Highly Controlled Organotellurium-Mediated Living Radical Polymerization (TERP) in Ionic Liquids (ILs). The New Role of ILs in Radical Reactions

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Ⓢ *Supporting Information*

ABSTRACT: Ionic liquids (ILs) served perfectly as solvents for the organotellurium-mediated living radical polymerization (TERP) of methyl methacrylate (MMA), methyl acrylate (MA), and styrene. The reaction rate of polymerizing MMA and MA was significantly increased as previously reported, and the controllability of the polydispersity index (PDI) was also improved by a great margin. The TERP of MMA can now give poly(methyl methacrylates) (PMMAs) with PDIs less than 1.1 and nearly full conversion in a half hour without the presence of $(TeMe)_2$. The kinetic study revealed that the improved control could be ascribed to a faster degenerative chain transfer (DT) reaction which plays a key role in the control of PDI for TERP. Besides the polar effect of ILs, the existence of Lewis acid–base interaction between ILs and the Te atom was proven by UV–vis spectroscopy and ^{125}Te NMR results. Such positive interaction lowered the activation energy of the DT process.
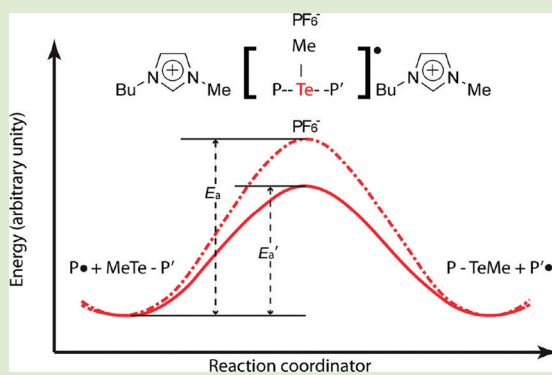
Living radical polymerization (LRP) has become an indispensable method for the synthesis of structurally well-defined polymers with improved and/or novel properties.[1−9] Among various LRP methods developed so far, organo-tellurium-mediated living radical polymerization (TERP) together with organostibine- and organobismuthine-mediated living radical polymerization (SBRP and BIRP, respectively) are one of the most synthetically valuable methods,[10−12] such as the high versatility of monomer families, high compatibility toward functional groups and solvents,[13−17] and ease of the living-end transformation for the synthesis of block copolymers[18−22] and end-functionalized polymers.[23−26] We have already reported that control of the polymerization is significantly enhanced by the addition of diheteroatom compounds[18,25,27,28] and by altering the substituent on the heteroatom.[29] However, the invention of new and practical methods is awaited to further increase the precise control of structure of macromolecules and their physical properties.

Ionic liquids (ILs) have been attracted a great deal of attention as a novel reaction medium not only due to their "green" nature, such as nonvolatileness, reusability, and low flammability,[30,31] but also because of their unique physical properties to increase the solubility of polar and nonpolar solutes and to alter the reactivities of reactive intermediates.[32] ILs have already used as a solvent for conventional radical polymerization and LRP,[33−37] such as atom transfer radical polymerization (ATRP),[38−44] single-electron transfer living

radical polymerization (SET-LRP),[45] reversible addition−fragmentation chain transfer polymerization (RAFT),[46,47] nitroxide mediated polymerization (NMP),[48,49] and SBRP.[50] Two significant features have been reported in methacrylate polymerization; one is the faster rate of the propagation in ILs than in bulk or conventional solvents due to the polar effect, which stabilizes the transition state involving a polar polymer-end radical and a monomer.[34,51−54] The other is the slower termination reaction in ILs due to the viscosity effect.[52,55] These features resulted in the formation of high molecular weight poly(methyl methacrylate) (PMMA) under conventional conditions. They would also benefit for LRP giving better livingness to preserve chain end functionality from low to high molecular weight polymers.[56]

During the course of utilizing ILs as a solvent for TERP, we found that not only TERP was compatible with ILs but also the control of TERP was significantly increased in ILs (Scheme 1). Kinetic studies revealed that the increase of the control is mainly due to the significant rate enhancement of the degenerative chain transfer (DT) reaction between polymer-end radical and organotellurium dormant species, which is the key mechanism for the control of molecular weight distribution in TERP.[57−59] This result represents the first example for a

Scheme 1. TERP in an Ionic Liquid (IL)
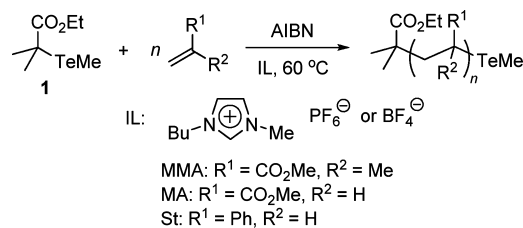
significant increase of the reactivity of this type of radical reaction by external media. The TERP of (meth)acrylates in ILs was also completed in a shorter period than in bulk and conventional solvents. Therefore, ILs serve as ideal media to carry out TERP.

