

Research on Imidazolium Ionic Liquids with Radical Polymerization Initiating Ability

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KEY WORDS: 1-Ethyl-2,3-dimethylimidazolium bromide, 1-Ethyl-2,3-dimethylimidazolium chloride, Methyl methacrylate, Methyl acrylate, Radical polymerization initiator

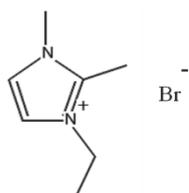
ABSTRACT: Under various polymerization conditions, the polymerizations of methyl methacrylate (MMA), methyl acrylate (MA), and *n*-butyl acrylate (*n*-BA) initiated with imidazolium ionic liquids such as 1-ethyl-2,3-dimethylimidazolium bromide ([edmim]Br) and 1-ethyl-2,3-dimethylimidazolium chloride ([edmim]Cl) are investigated in detail. Needless to say, these two ionic liquids have the identical polysubstituted imidazolium cation structure. In regard to the *N,N*-dimethylformamide (DMF) solution polymerization of MMA initiated with [edmim]Br at 80 °C, in contrast to the polymerization proceeds smoothly under air atmosphere, the polymerization under argon atmosphere is strongly inhibited. The oxygen molecules in air often play the role of the radical polymerization inhibitor, so this polymerization behavior is unique in contrast to the conventional radical polymerization. This unique polymerization behavior is also observed in the polymerization of MA and *n*-BA initiated with [edmim]Br under almost identical polymerization conditions. Another unique point of the MMA polymerization initiated with [edmim]Br under air atmosphere is that the polymerization reaction is strongly dependent on the polymerization solvent. To be more precise, at the polymerization temperature of 80 °C, only the DMF solution polymerization proceeds smoothly in contrast to the perfect inhibition of the carbon tetrachloride solution polymerization, the toluene solution polymerization, and the dimethylsulfoxide solution polymerization. This polymerization behavior that only the DMF solution polymerization proceeds smoothly can be observed in the *n*-BA polymerization initiated with [edmim]Br under air atmosphere at 90 °C, and the MMA polymerization initiated with [edmim]Cl under air atmosphere at 70 °C. Incidentally, it is very interesting to note that the DMF solution polymerization of MMA under air atmosphere at 80 °C shows that [edmim]Cl has the higher polymerization initiating activity than [edmim]Br, indicating that the halogen anion has a significant effect on their properties as polymerization initiators. On the other hand, in order to obtain the minimum necessary information on the polymerization mechanism, the study of adding the radical chain transfer agent such as 1-dodecanethiol (1-DT), and the radical polymerization inhibitors such as hydroquinone (HQ) and 2,6-di-*tert*-butyl-*p*-cresol (BHT) is important. With respect to the DMF solution polymerization of MMA initiated with [edmim]Br under air atmosphere at 80 °C, and the DMF solution polymerization of *n*-BA initiated with [edmim]Br under air atmosphere at 90 °C, 1-DT, HQ and BHT perfectly inhibit the polymerization. Furthermore, the DMF solution polymerization of MMA initiated with [edmim]Cl under air atmosphere at 70 °C and 80 °C, and the toluene solution polymerization of MMA initiated with [edmim]Cl under air atmosphere at 80 °C are completely inhibited by the addition of HQ and BHT. These results strongly suggest that the vinyl polymerization initiated with [edmim]Br or [edmim]Cl under air atmosphere proceeds via a radical pathway. From the viewpoint of polymerization temperature, the polymerization rate of the DMF solution polymerization of MA initiated with [edmim]Br under air atmosphere increases with increasing the polymerization temperature within the polymerization temperature range 70 °C to 90 °C. At the same time, regarding the rate of DMF solution polymerization of MMA initiated with [edmim]Cl under air atmosphere, in contrast to the polymerization rate increases with increasing the polymerization temperature at 70 °C and 80 °C, the polymerization at 60 °C is perfectly inhibited. Such polymerization behavior that the polymerization activity is lost with a slight polymerization temperature difference of about 10 °C can also be seen in the polymerization initiated with conventional radical polymerization initiators such as azobisisobutyronitrile and benzoylperoxide. Further, such polymerization behavior can be observed in the MMA-polymerization initiated with [edmim]Cl under air atmosphere in toluene, where the polymerization proceeds smoothly at 80 °C but the polymerization at 70 °C is perfectly inhibited. More interestingly, in the DMF solution polymerization, the polymerization rate increases with increasing the polymerization temperature, but in this toluene solution polymerization, the polymerization rate at 90 °C is slower than that at 80 °C. In the meanwhile, comparing the polymerizations at 80 °C, the polymerization rate is faster in the DMF solution polymerization, but the molecular weight of the resulting polymer is larger in the toluene solution polymerization. From these viewpoints about the MMA-polymerization initiated with [edmim]Cl under air atmosphere, it is suggested that the polymerization rate and the molecular weight of the resulting polymer can be controlled by the type of polymerization solvents. A large body of experimental results of [edmim]Br or [edmim]Cl as a polymerization initiator indicate their unique radical polymerization initiating ability. Following this study, the author is not only elucidating the detailed mechanism of this radical polymerization, but also researching the development of ionic liquids as more attractive radical polymerization initiators from the perspective of combinations of anions and cations.

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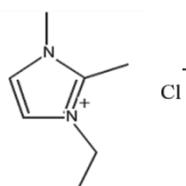
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INTRODUCTION

The existence of ionic liquids themselves has been known from Walden's report in the 1910s.¹⁾ However, it was only after the 1980s that the potential applications of ionic liquids in various fields began to attract attention.²⁾⁻¹²⁾ In this trend of the time, the author has clarified the radical polymerization initiating ability of ionic liquids for the first time in 2005.¹³⁾⁻¹⁵⁾ In the process of conducting extensive research on the radical polymerization initiating ability of various ionic liquids, the author has learned about the specific properties of ionic liquids, their various applications, and the historical aspects of their development. Incidentally, since this topic has been discussed in detail in the author's other papers,¹⁶⁾⁻³⁹⁾ the author does not discuss it further in this paper. On the other hand, since there are no other research examples to date that have examined ionic liquids as radical polymerization initiators, other than the author's investigations, they are the main source of information for providing an overall picture of research in this field. In this sense, some examples of reports in this field by authors other than those mentioned above are listed in the references.⁴⁰⁾⁻¹⁴³⁾ In such a meaning, although the author has clarified the radical polymerization initiating ability of many kinds of ionic liquids, elucidation of the detailed polymerization mechanism is currently in progress. This research is a part of elucidating the detailed polymerization mechanism by accumulating the data on polymerization under various polymerization conditions using ionic liquids as radical polymerization initiators. Through this study, the author investigates the polymerization of vinyl monomers such as methyl methacrylate (MMA), methyl acrylate (MA), and *n*-butyl acrylate (*n*-BA) initiated with the imidazolium ionic liquids such as 1-ethyl-2,3-dimethylimidazolium bromide ([edmm]Br) and 1-ethyl-2,3-dimethylimidazolium chloride ([edmm]Cl). These imidazolium ionic liquids are polysubstituted type, and have the common cation structure, as shown in Scheme 1 and Scheme 2, respectively.



