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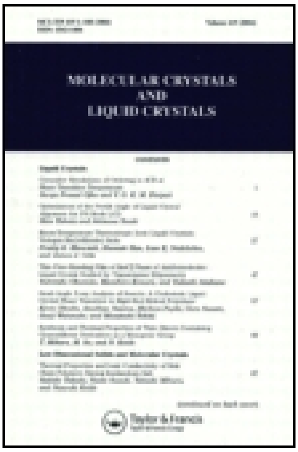

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New Aspects of Ionic Liquids as a Novel Initiator of Radical Polymerization

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New Aspects of Ionic Liquids as a Novel Initiator of Radical Polymerization

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This study focused on a simple approach to prove the initiating ability of radical polymerization in some types of imidazolium ionic liquids such as 1-butyl-3-methylimidazolium thiocyanate, 1-ethyl-3-methylimidazolium thiocyanate, and 1-ethyl-2,3-dimethylimidazolium bromide. Their utility has been demonstrated beyond doubt: they are indeed worthy initiators of unique radical polymerization of some types of vinyl monomers such as methyl methacrylate, methyl acrylate, ethyl acrylate, and butyl acrylate. This polymerization behavior is unique and marked different from that of traditional radical polymerization.

Keywords 1-butyl-3-methylimidazolium thiocyanate; 1-ethyl-2,3-dimethylimidazolium bromide; 1-ethyl-3-methylimidazolium thiocyanate; initiator; radical polymerization

Introduction

Macromolecular science plays a key role in the reflection and further reform of advanced modern human society. On the other hand, in recent years ionic liquids consisting of bulky organic cations paired with various kinds of different anions have generated much excitement among some sections of the science and industrial world because of their outstanding properties [1–3] and wide range of applications [4–8]. For instance, ionic liquids have become attractive solvents among the polymer synthetic field of the macromolecular science community because of their outstanding solution properties, vanishingly low vapor pressure, and recycling capability [9–21]. In other words, in the macromolecular science community, research and development relating to ionic liquids concentrated mainly on the use of replacement solvents for free radical polymerizations. The benefit in using of ionic liquids as replacement solvents can be seen in their nonflammability and negligible volatility, their dissolution potential for numerous organic and inorganic compounds, and their ability to influence the resulting polymers. In addition, it is possible to vary the physical and chemical properties of ionic liquids over a wide range by the selection of suitable cations and anions.

At present, it is generally known that some kinds of conventional free radical polymerizations in ionic liquids represent large increases in both the polymerization rate and the molecular weights of resulting polymers compared to the polymerizations in traditional volatile organic solvents. Part of these drastic increases is attributed to the high viscosity

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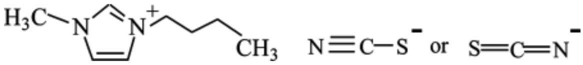
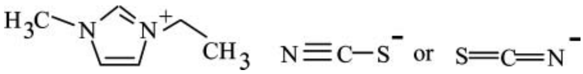
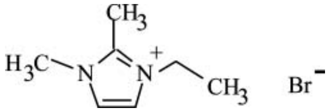
of the polymerization media, in which both terminations and/or chain transfers can be diminished in the viscous systems [22]. However, the details of the mechanism are still obscure. Of course, discussions and arguments about the use of ionic liquids as the replacement solvents for free radical polymerizations are still current in 2010. Nevertheless, the author has been targeting ionic liquids as a specific initiator of radical polymerization so far [23–27], while there are no reports about the application of ionic liquids as an initiator of radical polymerization except for the author's investigations. Generally, since ionic liquids are characterized by good thermal and chemical stability, nobody focuses on them as an initiator of radical polymerization. In this context, there is a basic doubt concerning the radical initiating ability of ionic liquids. On the other hand, the radical initiating ability of ionic liquids must be an additional benefit compared to further well-known applications of ionic liquids. By the way, the investigations of imidazolium ionic liquids were first reported in 1980s as far as the author knows [28,29]. In the investigations, it was proved that some kinds of imidazolium ionic liquids are useful catalysts/solvents for Friedel-Crafts acylations. In this communication, the author reports the simple approach to prove the initiating ability of radical polymerization on some kinds of imidazolium ionic liquids. In a word,1-butyl-3-methylimidazolium thiocyanate ([bmim]SCN; see Scheme 1), 1-ethyl-3-methylimidazolium thiocyanate ([emim]SCN; see Scheme 2), and 1-ethyl-2,3-dimethylimidazolium bromide ([edmim]Br; see Scheme 3) were explored as a novel initiator for the free radical polymerization of vinyl monomers.