We first examined the TERP of methyl methacrylate (MMA) (100 equiv) in 1-butyl-3-methylimidazolium ([Bmim]PF$_6$) (MMA/[Bmim]PF$_6$ = 1:4 v/v) in the presence of ethyl 2-methyltellanylisobutyrate (**1**) and AIBN (1.0 equiv). Quantitative monomer feed was observed upon heating at 60 °C for 0.5 h, and highly controlled PMMA with a predicted number-average molecular weight from MMA/**1** and narrow polydispersity index (PDI = 1.08) was formed (Table 1, entry 1). The TERP of MMA in [Bmim]BF$_4$ also gave well-controlled PMMA at an early stage of the polymerization, though the phase separation of PMMA started as the increase of MMA feed (entry 2).

The rate of monomer feed as well as the control of PDIs decreased with the increase of initial MMA concentration over the IL (MMA/[Bmim]PF$_6$ = 4:1 to 1:2 v/v, see Supporting Information for the kinetic plots), suggesting the importance of the bulk amount of IL (entry 1 vs 3 and 4). The observed effect of ILs on the rate of polymerization as well as the increase of the control are consistent with the previous reports; the observed dramatic increase of PDI control cannot be explained simply by the viscosity effect (see below). While the control of PDIs slightly decreased in entries 3 and 4 compared to that of entry 1, the rate of polymerization as well as the control of PDI was still better than the previous condition in bulk (entry 8). The PDI control was increased by the addition of dimethyl

ditelluride as already reported (entry 9),[18,27] but no significant rate enhancement was observed. PMMAs with high molecular weights ($\sim M_n$ = 1.7 × 10^5) were prepared in a highly controlled manner within 1 h by increasing the amount of MMA over **1** with keeping the same IL/MMA ratio (entries 6 and 7).

TERP of methyl acrylate (MA) was also investigated in [Bmim]PF$_6$ under otherwise identical conditions. Highly controlled poly(methyl acrylate) (PMA) with a PDI of 1.06 was obtained (entry 10). While the rate of polymerization in the IL could not be rigorously compared to that in bulk due to the high propagation rate constant, a faster monomer conversion was suggested in ILs than in bulk. In addition, PMA with a smaller PDI was formed in IL that in bulk (entry 10 vs 11). The TERP of styrene in [Bmim]PF$_6$ also showed higher PDI control than that in the bulk, while no significant rate enhancement was observed (entry 12 vs 13). The insensitivity of the rate of polymerization in styrene polymerization can be attributed to the less polar character of the addition reaction of polystyrene radical to styrene than that of PMMA or PMA radicals to MMA or MA, respectively.[54]
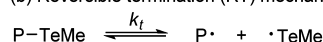
Kinetic experiments were carried out to clarify the origin of the PDI control in ILs. TERP predominantly proceeds by the DT mechanism for the activation/deactivation of dormant/radical species (Scheme 2a), and the increase of the rate of DT

Scheme 2. Activation/Deactivation Mechanism of Dormant/Radical Species in TERP
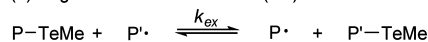
reaction (k_{ex}) relative to the rate of propagation reaction (k_p), namely, the larger exchange constant C_{ex} (= k_{ex}/k_p), leads to the narrower PDI.[58] Indeed, we have already reported that organotellurium-chain transfer agents with an aryl-substituted tellanyl group exhibit higher k_{ex} and thus higher PDI control than those having an alkyl-substituted tellanyl group.[29]