Scheme 1. 1-Ethyl-2,3-dimethylimidazolium bromide ([edmm]Br).



Scheme 2. 1-Ethyl-2,3-dimethylimidazolium chloride ([edmm]Cl).

MATERIALS AND METHODS

Chemicals

Imidazolium ionic liquids such as [edmm]Br and [edmm]Cl used as the polymerization initiator received from Merck KGaA were used without further purification. Commercial grade acrylic esters such as MA and *n*-BA

(FUJIFILM Wako Pure Chemical Corporation) were washed three times with 5 % wt sodium hydroxide aqueous solution to remove the inhibitor, then were washed three times with 20 % wt sodium chloride aqueous solution, and then were washed three times with distilled water. Washed these acrylic esters were dried on calcium chloride overnight and distilled under vacuum and stored in a freezer at $-20\text{ }^{\circ}\text{C}$ until use. Commercial grade MMA (FUJIFILM Wako Pure Chemical Corporation) was washed three times with 5 % wt sodium sulfite aqueous solution to remove the inhibitor, then was washed three times with a 5 % wt sodium hydroxide, and then was washed three times with a 20 % wt sodium chloride aqueous solution, and then was washed three times with distilled water. Washed MMA was dried on anhydrous sodium sulphate overnight and distilled under vacuum and stored in a freezer at $-20\text{ }^{\circ}\text{C}$ until use. The polymerization solvents used such as toluene, *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and carbon tetrachloride were spectroscopic ultra-pure grade for optical measurements (FUJIFILM Wako Pure Chemical Corporation). Commercial grade methanol or *n*-hexane used as the poor solvent purchased from FUJIFILM Wako Pure Chemical Corporation was used as it was. Commercially obtained hydroquinone (HQ) from FUJIFILM Wako Pure Chemical Corporation as the radical polymerization inhibitor was recrystallized from distilled water. 2,6-Di-*tert*-butyl-*p*-cresol (BHT), which is also the radical polymerization inhibitor, was purchased from FUJIFILM Wako Pure Chemical Corporation and purified by recrystallization using ethanol. The radical chain transfer agent such as 1-dodecanethiol (1-DT) was purchased from FUJIFILM Wako Pure Chemical Corporation, and 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, polymerization-solvent, and ionic liquid were placed in the brown glass ampoule, and it was sealed by the rubber septum-type cap. When using the additives such as HQ, BHT, and 1-DT, they were placed in the brown glass ampoule together with vinyl monomer, polymerization-solvent, and ionic liquid before sealing. Most of the polymerization was carried out under air atmosphere, and as a comparison, the polymerization was carried out after purging with argon for 10 minutes (250 ~ 350 ml/min) using two injection needles through the rubber septum-type cap. The brown glass ampoule was maintained in the predetermined temperature oil bath in order to proceed the polymerization reaction. After certain polymerization time intervals, the reaction mixture in the brown glass ampoule was slowly poured into poor solvent stirred in the beaker in order to precipitate the resulting polymer. Methanol was used as a poor solvent for polymerizing MMA, and *n*-hexane was used as a poor solvent for polymerizing MA and *n*-BA. The resulting polymer was washed with poor solvent and dried under

reduced pressure at 40 °C to 50 °C overnight. The monomer conversion was calculated gravimetrically.

Molecular Weight Measurements

Gel permeation chromatography (GPC) was used to measure number- and weight-average molecular weights (\overline{M}_n and \overline{M}_w , respectively) and the polydispersity ($\overline{M}_w/\overline{M}_n$) of resulting polymer. As the GPC apparatus, Shimadzu LC-VP system equipped with Shimadzu RID-10A differential refractometer, Shimadzu SCL-10AVP controller, Shimadzu LC-10ADVP pump, TSK gel column (GMH_{HR}-M), and Shimadzu DGU-12A on-line degasser were used. As the developing solvent of all the GPC-measurements, tetrahydrofuran (THF) was used at the flow rate of 0.8 mL/min at 40 °C. Data analysis of GPC was performed using Shimadzu LC solution software. The calibration curve was constructed from monodisperse polystyrene standards (Wako Pure Chemical Industries, Ltd.) ranging from 1.3×10^3 to 2.3×10^6 AMU.

RESULTS AND DISCUSSION

Polymerization of MMA Initiated with [edmin]Br Under Various Polymerization Conditions

As an opening gambit, in order to confirm the basic polymerization behavior, Figure 1 shows the relationship of monomer conversion and polymerization time with respect to the polymerization atmosphere on the DMF solution polymerization of MMA initiated with [edmin]Br at 80 °C.

As can be easily seen in this figure, the clear tendency for the polymerization atmosphere dependence to the polymerization rate can be confirmed. More concrete, in contrast to the polymerization proceeds smoothly under air atmosphere, the polymerization under argon atmosphere is strongly inhibited.

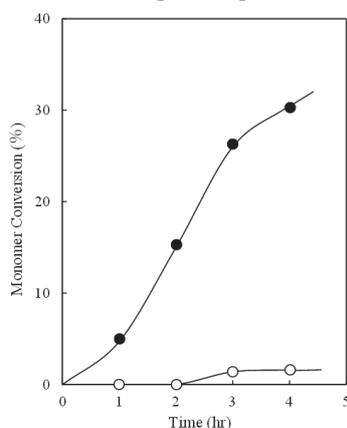


Figure 1. Effect of atmosphere on the Polymerization of MMA initiated with [edmin]Br. MMA 4.7 mmol, [edmin]Br 0.047 mmol, DMF 1.0 ml, 80 °C, (●) under air, (□) under argon.

