Chapter 8
Reversible Addition-Fragmentation Chain Transfer (RAFT) Polymerization in Ionic Liquids: A Sustainable Process

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Abstract Ionic liquid (IL) is an important class of materials which have asymmetric organic cation and inorganic anion. Most of the ILs remain as liquids at ambient temperature and are non-toxic in nature. They have low-to-zero vapor pressure and high thermal stability and have the potential to replace many volatile organic solvents. They have several advantages over conventional solvents and are considered as 'green' solvents. In polymer science, they are used as solvents for polymerization as well as an additive in polymer processing. In this case, IL was used as the solvent for the polymerization of different acrylates via a reversible addition-fragmentation chain transfer (RAFT) process, a method of controlled radical polymerization. RAFT polymerization in IL was observed to be remarkably fast. The IL used in the polymerization process was successfully recovered and reused without any loss in efficiency or efficacy. It was also observed that the presence of even a small amount of IL can increase the rate of polymerization.

Keywords Ionic liquids · RAFT polymerization · Green solvents · Sustainable solvents · Kinetics · Recycling · Furfuryl methacrylate · Butyl methacrylate

1 Introduction

Ionic liquids (ILs) are organic salts with asymmetric ions that remain as liquids below 100 °C. The common ILs are made of organic cations based on imidazolium, ammonium, and pyridinium organic compounds, and anions include halides, nitrates, hexaflluorophosphates, tetrafluoro borates, fluorosulfonylamides, etc. The properties of ILs depend on these constituting ions. There are numerous combinations of the ions including binary and ternary mixtures which can be used to tailor-make ILs with task-specific properties. The polarity, melting temperature, miscibility, and solvation are a few examples of properties that can be easily manipulated by changing

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the constituting ions of the ILs, which earned ILs its rightful name ‘designer solvents.’ For example, increasing the alkyl chain length of the imidazolium cation, from methyl (T_m 125 °C) to butyl (T_m 65 °C) will reduce the melting point of the IL with the same counter anion significantly. As they are salts, they have no measurable vapor pressure, even at high temperature. Thus, they can be employed for high-temperature solvent applications up to 350 °C at relatively low pressure. They have thermal stability, no volatile organic content (VOC), no vapor pressure at higher temperature, combined with its ability to recycle increases the environmental safety of these solvents. Hence, they are referred to as ‘green’ solvents. ILs are generally non-corrosive, non-flammable, and viscous solvents compared to common organic solvents. Their polarity is similar to that of alcohols. ILs have been used as solvents for organic reactions for more than a decade. They interact with the solutes through weak van der Waals forces [1], dispersion forces, strong hydrogen bonding [2], dipole–dipole, and ionic interactions [3]. In 1990, Carlin et al. [4] first used IL as a solvent for polymerization with Ziegler–Natta catalysis. Later in 2000, Noda et al. [5] described free radical polymerization in IL. In 2002, the first RAFT polymerization in IL was studied by Perrier et al. [6]. IL has been used as a solvent for a variety of polymerization reactions like polycondensation [7], cationic polymerization [8] other controlled radical polymerizations [9], and so on. It should be noted that the imidazolium-based ILs deactivate the anionic initiators, and hence anionic polymerization reaction is very tedious in ILs [10]. The ILs are known to increase the rate of polymerization reactions and increase the yield of polymer. For example, Vygodskii et al. [11] reported that PMMA produced in IL had molecular weight up to 5.7×10^6 Da. Even though it has been established that ILs increase the rate of polymerization, the exact mechanism for this positive effect is still speculative. There have been many reviews [12–16] and books [17–21] written on this topic.

2 Polymerization of Methacrylates in ILs

The RAFT polymerization of methacrylates such as furfuryl methacrylate (FMA) and butyl methacrylate (BMA) has been studied in different commercially available ionic liquids like 3-butyl-1-methyl imidazolium hexafluorophosphate (BMIM[PF_6]), 3-butyl-1-methyl imidazolium tetrafluoroborate (BMIM[BF_4]), and 3-ethyl-1-methyl imidazolium ethyl sulfate (EMIM[$EtOSO_3$]). These are room temperature ionic liquids with different counterions and varying polarity. FMA, a functional monomer, is polymerized using 2-cyano-2-propyl dodecyl trithiocarbonate (CPDTC) as a RAFT agent, thermally initiated and studied in both organic and ionic solvents and also in bulk conditions. BMIM[PF_6] is used, and it is relatively non-polar and is immiscible with water. The FMA is partially miscible with BMIM[PF_6], where mechanical stirring helps in achieving a homogenous mixture. The summary of the polymerization reactions and the polymers obtained are listed in the following table.