Table 1. TERP of Methyl Methacrylate (MMA), Methyl Acrylate (MA), and Styrene (St) in Bulk or ILs at 60 °C[a]

entry	monomer (equiv)	ratio (m/s)[b]	time (h)	conv.[c] (%)	M_n[d] (theo)	M_n[d] (exp)	PDI[d]
1	MMA (100)	1/4	0.5	98	9900	10200	1.08
2[e]	MMA (100)	1/4	0.1	30	3100	3600	1.09
3	MMA (100)	1/1	1	100	10100	11400	1.11
4	MMA (100)	4/1	1	90	9100	10100	1.15
5	MMA (500)	1/4	0.5	89	44600	45200	1.07
6	MMA (1000)	1/4	1	88	88100	89800	1.09
7	MMA (2000)	1/4	1	85	170100	169700	1.12
8[f]	MMA (100)		2	98	9900	11000	1.28
9[f,g]	MMA (100)		2	96	9700	9800	1.10
10	MA (100)	2/1	1	89	7770	8200	1.06
11[f]	MA (100)		1	70	6100	6900	1.13
12	St (100)	2/1	4	54	5700	5500	1.05
13[f]	St (100)		4	50	5300	5300	1.10

[a]All reactions were carried out in N$_2$ atmosphere by mixing **1**, AIBN (1.0 equiv), monomer, and [Bmim]PF$_6$. [b]Ratio (m/s) stands for volume ration of monomer and solvent. [c]The conversion were determined by ^{1}H NMR except for entries 2−4, 10, and 11, of which were determined gravimetrically. [d]M_n(exp) and PDIs were obtained by gel permeation chromatography calibrated by PMMA standards for entries 1−11 and polystyrene standards for others. [e]TERP was carried out in [Bmim]BF$_4$ instead of [Bmim]PF$_6$. [f]TERP was carried out in bulk. [g]Dimethyl ditelluride (1.0 equiv) was added.

A PMMA-TeMe macroinitiator was prepared and subjected to kinetic analysis using the protocol developed by Fukuda et al.[60] It was found that the k_{ex} in MMA polymerization in $[Bmim]PF_6$ was 11 times higher than that in the bulk (Table 2, entry 1 vs 2). While the k_p also increases two times more in $[Bmim]PF_6$ than that in bulk, the rate enhancement in k_{ex} is more pronounced than in k_p. The C_{ex} value in bulk (3.7) is not sufficient to obtain well-defined PMMA, but that in the IL (14) is sufficiently high to achieve efficient control. Therefore, the increase of the exchange constant C_{ex} ($= k_{ex}/k_p$) must be the major reason for the increase of PDI control. While reversible termination (RT) also contributes to the activation of the dormant species in TERP to a small extent (Scheme 2b),[57,59] the effect of ILs on RT was negligible.

We next analyzed the kinetics of TERP of MA using PMA-TeMe (Table 2). A slightly higher C_{ex} value was obtained in

Table 2. Kinetic Parameters, k_{ex}, k_p, and C_{ex} in TERP of MMA, MA, and Styrene in Bulk and $[Bmim]PF_6$ at 60 °C[a]

entry	P-TeMe	solvent[b]	k_{ex}[c] (M^{-1} s^{-1})	k_p[d] (M^{-1} s^{-1})	C_{ex}[c]
1	PMMA-TeMe	bulk	3.0×10^3	8.3×10^2	3.7
2	PMMA-TeMe	IL	3.6×10^4	2.6×10^3	14
3	PMA-TeMe	bulk	4.6×10^5	2.4×10^4	19
4	PMA-TeMe	IL			22
5	PSt-TeMe	bulk	5.8×10^3	3.4×10^2	17
6	PSt-TeMe	IL	8.5×10^3	3.4×10^2	25

[a]k_p and k_{ex} refer to the rate constants of propagation and degenerative chain transfer (Scheme 2), and C_{ex} ($= k_{ex}/k_p$) is the exchange constant. [b]The IL is denoted as $[Bmim]PF_6$. The volume ratio of monomer/solvent for MMA, MA, and St was 1:4, 2:1, and 2:1, respectively. [c]k_{ex} and C_{ex} of bulk polymerization of PMMA, PMA, and PSt are from ref 59. C_{ex} of $[Bmim]PF_6$ system are from this work (see Supporting Information), and the related k_{ex} are obtained by calculation from $C_{ex} = k_{ex}/k_p$. [d]Taken from ref 59 and ref 53 for the 1:4 MMA/$[Bmim]PF_6$ system; the k_p of 2:1 St/$[Bmim]PF_6$ system is assumed to be unchanged.

the IL than in bulk (run 3 vs 4), though the k_{ex} value could not be determined due to the lack of the k_p data of MA in ILs. The results suggest that the same level of rate enhancement occurs for both the propagation and the DT reactions in ILs. The C_{ex} value in styrene polymerization in the IL was 1.5 times faster than that in bulk (run 5 vs 6). Since the propagation rates are insensitive to the ILs, only the k_{ex} was slightly increased by the IL.