On the other hand, the completely opposite polymerization behavior is often observed in the polymerization initiated with azobisisobutyronitrile and benzoylperoxide, which are known as conventional radical polymerization initiators. This is because in conventional radical polymerization, oxygen molecules in the air often play the role of the radical polymerization inhibitor. The author has previously reported that the polymerization of MMA initiated with [edmin]Br proceeds via a radical pathway^{37-39, 130, 132, 133, 135-137, 139, 141}, and therefore the polymerization behavior observed here is significantly different from that of conventional radical polymerization. Additionally, in

regard to the THF solution polymerization of MMA initiated with [edmin]Br at 60 °C, as the author's recent investigation,³⁹ it could be observed that although the initial polymerization rate tends to be slightly suppressed under nitrogen atmosphere, but it appears that the polymerization under air atmosphere or under nitrogen atmosphere proceeds at approximately the same rate. At that time, the cause was attributed to the slight progression of the thermal self-initiated polymerization of MMA under nitrogen atmosphere in THF at 60 °C, but it can be confirmed here that the influence of the polymerization solvent may not be negligible. As the food for further discussion regarding this polymerization under air atmosphere, especially taking into consideration the such polymerization solvent effect, Figure 2 exhibits the time-conversion curves about the polymerization solvent effect of DMF, carbon tetrachloride, toluene, and DMSO on the polymerization of MMA initiated with [edmin]Br under air atmosphere at 80 °C. It can be recognized clearly from this figure, the polymerization reaction is strongly dependent on the polymerization solvent. To be more precise, only the DMF solution

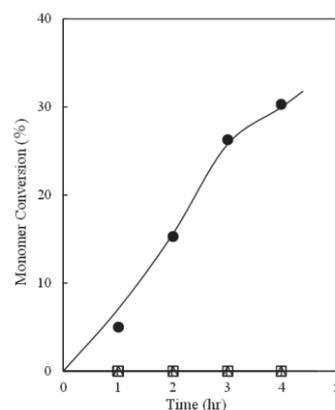


Figure 2. Effect of solvents on the polymerization of MMA initiated with [edmin]Br. MMA 4.7 mmol, [edmin]Br 0.047 mmol, solvent 1.0 ml, under air, 80 °C, solvent : (●) DMF, (□) CCl₄, (+) Toluene, (△) DMSO.

polymerization proceeds smoothly in contrast to the perfect inhibition of the carbon tetrachloride solution polymerization, the toluene solution polymerization, and the DMSO solution polymerization. Generally, radical polymerization is known to be characterized by being less affected by the polymerization solvent compared especially to ionic polymerization, and in this sense the strong solvent effect observed here is unique. Besides, from the viewpoint of the molecular weight of resulting polymer on this MMA-polymerization in DMF, Table 1 lists the time-conversion data and the GPC results (\overline{M}_n and $\overline{M}_w/\overline{M}_n$) as the corresponding data of Figure 2. As something of primary

Table 1. Polymerization of MMA Initiated with [edmin]Br in DMF^a

Entry	Time (hr)	Conversion (%)	\overline{M}_n^b	$\overline{M}_w/\overline{M}_n^b$
1	1	5.0	56000	1.56
2	2	15.3	52000	1.58
3	3	26.3	48000	1.59
4	4	30.3	58000	1.74
5 ^c	4	0.0	—	—

^aMMA 4.7 mmol, [edmin]Br 0.047 mmol, DMF 1.0 ml, under air, 80 °C.

^bDetermined by GPC with standard polystyrenes (eluent: THF). ^c[edmin]Br nil.

confirmation, the thermal self-initiated polymerization of MMA in DMF does not proceed under such polymerization conditions here (see Entry 5 in Table 1). That is to say, the important thing is that the certain polymerization initiating

ability of [edmin]Br itself under the given polymerization conditions can be confirmed from this data. And furthermore, the most striking characteristic of the data from Table 1 is that the molecular weight of the resulting polymer is small, for the polymer produced by radical polymerization. One possible cause is that since this polymerization is carried out under air atmosphere, oxygen biradicals in the air act as radical chain transfer agents. In the meanwhile, in order to more discuss the unexpected polymerization behaviors as described above and the polymerization mechanism,

the relationship between the polymerization initiator concentration and the polymerization rate is interested. In this sense, Figure 3 exhibits the time-conversion curves about the relationship between the polymerization initiator concentration and the polymerization rate on the bulk polymerization of MMA initiated with [edmin]Br under air atmosphere at 80 °C. Unexpectedly, it can be recognized from this figure, the polymerization rate is independent from the polymerization initiator concentration. One explanation for this polymerization behavior is that there is an effective amount of polymerization initiator. Actually, the upper limit of the amount of polymerization initiator is 0.5 mol % with respect to the amount of monomer, and the amount of polymerization initiator above this does not affect the polymerization rate. Needless to say, such polymerization behavior can not be observed in conventional radical polymerization. And in any event, the author finds that this kinetic study is difficult, so the author returns to the basic and next investigates the effect of radical polymerization inhibitors and radical chain transfer agent. In other words, the author reexamines the basic polymerization behavior of MMA initiated with [edmin]Br under different polymerization conditions from those of the author's previous investigation. More specifically, Figure 4 shows the effects of 1-DT as a radical chain transfer agent and radical inhibitors such as HQ and BHT with

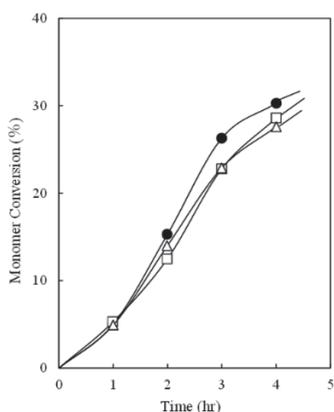


Figure 3. Effect of initiator concentration on the polymerization of MMA initiated with [edmin]Br. MMA 4.7 mmol, under air, 80 °C, [edmin]Br: (●) 0.047 mmol, (□) 0.094 mmol, (△) 0.141 mmol.

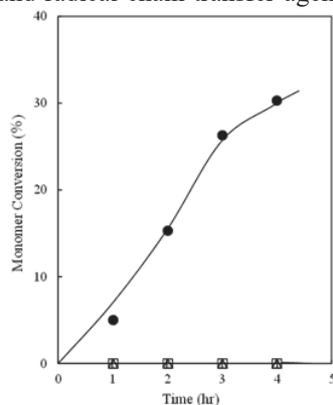


Figure 4. Effect of additives on the polymerization of MMA initiated with [edmin]Br. MMA 4.7 mmol, [edmin]Br 0.047 mmol, DMF 1.0 ml, under air, 80 °C, additive : (●) nil, (□) HQ 1.41 mmol, (△) BHT 1.41 mmol, (+) 1-DT 1.41 mmol.

respect to the DMF solution polymerization of MMA initiated with [edmin]Br under air atmosphere at 80 °C. Evidently, according to the data in this figure, 1-DT, HQ and BHT perfectly inhibit the polymerization. Taking this result into account, it can be confirmed that DMF solution polymerization of MMA using [edmin]Br as a polymerization initiator under air atmosphere proceeds via a radical pathway.