Table 1 shows that the IL offers a higher monomer conversion rate, both in case of high-temperature AIBN-initiated polymerization. It can also be noted that the

Table 1 Summary of RAFT polymerization of FMA using BMIM[PF_6] as IL and toluene as solvent[a]

S. no	RAFT agent	Solvent	Time (h)	Conversion (%)	$M_{n,\text{ GPC}}$ (g/mol)	$M_{n,\text{ theo}}$ (g/mol)	$Đ$
1	CPDTC	IL	1	98	9800	10,200	1.38
2	CPDTC	Toluene	1	27	5100	3100	1.28
3[b]	CPBDT	IL	5	40	3600	4400	1.05
6	CPDTC	Recycled IL	1.2	95	9100	9900	1.31
7[c]	CPDTC	–	1	98	Gelled	–	–
8	Without RAFT	IL	1	98	Gelled		

[a] [M]:[RAFT]:[Initiator] = 240:4:1, Temp^r = 70 °C, AIBN initiator, 2-cyano-2-propyl dodecyl trithiocarbonate as RAFT agent. [b] CPBDT, 2-cyano 2-propyl benzodithioate was used as RAFT reagent. [c] Polymerization is carried out in bulk at 70 °C

dispersity of the polymers obtained is narrow indicating a controlled polymerization reaction. In case of organic solvents, the monomer conversion is found to be low, and the molar mass distribution of the polymers is found to be broad in GPC. Also, it should be noted that the reactions in ILs are faster than the same in organic liquids. The polymerization is studied in bulk conditions with/without RAFT agents which resulted in gelation, rending the product useless. The IL used is recycled using chloroform/toluene, which is discussed later in the chapter, and the polymerization of FMA is studied in recycled IL also. It can be seen that the polymerization in recycled IL produces similar results as that of pure ILs, showing that ILs can be reused and it could be an alternate 'green' solvent to replace the organic solvents.

The question of the miscibility of monomer and the IL is important as it would directly affect the rate of polymerization. The FMA is polymerized with CPDTC which has a long aliphatic non-polar chain which could stabilize the monomer droplets in BMIM[PF_6]. This would form stabilized nano-droplets of monomer in IL and control the particle size of the polymer formed [22]. The particle size is measured to be 26 d.nm with Dynamic Light Scattering (DLS), and the histogram is shown in Fig. 1. To investigate further, another RAFT agent without a long-chain hydrocarbon is used to compare the particle size of the polymer. 2-cyano-2-propyl benzodithioate (CPBDT) is used, and the results are given in Table 1 and Fig 1. The absence of long-chain hydrocarbon leads to poor stabilization and Ostwald 'ripening,' and the particle size of the resulting polymer is not homogeneous (20, 1300 and 5100 d.nm) and it is found to be higher than that of the polymer polymerized by CPDTC. To show the stabilization effect of CPDTC RAFT, TEM images are taken of the FMA/BMIM[PF_6] mixture with CPDTC and shown in Fig. 2. The CPDTC provided good stabilization effect and a stable suspension with uniform particle size is obtained.

BMA is a relatively non-polar monomer found to be immiscible with the non-polar BMIM[PF_6] IL. This gives an opportunity to study the effects of IL on a monomer/IL