Scheme 1. 1-Butyl-3-methylimidazolium Thiocyanate ([bmim]SCN).



Scheme 2. 1-Ethyl-3-methylimidazolium Thiocyanate ([emim]SCN).



Scheme 3. 1-Ethyl-2,3-dimethylimidazolium Bromide ([edmim]Br).

The results were compared with the polymerization initiated with conventional radical initiator such as 2,2′-azobisisobutyronitrile (AIBN). By the way, most ionic liquids that have been used in the replacement solvent for free radical polymerization of methacrylates contain 1-alkyl-3-methylimidazolium cations. For this reason the author has gained interested to investigate the initiating ability of these type of ionic liquids such as [bmim]SCN and [emim]SCN. In addition, until now, only ionic liquids with di-substituents at the 1-position and the 3-position of the imidazolium ion have been investigated as solvents for free radical polymerization. In regard to [edmim]Br, although this ionic liquid is out of this group, namely, this ionic liquid is composed of the tri-substituted imidazolium ring with alkyl chains. In order to confirm about the influence of the alkyl substituents of the imidazolium ion, the author investigated [edmim]Br as a new initiator for radical polymerization, too.

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Anyhow, the author believes that the initiating ability of radical polymerization is the most fascinating and useful aspect of ionic liquids.

Experimental

Materials

Imidazolium-based ionic liquids such as [bmim]SCN and [emim]SCN were purchased from Fluka and used without further purification. Another imidazolium-based ionic liquid such as [edmim]Br was also used directly as it was received from Nippon Synthetic Chemical Industry Co., Ltd. Conventional radical initiator such as AIBN was purchased from Wako Pure Chemical Industries, Ltd. and recrystallized with methanol, and dried under vacuum at room temperature. Vinyl monomers such as methyl methacrylate (MMA), methyl acrylate (MA), ethyl acrylate (EA), and butyl acrylate (BA), were also purchased from Wako Pure Chemical Industries, Ltd. and purified by conventional methods. These distilled vinyl monomers were placed in brown glass bottles and stored in a freezer at −20°C after bubbling with argon. Tetrahydrofuran (THF), benzene, toluene, dioxane, carbon tetrachloride, *N,N*-dimethylformamide (DMF), and dimethylsulfoxide (DMSO) used as polymerization media were spectroscopic grade for optical measurements (Wako Pure Chemical Industries, Ltd.). Only diglyme used as polymerization media from Aldrich Chemical Co., Ltd. was anhydrous grade. Hydroquinone (HQ) and 2,6-di-*tert*-butyl-*p*-cresol (BHT) were purchased from Wako Pure Chemical Industries, Ltd. and recrystallized with distilled water and ethanol, and dried under vacuum at room temperature, respectively. Commercially obtained 1-dodecanethiol (1-DT) (Wako Pure Chemical Industries, Ltd.) was used without previous purification. Research-grade quality argon (oxygen < 0.2 ppm) was supplied by Toho Acetylene Co., Ltd. and used as received.

Polymerization

Vinyl monomer, solvent, and imidazolium-based ionic liquid were placed in a brown glass ampoule, which was stoppered with a rubber septum. The polymerization was carried out under air or after purging with ultra-pure grade quality argon for 10 minutes (250∼350 ml/min) using two injection needles through the septum of the brown glass ampoule which was cooled in an ice bath. And then, the brown glass tube was maintained at a predetermined temperature. After certain time intervals, the polymer solution thus obtained was slowly poured into a miscible nonsolvent and a precipitate was obtained. The obtained polymer was washed by the nonsolvent and dried under vacuum at 40°C∼50°C. The conversion was determined gravimetrically.