Polymerization of Acrylic Esters Initiated with [edmin]Br Under Various Polymerization Conditions

Against the above-mentioned polymerization of MMA initiated with [edmin]Br, the polymerization of acrylic esters initiated with [edmin]Br is discussed below. First things first, as one of the typical fundamental polymerization behaviors, Figure 5 shows the relationship of monomer conversion and polymerization time with respect to the polymerization temperature on the DMF solution polymerization of MA initiated with [edmin]Br under air atmosphere. In short, the time-conversion curves of the polymerizations at 70 °C, 80 °C, and 90 °C are shown together in this figure. As can be seen from this figure, the clear evidence for the polymerization

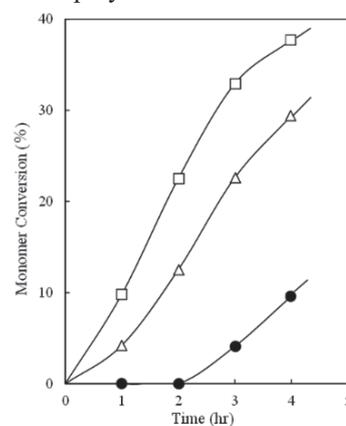


Figure 5. Effect of temperature on the polymerization of MA initiated with [edmin]Br. MA 5.6 mmol, DMF 1.0 ml, under air, [edmin]Br 0.028 mmol, (●) 70 °C, (△) 80 °C, (□) 90 °C.

temperature dependence to the polymerization rate can be easily confirmed. More concrete, the polymerization rate increases with increasing the polymerization temperature within the polymerization temperature range 70 °C to 90 °C. Especially, the polymerization at 70 °C is initially inhibited and then proceeds gradually. Such polymerization behavior in which the polymerization progresses dramatically with a slight difference at the polymerization temperature can also be seen in the polymerization initiated with conventional radical polymerization initiators such as azobisisobutyronitrile and benzoylperoxide. Subsequently, as another important factor that influences the polymerization behavior, the author examines the influence of the polymerization atmosphere, which was also noted during the above-mentioned MMA polymerization. As a typical example, Figure 6 exhibits the time-conversion curves about the polymerization atmosphere effect on the polymerization of MA initiated with [edmin]Br at 80 °C. It can be recognized clearly from this figure, the polymerization reaction is strongly dependent on the polymerization atmosphere. That is, in contrast to the strong inhibition of the polymerization under argon atmosphere, the polymerization proceeds smoothly under air atmosphere. The strong dependence of the polymerization reaction on

the polymerization atmosphere revealed here has also been confirmed in the MMA polymerization under the same polymerization condition as described above (see Figure 1). Specifically, the DMF solution polymerization of MMA at 80 °C proceeds smoothly under air atmosphere, whereas the polymerization is strictly inhibited under argon atmosphere. As mentioned there, this kind of polymerization behavior is significantly different from that of conventional radical polymerization, and this unique polymerization behavior has been reconfirmed once again. Regarding this influence of the polymerization atmosphere, the similar

polymerization behavior can be observed in *n*-BA polymerization. For example, Figure 7 shows the time-conversion curves about the effect of polymerization atmosphere on the DMF solution polymerization of *n*-BA initiated with [edmm]Br at 90 °C. As can be seen at a glance in the figure, in contrast to the polymerization proceeds smoothly under air atmosphere, it is certainly inhibited under argon atmosphere. Furthermore, in order to confirm the another basic polymerization

behavior of the *n*-BA polymerization, Figure 8 shows the time-conversion plots of the DMF solution polymerization of *n*-BA initiated with [edmm]Br under air atmosphere at 90 °C with respect to the effects of 1-DT as a radical chain transfer agent and radical inhibitors such as HQ and BHT. Evidently,

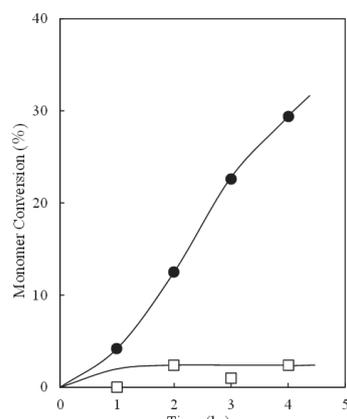


Figure 6. Effect of atmosphere on the polymerization of MA initiated with [edmm]Br. MA 5.6 mmol, DMF 1.0 ml, 80 °C, (●) under air, (□) under argon.

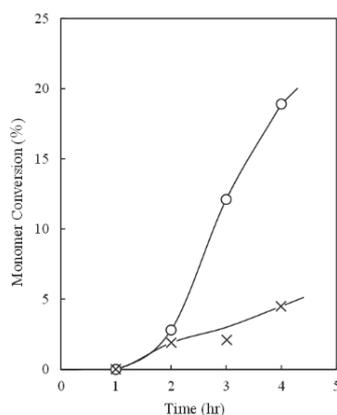


Figure 7. Effect of atmosphere on the polymerization of *n*-BA initiated with [edmm]Br. *n*-BA 3.5 mmol, DMF 1.0 ml, [edmm]Br 0.035 mmol, 90 °C, (○) under air, (×) under argon.

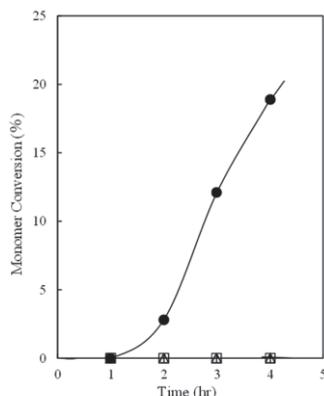


Figure 8. Effect of additives on the polymerization of *n*-BA initiated with [edmm]Br. *n*-BA 3.5 mmol, [edmm]Br 0.035 mmol, DMF 1.0 ml, under air, 90 °C, additive: (●) nil, (□) BHT 0.105 mmol, (△) HQ 0.105 mmol, (+) 1-DT 0.105 mmol.