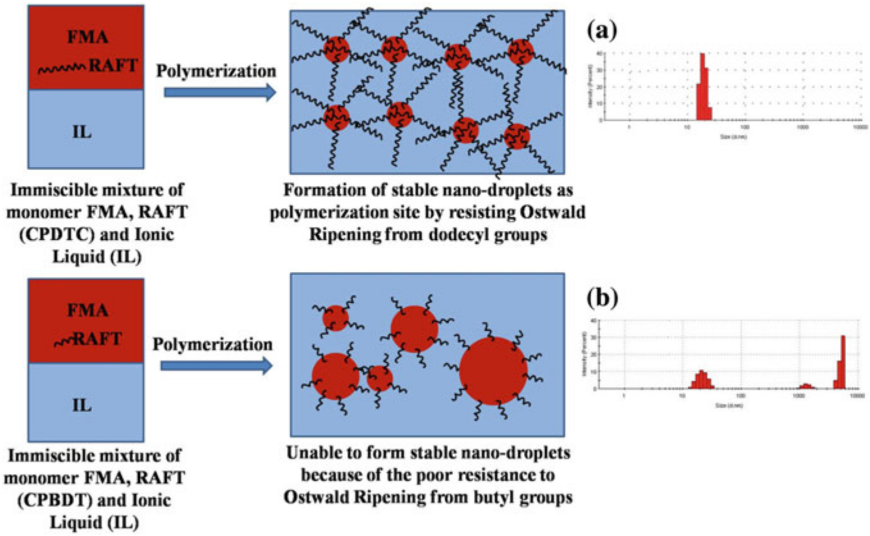


Fig. 1 Schematic representation of size variation of the particles in the presence of CPDTC (**a**) and CPBDT (**b**) RAFT reagent in FMA and IL mixture. Reproduced from Ref. [24] with permission from the Royal Society of Chemistry

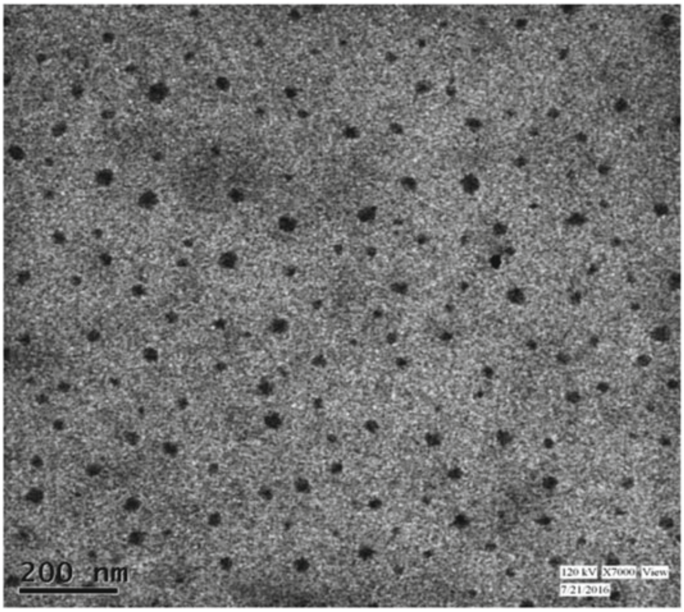


Fig. 2 TEM image of FMA in IL in the presence of CPDTC as the RAFT reagent. Reproduced from Ref. [25] with permission from the Royal Society of Chemistry

Table 2 Polymerization of BMA at different reaction conditions using AIBN as initiator[a]

S. no	Solvent	Time (h)	[M]/[RAFT]	Conversion (%)	$M_{n,\text{ Theo}}$ (g/mol)	$M_{n,\text{ GPC}}$ (g/mol)	Dispersity (Đ)
1	Bulk	2	120	81.3	13,900	12,700	1.31
2	Toluene	12	120	68.2	11,800	10,100	1.36
3	DMF	12	120	58.8	10,300	9500	1.33
4	BMIM[PF$_6$]	2	130	91.3	16,900	14,500	1.16

[a] [RAFT]:[Initiator] = 4:1, reactions carried out at 70 °C under N_2 atmosphere, 2-cyano-2-propyl dodecyl trithiocarbonate as RAFT agent. $M_{n,\text{Theo}} = \left(\rho \times \frac{[\text{Monomer}]}{[\text{RAFT}]} \times M_{w,\text{Monomer}}\right) + M_{w,\text{RAFT}}$; where ρ is the monomer conversion. Reproduced from Ref. [24] with permission from Elsevier

immiscible system. The polymerization of BMA is studied using RAFT agents like CPDTC and CPBDT in BMIM[PF$_6$] IL, DMF, toluene, and in bulk conditions. The summary of the study with the molecular weight and dispersity index of the polymer obtained are given in Table 2.

It is observed that ILs increase the rate of polymerization even in the case of immiscible monomer. The monomer conversion is also found to be high and the dispersity obtained is low compared to the organic solvents, indicating a narrow molar mass distribution. The polymerization is found to be faster than the organic solvents. At high polymerization rate, ILs also help to diffuse the heat generated during the reaction [23]. BMA is also polymerized in different ILs like BMIM[PF$_6$], BMIM[BF$_4$], and EMIM[EtOSO$_3$] and found to have varying rates of polymerization. This shows that ILs with different counter ions or different alkyl chain lengths have varying influence on the rate of polymerization. The synthesized PBMA polymer has been successfully used as a macro-RAFT to polymerize MMA monomer in IL, demonstrating block copolymerization in IL [24].