Measurement

Molar mass (M_n) and molecular-weight distribution (M_w/M_n) were determined with a gel-permeation chromatography (GPC); a Shimadzu high-speed liquid chromatography system equipped with an LC-10AD$_{\mathrm{VP}}$ solvent pump, a DGU-12A degasser, a RID-10A refractive index detector, a SCL-10A$_{\mathrm{VP}}$ system controller, a CTO-10AC$_{\mathrm{VP}}$ column oven, and TSK gel column (GMH$_{\mathrm{HR}}$-M). All samples were dissolved in THF, and analyzed at 40°C. The polystyrene standards were used for the calibration, and the eluent THF was delivered at a flow rate of 0.8 mL/min.

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Results and Discussion

Table 1 is a one typical example of the direct proof about the initiating ability of ionic liquid. In a word, Table 1 exhibits the conversion percentages about the polymerizations of EA initiated with the combination system of AIBN as a conventional radical initiator and [bmim]SCN as an ionic liquid and AIBN, and [bmim]SCN under air at 40°C. Needless to say, AIBN was used as the reference in order to compare the initiating ability of [bmim]SCN. In addition, polymerization experiment in the absence of initiator was performed under otherwise similar reaction conditions as a reference polymerization reaction. Because, it is well-known that THF easily form peroxide under air. Consequently, one may speculate that the polymerization behavior is due to the thermal polymerization of EA under otherwise similar reaction conditions. Either way the description of Table 1 is as follows. The most striking characteristic of these polymerizations is that only AIBN did not exhibit the initiating ability at 40°C. Contrary to the fact, [bmim]SCN-initiated polymerization proceeded most smoothly, in which 26.9% conversion was observed after 4 hours. In other words, interestingly, the polymerization activity of the combination system of AIBN and [bmim]SCN was lower than that of [bmim]SCN, in which only 16.3% conversion was observed after 4 hours. Moreover, the strong inhibitory effects of HQ and BHT as radical inhibitors and 1-DT as a radical chain transfer agent were clearly observed concerning the EA-polymerization initiated with the combination system of AIBN and [bmim]SCN. Consequently, it is expected that the EA-polymerization proceeds via a radical pathway. To be more precise, these facts obtained here suggest that only [bmim]SCN has the initiating ability of radical polymerization. Needless to say, a purely thermal, self-initiated polymerization of EA in THF under the same reaction conditions did not proceed (see Entry 8 in Table 1).

In order to compare the results of the EA-polymerization and to shed more light on the nature of the radical polymerization initiated with [bmim]SCN, the polymerization of another vinyl monomer initiated with [bmim]SCN was realized. Table 2 shows the relationship between the time-conversion and the GPC results (M_n and M_w/M_n) of the MMA-polymerization initiated with [bmim]SCN in THF under air, in which the effects of radical inhibitors and the reaction temperature of the polymerization are listed. The description of Table 2 is as follows. In regard to the MMA-polymerization at 60°C, the polymerization proceeded smoothly, but the polymerizations in the presence of HQ and

Table 1. Polymerization of EA initiated with AIBN and [bmim]SCN[a]

			Conversion (%)		
Entry	Time (min)	Additive[c]	AIBN and [bmim]SCN	AIBN	[bmim]SCN
1	10	(Nil)	5.1	0.0	6.8
2	30	(Nil)	5.7	0.0	19.6
3	60	(Nil)	9.5	0.0	24.2
4	120	(Nil)	16.3	0.0	26.9
5	120	1-DT	4.9	—	—
6	120	HQ	7.6	—	—
7	120	BHT	5.0	—	—
8[b]	120	(Nil)	0.0	—	—

[a]EA 4.6 mmol, AIBN 0.046 mmol, [bmim]SCN 0.046 mmol, THF 1.0 ml, under air, 40°C. [b][emim]SCN and AIBN nil. [c]0.138 mmol.

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Table 2. Polymerization of MMA initiated with [bmim]SCN[a]

Entry	Time (h)	Temperature (°C)	Additive[b]	Conversion (%)	*Mn*[c]	*Mw/Mn*[c]
1	2	60	(Nil)	8.9	13000	2.00
2	4	60	(Nil)	16.0	13000	2.15
3	6	60	(Nil)	17.1	13000	2.31
4	8	60	(Nil)	25.2	14000	2.61
5	4	60	HQ	0.0	—	—
6	8	60	HQ	0.0	—	—
7	4	60	BHT	2.7	—	—
8	8	60	BHT	2.7	—	—
9	4	50	(Nil)	0.0	—	—
10	8	50	(Nil)	0.0	—	—
11	4	40	(Nil)	0.0	—	—
12	8	40	(Nil)	0.0	—	—
13	4	30	(Nil)	0.0	—	—
14	8	30	(Nil)	0.0	—	—

[a]MMA 4.7 mmol, THF 1.0 ml, under air. [b]0.14 mmol. [c]Determined by GPC with standard polystyrenes (eluent:THF).