according to the data in this figure, 1-DT, HQ, and BHT perfectly inhibit the polymerization. The perfect inhibitory effect of these additives on the polymerization of *n*-BA revealed here has also been observed above, that is the MMA polymerization under similar polymerization (see Figure 4). There, 1-DT, HQ, and BHT perfectly inhibit the DMF solution polymerization of MMA initiated with [edmm]Br under air atmosphere at 80 °C. In this sense, the common effect of the radical chain transfer agent and radical inhibitors has been reconfirmed here. In other words, it goes without saying that the result strongly suggests again that the polymerization initiated with [edmm]Br under air atmosphere proceeds via a radical pathway. From another point of view about the basic polymerization behavior, it is mentioned above that the effect of polymerization solvent is particularly important in this case. Therefore, as a representative example of the influence of the polymerization

solvent, Figure 9 exhibits the time-conversion curves about the polymerization solvent effect of DMF, toluene, and DMSO on the polymerization of *n*-BA initiated with [edmm]Br under air atmosphere at 90 °C. It can be clearly observed from this figure,

the polymerization reaction is strictly dependent on the kind of polymerization solvent. More specifically, in contrast to the perfect inhibition of the toluene solution polymerization and the DMSO solution polymerization, the DMF solution polymerization proceeds smoothly. In this regard, the very similar trend of the polymerization can be observed in the MMA-polymerization as described above (see Figure 2). As also mentioned there, such a effect of the polymerization solvent is unlikely in conventional radical polymerization. In brief, in this case as well, the unique polymerization behavior in spite of radical polymerization can be confirmed once again. In particular, the large difference in polymerization activity depending on the polymerization solvent suggests the possibility of controlling the polymerization reaction by selecting or mixing the polymerization solvent, and the author plans to reexamine this possibility in the near future. Taking all of this into account, regarding the polymerization using [edmm]Br as an polymerization initiator, when the target vinyl monomer is MMA, MA, or *n*-BA, the polymerization behavior is common and that is different from conventional radical polymerization. In this sense, the versatility of [edmm]Br as a special radical polymerization initiator can be confirmed.

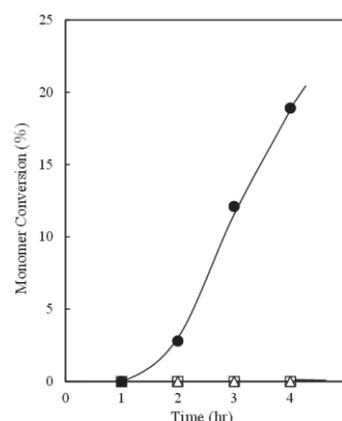


Figure 9. Effects of solvents on the polymerization of *n*-BA initiated with [edmm]Br. *n*-BA 3.5 mmol, [edmm]Br 0.035 mmol solvent 1.0 ml, under air, 90 °C, solvent: (●) DMF, (□) toluene, (△) DMSO.

Polymerization of MMA Initiated with [edmim]Cl Under Various Polymerization Conditions

Meanwhile, in the same idea as experiments so far, in this section, the author examines the polymerization behavior of MMA initiated with [edmim]Cl, in which the anion structure of [edmim]Br, discussed in the previous section, is replaced with another halogen. Continuing from the previous section, the author first considers the influence of the polymerization solvent as a basic polymerization behavior. So, as an example roughly corresponding to

Figure 2, Figure 10 shows the conversion percentages versus the reaction time together on the MMA-polymerization in DMF, DMSO, and toluene initiated with [edmim]Cl under air atmosphere at 70 °C. Observing Figure 10, although the reactivity of the DMF solution polymerization is superior as compared with the perfect inhibition of the DMSO solution polymerization and the toluene solution polymerization. As has been repeatedly stated, the polymerization solution effect observed here is difficult to imagine in conventional radical polymerization, and in this sense, it can be said that this polymerization is unique. Simultaneously, this polymerization behavior is almost the same as that of the polymerization of MMA using [edmim]Br as an initiator under the roughly same polymerization conditions described above (see Figure 2), but it can be confirmed that the polymerization activity of MMA-polymerization initiated with [edmim]Cl is higher than that initiated with [edmim]Br. As an important fundamental polymerization behavior, the effect of polymerization temperature is discussed next. Specifically, Figure 11 illustrates the time-conversion plots with respect to the polymerization temperature at 60 °C, 70 °C, and 80 °C on the DMF solution polymerization of MMA initiated with [edmim]Cl under air atmosphere. As Figure 11 shows, the tendency that the polymerization rate increases with increasing the polymerization temperature can be observed. In a word, in contrast to the polymerization rate

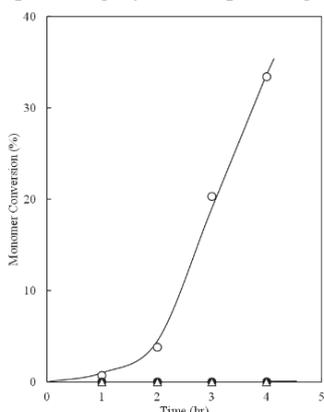


Figure 10. Effect of solvents on the polymerization of MMA initiated with [edmim]Cl. MMA 4.7 mmol, [edmim]Cl 0.047 mmol, under air, 70 °C, solvent: (○) DMF, (●) toluene, (△) DMSO.

increases with increasing the polymerization temperature at 70 °C and 80 °C, the polymerization at 60 °C is perfectly inhibited. As mentioned above, the polymerization behavior obtained here in which the polymerization activity is lost with a slight polymerization temperature difference of about 10 °C can also be seen in the polymerization initiated with conventional radical polymerization initiators such as azobisisobutyronitrile and benzoylperoxide. In the meanwhile, for the more detailed discussion about the effects of polymerization temperature, as the additional data of Figure 11, Table 2 lists the time-conversion data and the GPC results (\overline{M}_n and $\overline{M}_w / \overline{M}_n$) of the MMA-

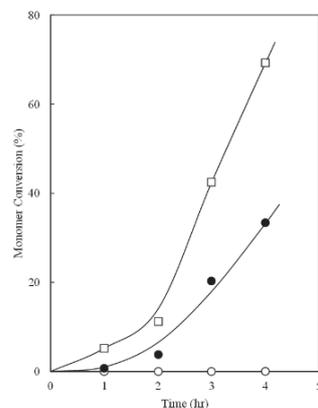


Figure 11. Effect of temperature on the polymerization of MMA initiated with [edmim]Cl in DMF. MMA 4.7 mmol, [edmim]Cl 0.047 mmol, DMF 1.0 ml, under air, temperature: (○) 60 °C, (●) 70 °C, (□) 80 °C.

increases with increasing the polymerization temperature at 70 °C and 80 °C, the polymerization at 60 °C is perfectly inhibited. As mentioned above, the polymerization behavior obtained here in which the polymerization activity is lost with a slight polymerization temperature difference of about 10 °C can also be seen in the polymerization initiated with conventional radical polymerization initiators such as azobisisobutyronitrile and benzoylperoxide. In the meanwhile, for the more detailed discussion about the effects of polymerization temperature, as the additional data of Figure 11, Table 2 lists the time-conversion data and the GPC results (\overline{M}_n and $\overline{M}_w / \overline{M}_n$) of the MMA-