The polymers obtained, PBMA and PFMA, were characterized by NMR, GPC, MALDI-ToF, and DSC analyses [24, 25]. The absence of the resonances at $\delta = 6.4$ ppm corresponding to vinyl protons in ^{1}H NMR proved that there is no unreacted monomer in the polymer. Also, the NMR spectra did not show any impurities related to ILs being entrapped in the polymer. The chemical shift corresponding to –SCH$_2$ proton of the RAFT, which resonates at 3.2 ppm was used to calculate the molecular weight of the polymer. GPC analyses were carried with THF eluent to determine the molecular weight and dispersity of the polymers. In the block copolymerization of BMA and MMA, unimodal GPC traces were obtained, which confirmed the formation of block copolymers.

2.1 Polymerization Kinetics of Methacrylates in ILs

The ILs increase the rate of polymerization in both miscible and immiscible monomer systems. To investigate the influence of ILs, we studied the polymerization kinetics of both FMA and BMA in ILs with various reaction conditions. The kinetic plot of FMA polymerization is linear with the R^2 value approaching unity (0.99) showing the controlled nature of the RAFT polymerization in IL. The rate of polymerization is higher than that of organic solvents with k_{app} approximately 16 times higher in IL. Also, the dispersity of the polymer was below 1.4 throughout the molecular weight evolution which shows that ILs do not interfere with the RAFT process.

The polymerization kinetics of BMA has been studied in different ILs and also compared with different organic solvents. Figure 3 shows that the rate of polymerization is high in IL when compared to the same in organic solvents. The k_{app} in IL is approximately seven times higher than that of toluene, a common organic solvent used to polymerize BMA. When comparing the rate of polymerization in different ILs, the relatively non-polar BMIM[PF$_6$] accelerates the rate of polymerization more than the relatively polar BMIM[BF$_4$] [26]. When compared, the K_{app} of FMA (6.4×10^{-2} min^{-1}) and BMA (1.4×10^{-2} min^{-1}) in the same BMIM[PF$_6$], where the polarity of the FMA is closer to the IL, it is evident that the polarity of IL has a greater influence on the rate of polymerization of the monomer.

Taking BMIM[PF$_6$] as a model IL solvent, we studied the kinetics of BMA polymerization using different RAFT agents such as 2-(Dodecylthiocarbonothioylthio)-2-methylpropionic acid (CPCTP), 2-cyano-2-propyl dodecyl trithiocarbonate (CPDTC) with long-chain end groups and 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (DCTMP), 2-cyano-2-propyl benzodithioate (CPBDT) with phenyl group. As seen in Fig. 4, the RAFT agents with dodecyl functional groups offer a higher rate of polymerization. It was speculated that the long aliphatic chain (dodecyl) would stabilize the monomer in IL polymerization system to form nano-suspensions of monomer droplets. This explains the higher rate of propagation in long chain containing RAFT agents compared to those of phenyl active groups. Therefore, a careful selection of RAFT

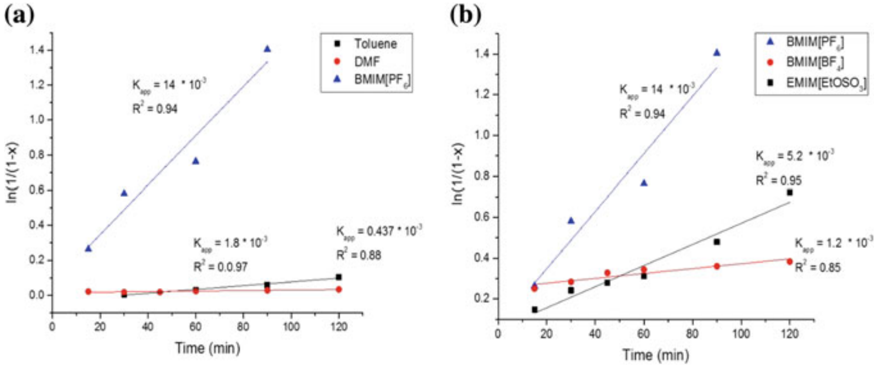
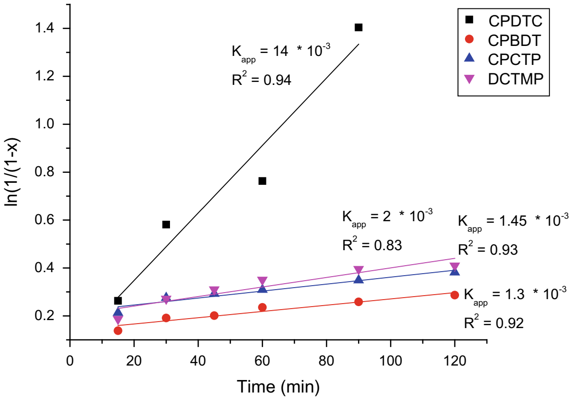