BHT were completely inhibited or scarcely proceeded (see Entries 1–9 in Table 2). Without doubt, the MMA-polymerization initiated with [bmim]SCN in THF under air proceeds via a radical pathway. Furthermore, the molecular weights of obtained polymers at 60°C were constancy and relatively small during the entire polymerization process. It is generally accepted that the molecular weights of traditional radical polymerization reach high level in the early stage of polymerization and keep the level till the final stage of polymerization. In these meaning, the MMA-polymerization initiated with [bmim]SCN in THF under air is a little different from traditional radical polymerization. However, in regard to traditional radical polymerization under air, it is well known that the chain transfer and other side reactions easily take place by oxygen molecules in the air. Furthermore, the chain transfer reaction is widely used to reduce the molecular weight of obtained polymer by radical polymerization method. Consequently, one reason of the fact that the molecular weights of obtained polymers are relatively small may be attributed to the chain transfer and other side reactions by oxygen molecules in the air. On the other hand, since it is well known that the traditional radical initiator exhibits a high sensitivity to the reaction temperature, it could be easily estimated that the reaction activity of this [bmim]SCN-initiated polymerization is influenced by the reaction temperature as well as the radical inhibitors. As we estimated above, in contrast to the MMA-polymerization initiated with [bmim]SCN in THF under air at 60°C, it can be seen from Table 2 that the polymerizations at 50°C, 40°C, and 30°C were completely inhibited. This fact strongly suggests that the initiator is a thermally decomposing species, in which the initiator generates free radicals as the active species through its appreciable thermal decomposition.

In order to further understand the radical polymerization initiated with [bmim]SCN, the effect of solvent on the polymerization reaction was investigated. As a typical example of the effect of solvent on the [bmim]SCN-initiated polymerization, the conversion percentages of the MA-polymerizations initiated with [bmim]SCN under air in THF and toluene at 60°C are summarized together in Table 3. From Table 3, it is immediately clear that the polymerization in THF proceeds smoothly, but the polymerization in toluene scarcely

Table 3. Effect of solvent on the polymerization of MA initiated with [bmim]SCN[a]

Entry	Time (min)	Conversion in THF (%)	Conversion in Toluene (%)
1	10	16.1	(Trace)
2	30	24.2	1.1
3	60	27.4	1.8
4	120	29.6	3.1
5	240	44.7	2.0
6[b]	240	0.0	(Trace)

[a]MA 5.6 mmol, [bmim]SCN 0.056 mmol, solvent 1.0 ml, under air, 60°C. [b][bmim]SCN nil.

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proceeds; e.g., 44.7% and 2.0% conversions can be observed respectively after 4 hours. And furthermore, as described above it is well-known that THF easily form peroxide under air, but the self-thermal polymerization of MA in THF was perfectly inhibited under the same reaction conditions to say nothing of reacted having been inhibited in toluene. That is to say, it is clear that the MA-polymerization initiated with [bmim]SCN is apparently influenced by the selection of the solvent. In other words, [bmim]SCN has prominent effect on the initiating activity of radical polymerization in limited kinds of solvents. As the results of many investigations about the solvent effects on traditional radical polymerization, it is widely accepted that the solvent effects in traditional radical polymerization are usually much less significant than for ionic polymerization. In this manner, the MA-polymerization initiated with [bmim]SCN is different from traditional radical polymerization at this point. In addition with regard to traditional radical polymerization, to the author's best knowledge, the oxygen as a biradical acts as an inhibitor. Accordingly, the phenomenon that the polymerization proceeds under air via radical pathway is very important. In other words, this is an additional benefit compared to traditional radical polymerization.