Table 2. Effect of Temperature on the Polymerization of MMA Initiated with [edmim]Cl in DMF^a

Entry	Time (min)	Temperature (°C)	Conversion (%)	\overline{M}_n^b	$\overline{M}_w/\overline{M}_n^b$
1	60	60	0.0	—	—
2	120	60	0.0	—	—
3	180	60	0.0	—	—
4	240	60	0.0	—	—
5 ^c	240	60	0.0	—	—
6	60	70	0.7	—	—
7	120	70	3.8	—	—
8	180	70	20.3	83000	2.37
9	240	70	33.4	88000	2.24
10 ^c	240	70	0.0	—	—
11	60	80	5.2	92000	1.62
12	120	80	11.2	53000	1.59
13	180	80	42.5	50000	1.70
14	240	80	69.3	61000	1.94
15 ^c	240	80	0.0	—	—
16	10	90	5.2	—	—
17	20	90	12.7	—	—
18	40	90	22.8	78000	1.95
19 ^c	40	90	23.3	83000	1.67

^aMMA 4.7 mmol, [edmim]Cl 0.047 mmol, DMF 1.0 ml, under air.

^bDetermined by GPC with standard polystyrenes (eluent: THF). ^c[edmim]Cl nil.

polymerization initiated with [edmim]Cl under air atmosphere in DMF at 60 °C, 70 °C, 80 °C, and 90 °C. One important thing to note from this table is that since the thermal self-initiated auto acceleration polymerization is perfectly inhibited at 60 °C, 70 °C, and 80 °C, it can be confirmed that [edmim]Cl itself certainly has the polymerization initiating ability (see Entries 5, 10, and 15 in Table 2). Contrary to this fact, the thermal self-initiated auto acceleration polymerization proceeds significantly at 90 °C. This fact suggests that the effect of thermal self-initiated auto acceleration polymerization at 90 °C is so great that [edmim]Cl cannot be evaluated as the polymerization initiator. Besides, the effects of radical polymerization inhibitor and radical chain transfer agent need to be discussed in order to obtain the minimum necessary information on the polymerization mechanism of MMA initiated with [edmim]Cl. As an example, Figure 12 shows the time-conversion plots of the DMF solution polymerization of MMA initiated with [edmim]Cl under air atmosphere at 80 °C with respect to the

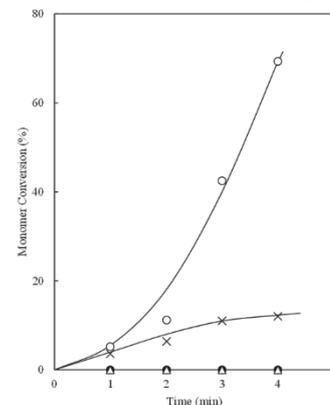


Figure 12. Effect of additives on the polymerization of MMA initiated with [edmim]Cl in DMF. MMA 4.7 mmol, [edmim]Cl 0.047 mmol, DMF 1.0 ml, additive 0.14 mmol, under air, 80 °C, additive: (○) nil, (●) HQ, (△) BHT, (×) 1-DT.

effects of 1-DT as a radical chain transfer agent and radical inhibitors such as HQ and BHT. It can be seen from this table that HQ and BHT completely inhibit the polymerization, and 1-DT strongly inhibits the polymerization. This polymerization behavior strongly suggests that the DMF solution polymerization of MMA initiated with [edmin]Cl under air atmosphere proceeds via a radical pathway. Furthermore, for the more detailed discussion about the effect of 1-DT, as the corresponding data of Figure 12, Table 3 lists the time-conversion data and the GPC results (\overline{Mn} and $\overline{Mw}/\overline{Mn}$) of the MMA-

Table 3. Effect of Additives on the Polymerization of MMA Initiated with [edmin]Cl in DMF^a

Entry	Time (hr)	Additive ^b	Conversion (%)	\overline{Mn}^c	$\overline{Mw}/\overline{Mn}^c$
1	1	(Nil)	5.2	92000	1.62
2	2	(Nil)	11.2	53000	1.59
3	3	(Nil)	42.5	50000	1.70
4	4	(Nil)	69.3	61000	1.94
5	1	HQ	0.0	-----	-----
6	2	HQ	0.0	-----	-----
7	3	HQ	0.0	-----	-----
8	4	HQ	0.0	-----	-----
9	1	BHT	0.0	-----	-----
10	2	BHT	0.0	-----	-----
11	3	BHT	0.0	-----	-----
12	4	BHT	0.0	-----	-----
13	1	1-DT	3.6	17000	1.27
14	2	1-DT	6.4	13000	1.76
15	3	1-DT	11.0	23000	1.68
16	4	1-DT	12.0	21000	1.66
17 ^d	4	(Nil)	0.0	-----	-----

^aMMA 4.7 mmol, [edmin]Cl 0.047 mmol, DMF 1.0 ml, under air, 80 °C. ^b0.14 mmol.

^cDetermined by GPC with standard polystyrenes (eluent:THF). ^d[edmin]Cl nil.

polymerization initiated with [edmin]Cl under air atmosphere in DMF at 80 °C. The review of this table, it can be confirmed that the addition of 1-DT not only retards the polymerization rate, but also tends to reduce the molecular weight of the resulting polymer. This result again supports that the DMF solution polymerization of MMA initiated with [edmin]Cl under air atmosphere proceeds via a radical pathway. Regarding the influence of these additives, the study is also presented below when the polymerization temperature is lowered. In this sense, Table 4 exhibits the time-conversion data and the GPC results (\overline{Mn} and $\overline{Mw}/\overline{Mn}$) about the effects of 1-DT, HQ, and BHT on the DMF solution polymerization of MMA initiated with [edmin]Cl under air atmosphere at 70 °C. What should be noted in this

Table 4. Effect of Additives on the Polymerization of MMA Initiated with [edmin]Cl in DMF^a

Entry	Time (hr)	Additive ^b	Conversion (%)	\overline{Mn}^c	$\overline{Mw}/\overline{Mn}^c$
1	1	(Nil)	0.7	-----	-----
2	2	(Nil)	3.8	-----	-----
3	3	(Nil)	20.3	83000	2.37
4	4	(Nil)	33.4	88000	2.24
5	1	HQ	0.0	-----	-----
6	2	HQ	0.0	-----	-----
7	3	HQ	0.0	-----	-----
8	4	HQ	0.0	-----	-----
9	1	BHT	0.0	-----	-----
10	2	BHT	0.0	-----	-----
11	3	BHT	0.0	-----	-----
12	4	BHT	0.0	-----	-----
13	1	1-DT	0.8	-----	-----
14	2	1-DT	4.9	-----	-----
15	3	1-DT	4.1	-----	-----
16	4	1-DT	6.0	16000	1.37
17 ^d	4	(Nil)	0.0	-----	-----

^aMMA 4.7 mmol, [edmin]Cl 0.047 mmol, DMF 1.0 ml, under air, 70 °C. ^b0.14 mmol.