The UV−vis and ^{125}Te NMR were measured to obtain insight into the effect of ILs (see Figure 1). The specific UV absorption of **1** corresponding to the $n(Te)−\sigma^*(C\text{-Te})$ transition at λ_{max} = 388 nm (in CH_2Cl_2)[16] was blue-shifted to 382, 381, and 375 nm by the addition of $[Bmim]X$ (X = PF_6, BF_4, and Cl), respectively. The results may suggest that, in addition to the effects of polar solvents, the existence of Lewis acid−base type or charge-transfer interaction between ILs and Te atom, thus lowering the energy level of the n orbital.

The ^{125}Te NMR of **1** in CD_2Cl_2 ($= 641.66$ ppm) showed downfield shifts upon the addition of $[Bmim]PF_6$ (see Supporting Information for details). A downfield shift at about 1 ppm was observed by the addition of ca. 0.5 equiv of $[Bmim]PF_6$ to **1**, and the chemical shift further shifted downfield about 1.6 and 2.7 ppm upon the addition of 2 and 10 equiv of $[Bmim]PF_6$, respectively. The results are also
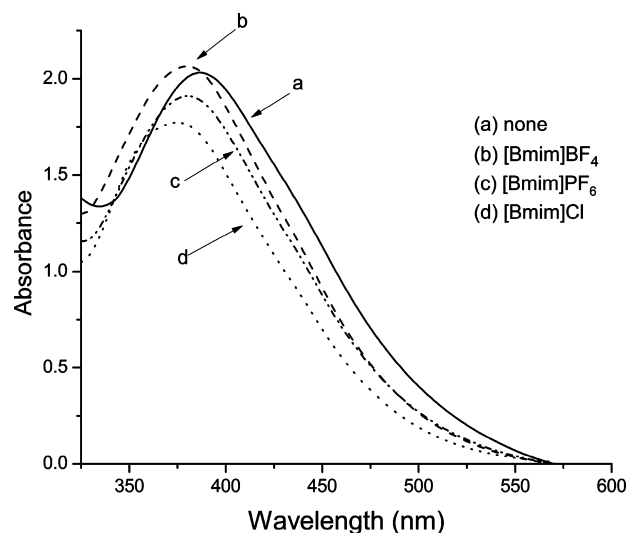

Figure 1. UV−vis spectra of **1** in CH_2Cl_2 and 2.5 g of $[Bmim]X$ (X = PF_6 or BF_4 or Cl) in 5 mL of CH_2Cl_2.

consistent with the existence of the Lewis acid−base type interaction between $[Bmim]PF_6$ and **1**.

The polystyrene radical and styrene are classified as a nonpolar radical and a radical acceptor, respectively, whereas P(M)MA radicals and (M)MA are polar radicals and radical acceptors, respectively.[54] Therefore, the reaction of the former pair is less polarized than the latter pair and less prone to be stabilized by polar media, such as ILs. While there is no report on the effect of polar media on the DT reaction so far, the transition state of the DT which involves P(M)MA radical and dormant species may be significantly polarized and is stabilized by ILs. The transition state in the DT reaction may be more polarized than that in the addition reaction, and the former reaction is more stabilized by ILs than the latter. More experimental as well as theoretical studies must be needed to clarify this point.

In summary, we have demonstrated that TERP is positively affected by ILs. The faster reaction speed, no need of $(TeMe)_2$ to gain high control, ease of separation of polymer from the IL, and recycling of ILs would be highly advantageous for the industrial processes. These features suggest that ILs serve as ideal media to carry out TERP. Furthermore, the striking rate enhancement of the DT reaction is highly intriguing. Since this type of radical reaction also plays important role in the atom- and group transfer radical addition reaction in organic synthesis,[61,62] the use of ILs for these reactions would be also of great interest.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Experimental details, kinetic plots, and ^{125}Te NMR results. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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