Radical initiating ability of [bmim]SCN about some kinds of vinyl monomers was evident from the results described above. Subsequent experiments were carried out to prove the radical initiating ability of similar ionic liquid such as [emim]SCN. Table 4 exhibits the data about the effect of temperature on the polymerization of EA initiated with the combination system of AIBN as a conventional radical initiator and [emim]SCN as an ionic liquid under air. As reference, the polymerization initiated with AIBN and the polymerization initiated with [emim]SCN were carried out under the identical reaction conditions. The description of Table 4 is as follows. The polymerization proceeded almost same at 50°C and 60°C, but that was clearly depressed at 40°C. Furthermore, the inhibitory effects of a radical chain transfer agent and radical inhibitors were observed in the every case. Needless to say, a purely thermal, self-initiated polymerization of EA in THF was completely inhibited in the every case. It is noteworthy that a 22.9% conversion of EA was observed in [emim]SCN-initiated polymerization at 40°C, but AIBN did not initiate the polymerization under the same reaction conditions. Very similar results were obtained in the polymerization of EA initiated with [bmim]SCN and the polymerization of EA initiated with AIBN under the same reaction conditions as described above (see Table 1). Anyhow, the obtained results indicate that [emim]SCN has the initiating ability of radical polymerization. Furthermore, the temperature range on the initiating activity of [emim]SCN is more wide than that of AIBN.

Table 4. Polymerization of EA initiated with AIBN and [emim]SCN[a]

			Conversion (%)		
Entry	Time (min)	Additive[e]	60°C	50°C	40°C
1	10	(Nil)	7.5	9.0	5.8
2	30	(Nil)	15.6	18.7	8.8
3	60	(Nil)	23.2	20.8	7.6
4	120	(Nil)	33.4	28.3	14.5
5	120	1-DT	2.1	0.7	2.7
6	120	HQ	4.1	3.1	4.4
7	120	BHT	1.1	2.1	2.0
8[b]	120	(Nil)	29.5	15.7	0.0
9[c]	120	(Nil)	35.0	45.8	22.9
10[d]	120	(Nil)	0.0	0.0	0.0

[a]EA 4.6 mmol, AIBN 0.046 mmol, [emim]SCN 0.046 mmol, THF 1.0 ml, under air. [b][emim]SCN nil. [c]AIBN nil. [d][emim]SCN and AIBN nil. [e]0.138 mmol.

In regard to subsequent experiments, the radical initiating ability of completely different ionic liquid compared with the ionic liquids as mentioned above was examined. Table 5 is a one typical example of the simple approach to prove the radical initiating ability of [edmim]Br as an initiator. Viewed from different angle, Table 5 is an example of the

Table 5. Polymerization of MMA initiated with [edmim]Br[a]

Entry	Time (h)	[edmim]Br (mmol)	Additive[b]	Conversion (%)	*Mn*[c]	*Mw/Mn*[c]
1	2	0.047	(Nil)	(Trace)	—	—
2	4	0.047	(Nil)	8.5	64000	2.66
3	6	0.047	(Nil)	21.7	64000	2.56
4	8	0.047	(Nil)	26.3	48000	2.15
5	2	0.047	HQ	0.0	—	—
6	4	0.047	HQ	0.0	—	—
7	6	0.047	HQ	0.0	—	—
8	8	0.047	HQ	0.0	—	—
9	8	0.047	BHT	0.0	—	—
10	2	0.047	1-DT	0.0	—	—
11	4	0.047	1-DT	(Trace)	—	—
12	6	0.047	1-DT	4.0	—	—
13	8	0.047	1-DT	6.0	10000	1.22
14	2	(Nil)	(Nil)	0.0	—	—
15	4	(Nil)	(Nil)	0.0	—	—
16	6	(Nil)	(Nil)	0.0	—	—
17	8	(Nil)	(Nil)	0.0	—	—

[a]MMA 4.7 mmol, DMF 1.0 ml, under air, 70°C. [b]0.14 mmol. [c]Determined by GPC with standard polystyrenes (eluent:THF).