^cDetermined by GPC with standard polystyrenes (eluent:THF). ^d[edmin]Cl nil.

table is that HQ and BHT perfectly inhibit the polymerization, and 1-DT not only strongly inhibits the polymerization, but also reduces the molecular weight of the resulting polymer. That is to say, since it can be confirmed that the main polymerization behavior is the same as that of the polymerization at 80 °C under the same polymerization conditions shown in Figure 12 and Table 3, again supporting the idea that this polymerization proceeds via a radical pathway. So far, the author has shown the case where highly polar DMF is used as the polymerization solvent, but below, for comparison, the author describes the results of solution polymerization using toluene, which has a low polarity. As a representative example, Table 5 lists the time-conversion data together with the corresponding GPC results of the MMA-polymerization initiated with

Table 5. Effect of Temperature on the Polymerization of MMA Initiated with [edmin]Cl in Toluene^a

Entry	Time (min)	Temperature (°C)	Conversion (%)	\overline{Mn}^b	$\overline{Mw}/\overline{Mn}^b$
1	60	70	0.0	-----	-----
2	120	70	0.0	-----	-----
3	180	70	0.0	-----	-----
4	240	70	0.0	-----	-----
5 ^c	240	70	0.0	-----	-----
6	60	80	2.0	-----	-----
7	120	80	22.3	80000	1.92
8	180	80	28.3	80000	1.65
9	240	80	31.1	85000	1.65
10 ^c	240	80	0.0	-----	-----
11	10	90	1.0	100000	2.72
12	20	90	8.6	47000	1.80
13	30	90	14.6	51000	2.12
14	40	90	21.8	43000	1.69
15 ^c	40	90	0.0	-----	-----

^aMMA 4.7 mmol, [edmin]Cl 0.047 mmol, toluene 1.0 ml, under air.

^bDetermined by GPC with standard polystyrenes (eluent:THF). ^c[edmin]Cl nil.

[edmin]Cl under air atmosphere in toluene at 70 °C, 80 °C, and 90 °C. Seen from this table, in contrast to the data of the DMF solution polymerization under the almost same polymerization condition that is summarized in Table 2, the thermal self-initiated auto acceleration polymerization is perfectly inhibited even at high temperatures of 90 °C. (see Entry 15 in Table 5). This means that [edmin]Cl itself certainly has the polymerization initiating ability at 90 °C. Furthermore, the significant difference between the DMF solution polymerization and the toluene solution polymerization can be recognized as follows. First, the polymerization initiating temperature is 70 °C or higher in the DMF solution polymerization, whereas it is 80 °C or higher in the toluene solution polymerization. More interestingly, in the DMF solution polymerization, the polymerization rate increases with increasing the polymerization temperature, but in the toluene solution polymerization, the polymerization rate at 90 °C is slower than that at 80 °C. Furthermore, comparing the polymerizations at 80 °C, the polymerization rate is faster in the DMF solution polymerization, but the molecular weight of the resulting polymer is larger in the toluene solution polymerization (see Entries 11-14 in Table 2, and see Entries 6-9 in Table 5). From these viewpoints, the polymerization rate and the molecular weight of the resulting polymer are controlled by the type of polymerization solvents can be suggested. On the other hand, here again, as their part of obtaining basic information

on the polymerization mechanism, the effects of adding radical polymerization inhibitors and radical chain transfer agents are discussed. Figure 13 shows the time-conversion plots of the toluene solution polymerization of MMA initiated with [edmim]Cl under air atmosphere at 80 °C with respect to the effects of 1-DT as a radical chain transfer agent and radical inhibitors such as HQ and BHT. Incidentally, Figure 13 corresponds to Figure 12, which shows DMF solution polymerization. As can be seen from this table, that since HQ and BHT perfectly inhibit the polymerization, it can be strongly suggests that the toluene solution polymerization of MMA initiated with [edmim]Cl under air atmosphere proceeds via a radical pathway as well as the DMF solution polymerization as mentioned above. However, unlike Figure 12, the unique polymerization behavior can be observed in which the polymerization is accelerated by the addition of 1-DT. Furthermore, as shown in Table 6, which is the corresponding data of Figure 13

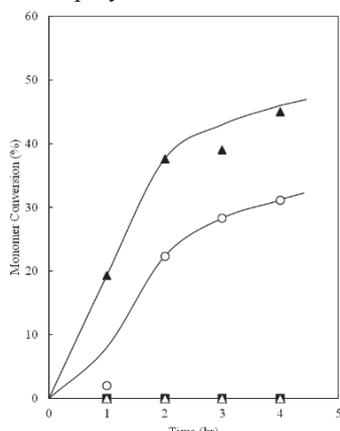


Figure 13. Effect of additives on the polymerization of MMA initiated with [edmim]Cl in toluene. MMA, 4.7 mmol; [edmim]Cl, 0.047 mmol; toluene, 1.0 ml; additive, 0.14 mmol, under air, 80 °C; additive: (○) nil, (●) HQ, (△) BHT, (▲) 1-DT.

Table 6. Effect of Additives on the Polymerization of MMA Initiated with [edmim]Cl in Toluene^a

Entry	Time (hr)	Additive ^b	Conversion (%)	M_n^c	M_w/M_n^c
1	1	(Nil)	2.0	—	—
2	2	(Nil)	22.3	80000	1.92
3	3	(Nil)	28.3	80000	1.65
4	4	(Nil)	31.1	85000	1.65
5	1	HQ	0.0	—	—
6	2	HQ	0.0	—	—
7	3	HQ	0.0	—	—
8	4	HQ	0.0	—	—
9	1	BHT	0.0	—	—
10	2	BHT	0.0	—	—
11	3	BHT	0.0	—	—
12	4	BHT	0.0	—	—
13	1	1-DT	19.3	9000	1.31
14	2	1-DT	37.6	8000	1.52
15	3	1-DT	39.0	8000	1.54
16	4	1-DT	45.0	3000	2.68
17 ^d	4	(Nil)	0.0	—	—

^aMMA 4.7 mmol, [edmim]Cl 0.047 mmol, toluene 1.0 ml, under air, 80 °C. ^b0.14 mmol.