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ionic liquid-initiated polymerization that proceeds in solvents other than THF. Specifically, Table 5 shows the relationship between the conversion percentages and the GPC results (Mn and Mw/Mn) of the MMA-polymerization initiated with [edmim]Br in DMF under air at 70°C, and the effects of radical inhibitors and radical chain transfer agent under the same reaction conditions are summarized together. In addition, the MMA-polymerization experiments in the absence of [edmim]Br were performed under the identical conditions as a reference reaction to confirm the possibility of a purely thermal, self-initiated polymerization of MMA. As shown in Table 5, in contrast to the fact that the purely thermal, self-initiated polymerization was completely inhibited, the MMA-polymerization in the presence of [edmim]Br proceeded smoothly. Moreover, the radical inhibitors such as HQ and BHT perfectly inhibited the [edmim]Br-initiated polymerization of MMA. Therefore, it is strongly suggested that [edmim]Br has an initiating ability of radical polymerization. This is supported by the experimental result of the polymerization using 1-DT as a radical chain transfer agent. In a word, the degree of polymerization is remarkably lower when the polymerization is carried out in the presence of 1-DT compared to the polymerization in the absence of 1-DT. By the way, the molecular weights of resulting polymers were relatively small ($M_n = 48000$–64000) in spite of radical polymerization. The lower molecular weights of the resulting polymers may be a result of favored termination in respect to propagation. Viewed from a different angle, it can be estimated that oxygen molecules as biradicals in the air act as a radical transfer agent to a certain extent.

In order to confirm the application about the radical initiating ability of [edmim]Br to another vinyl monomer and another polymerization condition, the EA-polymerization initiated with [edmim]Br in toluene under argon at 70°C was carried out. Especially, a lot of experimental data on the polymerization initiated with ionic liquid under air are shown in this paper, in contrast the data summarized in Table 6 is an example of the ionic liquid-initiated polymerization that proceeds under argon. Namely, Table 6 presents the data about effects of radical inhibitors and radical chain transfer agent on the EA-polymerization initiated with [edmim]Br in toluene under argon at 70°C, and a purely thermal, self-initiated polymerization of EA under the same reaction conditions. From Table 6, as qualitatively similar comments about the basic polymerization features of the MMA-polymerization initiated with [edmim]Br were made above, the polymerization features of EA are very similar to those of MMA. That is to say, it is clearly indicated that the EA-polymerization initiated with [edmim]Br proceeds via a radical pathway. The most striking characteristic of the EA-polymerization is that the molecular weights of obtained polymers are bigger than those of the MMA-polymerization as described above. The experimental observation supports the radical initiating ability of [edmim]Br again. Meaning that the EA-polymerization is carried out under argon, and accordingly the effects of oxygen molecules as biradicals in the air can be neglected.

As pointed out above, subsequent experiments were carried out to confirm the application about the radical initiating ability of [edmim]Br to another vinyl monomer and another polymerization condition. The results of the polymerization of BA initiated with [edmim]Br in diglyme under air at 70°C are summarized in Table 7. From the data summarized in Table 7, as qualitatively similar comments about the polymerization behaviors of the MMA-polymerization and the EA-polymerization initiated with [edmim]Br were made above, it is strongly indicated that the BA-polymerization initiated with [edmim]Br proceeds via a radical pathway.

In order to clarify the detailed reaction mechanism of the BA-polymerization initiated with [edmim]Br, parallel experiments about the effect of temperature and the effect of solvents were carried out and the results are summarized in Table 8 and Table 9, respectively.

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Table 6. Polymerization of EA initiated with [edmim]Br[a]

Entry	Time (h)	[edmim]Br (mmol)	Additive[b]	Conversion (%)	*Mn*[c]	*Mw/Mn*[c]
1	2	0.046	(Nil)	6.3	—	—
2	4	0.046	(Nil)	27.0	257000	2.09
3	6	0.046	(Nil)	30.8	111000	2.35
4	8	0.046	(Nil)	45.5	149000	2.19
5	2	0.046	HQ	0.0	—	—
6	4	0.046	HQ	2.9	—	—
7	6	0.046	HQ	2.0	—	—
8	8	0.046	HQ	3.5	—	—
9	8	0.046	BHT	0.0	—	—
10	2	0.046	1-DT	0.0	—	—
11	4	0.046	1-DT	7.9	4000	1.22
12	6	0.046	1-DT	18.6	—	—
13	8	0.046	1-DT	17.7	4000	1.20
14	2	(Nil)	(Nil)	0.0	—	—
15	4	(Nil)	(Nil)	0.0	—	—
16	6	(Nil)	(Nil)	0.0	—	—
17	8	(Nil)	(Nil)	0.0	—	—

[a]EA 4.6 mmol, toluene 1.0 ml, under argon, 70°C. [b]0.14 mmol. [c]Determined by GPC with standard polystyrenes (eluent:THF).

In comparison with the BA-polymerization initiated with [edmim]Br in diglyme under air at 70°C, it can be seen from Table 8 that the BA-polymerization at 60°C under otherwise similar reaction conditions was completely inhibited. Very similar results were observed in the case of the MMA-polymerization initiated with [bmim]SCN in THF under air (see Table 2). Suffice it to say that the initiating species is thermally unstable and decomposes into radicals at a temperature.

Table 7. Polymerization of BA initiated with [edmim]Br under Air at 70°C[a]

Entry	Time (h)	[edmim]Br (mmol)	Additive[b]	Conversion (°C)	*Mn*[c]	*Mw/Mn*[c]
1	1	0.035	(Nil)	19.4	—	—
2	2	0.035	(Nil)	40.8	—	—
3	3	0.035	(Nil)	61.7	—	—
4	4	0.035	(Nil)	62.0	45000	2.62
5	4	0.035	HQ	0.0	—	—
6	4	0.035	BHT	0.0	—	—
7	4	0.035	1-DT	0.0	—	—
8	4	(Nil)	(Nil)	0.0	—	—

[a]BA 3.5 mmol, diglyme 1.0 ml. [b]0.11 mmol. [c]Determined by GPC with standard polystyrenes (eluent:THF).

Table 8. Polymerization of BA initiated with [edmim]Br under Air at 60°C[a]

Entry	Time (h)	[edmim]Br (mmol)	Additive	Conversion (°C)
1	1	0.035	(Nil)	0.0
2	2	0.035	(Nil)	0.0
3	3	0.035	(Nil)	0.0
4	4	0.035	(Nil)	0.0

[a]BA 3.5 mmol, diglyme 1.0 ml.

As described above, the other polymerization solvents such as benzene, toluene, dioxane, carbon tetrachloride, DMF, and DMSO were used as reference in order to have a general impression on the role of the chemical nature of the solvent on the BA-polymerization initiated with [edmim]Br under air at 70°C. As evidenced in Table 7 the BA-polymerization in diglyme proceeds smoothly, in contrast to the fact, as seen in Table 9, these solution polymerizations are completely inhibited. Noteworthy, the bulk polymerization of BA initiated with [edmim]Br under air at 70°C is perfectly inhibited, too. The results obtained from Tables 7 and 9 suggest that variation of the polymerization solvent markedly affects the initiating ability of the BA-polymerization initiated with [edmim]Br. To be more precious, these results demonstrate the prominent importance of the selection of organic solvent as the polymerization media in order to obtain the radical initiating activity of [edmim]Br. Most of the solvent effects in traditional radical polymerization are usually much less significant than for ionic polymerization, but not negligible, and can be explained by interaction of the solvent with the propagating radical. In particular, to our best knowledge about traditional radical polymerization, there is no example that the solution polymerization proceeds in spite of the perfect inhibition of bulk polymerization under the same reaction conditions of the solution polymerization. For this reason, the radical initiating activity of [edmim]Br is completely different from that of conventional radical initiator. On the other hand, this observation agrees with the MA-polymerization initiated with [bmim]SCN as mentioned above (see Table 3) and the previous report on the phosphonium-based ionic

Table 9. Effect of solvents on the polymerization of BA initiated with [edmim]Br under Air at 70°C[a]

Entry	Time (h)	Solvent	Conversion (%)
1[b]	4	(Nil)	0.0
2	4	Benzene	0.0
3	4	Toluene	0.0
4	4	Dioxane	0.0
5	4	Carbon Tetrachloride	0.0
6	4	DMF	0.0
7	4	DMSO	0.0

[a]BA 3.5 mmol, [edmim]Br 0.035 mmol, solvent 1.0 ml. [b]BA 7.0 mmol, [edmim]Br 0.07 mmol.

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liquids-initiated polymerization that is called "solvent-assisted" radical polymerization, in which the polymerization proceeds in limited kinds of solvents [30].