^cDetermined by GPC with standard polystyrenes (eluent:THF). ^d[edmim]Cl nil.

including the GPC results, there is no clear tendency for the addition of 1-DT to decrease the molecular weight of resulting polymer. The significant difference in the effect of adding such a radical chain transfer agent in the DMF solution polymerization and the toluene solution polymerization may be related to the polarity of the solvent, and this will be examined in detail in the future. As an overview, this study summarizes the results of investigating the polymerization behavior of MMA, MA, and *n*-BA under various polymerization conditions using imidazolium ionic liquids [edmim]Br and [edmim]Cl as polymerization initiators. Following this study, the author's laboratory is currently conducting the industrial applications in regard to

the polymerization initiated with many kinds of imidazolium ionic liquids.

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イミダゾリウムイオン液体のラジカル重合開始能に関する研究

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キーワード : 1-エチル-2,3-ジメチルイミダゾリウム臭化物, 1-エチル-2,3-ジメチルイミダゾリウム塩化物, メタクリル酸メチル, アクリル酸メチル, ラジカル重合開始剤

2005年に著者はイオン液体がラジカル重合を開始する能力があることを初めて明らかにした。しかし、著者はこの重合の詳細な重合機構を明らかにするには至っていない。本研究の目的は、イオン液体を開始剤とするラジカル重合の重合機構を明らかにする一環として、様々な重合条件下における重合挙動を検討することにある。本研究では、イミダゾリウムイオン液体に着目しているが、その理由としては、イミダゾリウムイオン液体は1980年代からイオン液体の研究が活発になった際にさかんに扱われた物質であることも考慮している。様々な重合条件下で、1-エチル-2,3-ジメチルイミダゾリウム臭化物 ([edmim]Br) や1-エチル-2,3-ジメチルイミダゾリウム塩化物 ([edmim]Cl) などのイミダゾリウムイオン液体で開始したメタクリル酸メチル (MMA)、アクリル酸メチル (MA)、アクリル酸-*n*-ブチル (*n*-BA) の重合を詳細に検討している。言うまでもなく、これら2つのイオン液体は同一の多置換イミダゾリウムカチオン構造を有する。80 °Cで[edmim]Brで開始したMMAの*N,N*-ジメチルホルムアミド (DMF) 溶液重合に関しては、空気雰囲気下では重合がスムーズに進行するのに対し、アルゴン雰囲気下では重合が強く阻害される。空気中の酸素分子がラジカル重合禁止剤の役割を果たしている場合が多いため、この重合挙動は従来のラジカル重合とは異なり独特である。この独特な重合挙動は、ほぼ同じ重合条件下で[edmim]Brで開始されたMAおよび*n*-BAの重合でも観察される。空気雰囲気下で[edmim]Brを用いて開始されるMMA重合のもう一つのユニークな点は、重合反応が重合溶媒に強く依存することである。より正確には、重合温度80 °Cでは、四塩化炭素溶液重合、トルエン溶液重合、およびDMSO溶液重合が完全に阻害されるのとは対照的に、DMF溶液重合のみがスムーズに進行する。DMF溶液重合のみが円滑に進行するというこの重合挙動は、空気雰囲気下90 °Cで[edmim]Brで開始した*n*-BA重合、および空気雰囲気下70 °Cで[edmim]Clで開始したMMA重合において観察される。ちなみに、80 °Cの空気雰囲気下でのMMAのDMF溶液重合では、[edmim]Clが[edmim]Brよりも高い重合開始活性を示しており、ハロゲンアニオンが重合開始剤としての特性に大きな影響を与えていることが示されており、非常に興味深い。一方、重合機構に関する必要最低限の情報を得るためには、1-ドデカンチオール (1-DT) などのラジカル連鎖移動剤や、ヒドロキノン (HQ)、2,6-ジ-*tert*-ブチル-*p*-クレゾール (BHT) などのラジカル重合禁止剤を添加した検討が重要である。80 °Cの空気雰囲気下で[edmim]Brで開始されるMMAのDMF溶液重合、および90 °Cの空気雰囲気下で[edmim]Brで開始される*n*-BAのDMF溶液重合については、1-DT・HQ・BHTは重合を完全に阻害する。さらに、70 °Cおよび80 °Cの空気雰囲気下で[edmim]Clで開始したMMAのDMF溶液重合、および80 °Cの空気雰囲気下で[edmim]Clで開始したMMAのトルエン溶液重合は、HQおよびBHTの添加によって完全に阻害される。これらの結果は、空気雰囲気下で[edmim]Brまたは[edmim]Clによって開始されるビニル重合がラジカル経路を介して進行することを強く示唆される。重合温度の観点から見ると、空気雰囲気下で[edmim]Brで開始したMAのDMF溶液重合の重合速度は、重合温度範囲70 °C~90 °C内で重合温度の上昇とともに増加する。同時に、空気雰囲気下で[edmim]Clで開始したMMAのDMF溶液重合速度に関しては、70 °Cおよび80 °Cでの重合温度の上昇とともに重合速度が増加するのとは対照的に、60 °Cでの重合は完全に阻害される。10 °C程度のわずかな重合温度差で重合活性が失われるという重合挙動は、アゾビスイソブチロニトリルや過酸化ベンゾイルなどの従来のラジカル重合開始剤で開始した重合でも見られる。さらに、このような重合挙動は、トルエン溶媒中、空気雰囲気下で[edmim]Clで開始したMMA重合でも観察され、80 °Cでは重合はスムーズに進行しますが、70 °Cでは重合は完全に阻害される。さらに興味深いのは、DMF溶液重合では重合温度の上昇とともに重合速度が増加するが、このトルエン溶液重合においては90 °Cでの重合速度は80 °Cでの重合速度よりも遅いことである。一方、80 °Cでの重合を比較すると、DMF溶液重合の方が重合速度は速いが、得られるポリマーの分子量はトルエン溶液重合の方が大きい。これらの観点から、空気雰囲気下で[edmim]Clを用いて開始したMMA重合では、重合速度と得られるポリマーの分子量は重合溶媒の種類によって制御できることが示唆される。重合開始剤としての[edmim]Brまたは[edmim]Clの多数の実験結果は、それらの独特のラジカル重合開始能力を示している。著者は、このラジカル重合の詳細なメカニズムを解明するだけでなく、陰イオンと陽イオンの組み合わせの観点から、より魅力的なラジカル重合開始剤としてのイオン液体の開発についても引き続き検討している。

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