Concluding Remarks

In conclusion, the objective of this study focuses on the simple approach to prove the initiating ability of radical polymerization on some kinds of imidazolium ionic liquids such as [bmim]SCN, [emim]SCN, and [edmim]Br. Their utility has been demonstrated beyond doubt: they are indeed worthy initiators of unique radical polymerization of some kinds of vinyl monomers such as MMA, MA, EA, and BA. However, this investigation is progressing exactly now, hence, the detailed pathway that some initiators could homolytically dissociate to form the initiating radical will be examined in the near feature (including end-group analysis by NMR measurements). On the other hand, it is not expected that ionic liquids simply dissociate to form radicals that initiate polymerization. In other words, the author estimates that a solvent has an important role in the initiating system of this ionic liquid-initiated polymerization. Anyhow, the distinctive features of these imidazolium ionic liquids as an initiator of unique radical polymerization are as follows. As an example, the EA-polymerization initiated with [bmim]SCN under air in THF at 40°C proceeds smoothly, but the AIBN-initiated polymerization under otherwise similar reaction conditions is perfectly inhibited. As another example, suffice it to say that the inhibitory effect of HQ and BHT is observed on the MMA-polymerization initiated with [bmim]SCN under air in THF at 60°C. In addition, the MMA-polymerizations at 40°C and 50°C under otherwise similar reaction conditions are completely inhibited. As a further example, the MA-polymerization initiated with [bmim]SCN under air in THF at 60°C proceeds smoothly, but the MA-polymerization in toluene under otherwise similar reaction conditions is strongly inhibited. In regard to [emim]SCN, as an example, the EA-polymerizations initiated with [emim]SCN under air in THF at 40°C, 50°C, and 60°C proceed smoothly, respectively. As reference, the AIBN-initiated polymerization at 40°C under otherwise similar reaction conditions is perfectly inhibited. Needless to say, the AIBN-initiated polymerizations at 50°C and 60°C proceed, but the reaction activities are lower in comparison with those of the [emim]SCN-initiated polymerizations. That is to say, the use of [emim]SCN as an initiator of radical polymerization of EA improves the temperature range on the initiating activity in comparison with that of the conventional radical initiator such as AIBN. In this manner the use of ionic liquid as a new initiator for radical polymerization opens new possibility to obtain polymer at wider temperature range in comparison with the use of conventional radical initiator. On the other hand, viewed from a different angle, [bmim]SCN and [emim]SCN contain the di-substituted imidazolium ring with alkyl chains, but [edmim]Br contains the tri-substituted imidazolium ring with alkyl chains. Therefore, in contrast to the initiating ability of [bmim]SCN and [emim]SCN, that of [edmim]Br is intriguing. As an example of [edmim]Br as an initiator, the MMA-polymerization initiated with [edmim]Br under air in DMF at 70°C proceeds smoothly, and the molecular weight of resulting polymer is very small when the polymerization is carried out in the presence of 1-DT. Moreover, HQ and BHT completely inhibit the MMA-polymerization. The results of the EA-polymerization initiated with [edmim]Br under argon in toluene at 70°C are very similar to those of the MMA-polymerization as described above. Noteworthy, the molecular weight of obtained polymer of the EA-polymerization is bigger than that of the MMA-polymerization. One reason of this phenomenon is that the EA-polymerization is carried out under argon contrary to the MMA-polymerization that is carried out under air, and accordingly the effects of oxygen molecules as biradicals in the air can be neglected. As a more specific example

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of the radical initiating ability of [edmim]Br, the BA-polymerization initiated with [edmim]Br under air in diglyme at 70°C proceeds smoothly, but the polymerizations in the presence of HQ, BHT, and 1-DT are perfectly inhibited. The BA-polymerization at 60°C under otherwise similar reaction conditions is completely inhibited, too. These results suggest that the initiator is thermally unstable and decomposes into radicals at a temperature. Furthermore, special regard should be paid on the fact that the BA-polymerizations in benzene, toluene, dioxane, carbon tetrachloride, DMF, and DMSO at 70°C under otherwise similar reaction conditions are completely inhibited, too. This polymerization behavior is unique and marked different from that of traditional radical polymerization. In a word, the solvents have the marked impact on the initiating activity of the polymerization. Consequently, the BA-polymerization initiated with [edmim]Br can be called "solvent-assisted" radical polymerization. As a result, even though there are several complicating factors that prevent quantitative descriptions of the initiating radical, the qualitative features of this polymerization are very important for the nature of ionic liquids.

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