Fig. 3 Kinetic plots of BMA polymerization with CPDTC as RAFT agent in **a** different solvents such as toluene, DMF, and BMIM[PF6] and **b** different ionic liquids such as BMIM[PF$_6$], BMIM[BF$_4$], and EMIM[EtOSO$_3$]. Reproduced from Ref. [24] with permission from Elsevier

Fig. 4 Kinetic plots of BMA polymerization in BMIM[PF_6] solvent with different RAFT agents



agent would facilitate synthesis of polymer nanoparticles by stabilizing monomers into a nano-suspension in IL solvents.

To investigate further, we formed two binary solvents of IL and organic solvents and studied the polymerization kinetics of BMA in them as shown in Fig. 4. The binary solvents are made by mixing BMIM[PF_6] IL with toluene and DMF in two proportions 50:50 and 25:75 with IL as minor portion. The DMF:IL system is miscible with BMA, and the toluene:IL system is immiscible. From the polymerization kinetics of these two systems, it is evident that IL would increase the rate of polymerization irrespective of the miscibility with the monomer. This can be explained with the previously existing hypotheses that the IL being a viscous liquid would show 'solvent cage' effect [27] or diffusion-controlled termination [28, 29] which would increase the rate of polymerization. This would justify the increase in the polymerization rate in the immiscible system. But in the miscible system like DMF(75%):IL(25%), both the 'solvent cage' effect and the diffusion-controlled termination are negligible. This phenomenon as explained before by Thurecht et al. [30] proves the existence of ionic interaction between the IL and the propagating radical which forms a radical-IL 'complex' [24] or a 'protected' radical [30, 31] which would decrease the rate of termination and thus accelerating the rate of polymerization. From Fig. 5, it can also be inferred that the presence of even a small amount of IL would increase the rate of polymerization.

2.2 *Recovery and Reuse of ILs*

After the polymerization of the methacrylates, FMA and BMA, a small amount of chloroform was added to the reaction mixture. The chloroform dissolves the polymer formed but is immiscible with ionic liquid as it is a non-polar solvent. This forms a bilayer as seen in Fig. 6. The chloroform with polymer solution forms the upper layer, and the ionic liquid forms the bottom layer which can be easily

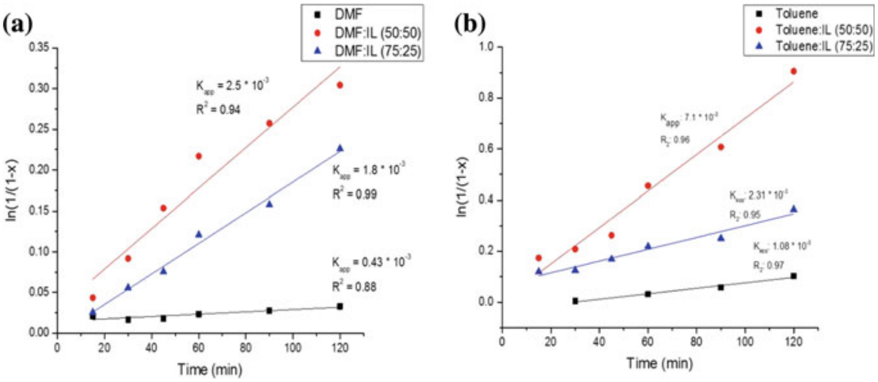


Fig. 5 Kinetic plots of BMA polymerization using CPDTC RAFT agent **a** DMF and BMIM[PF_6] binary solvent mixtures and **b** toluene and BMIM[PF_6] binary solvent mixtures. Reproduced from Ref. [24] with permission from Elsevier

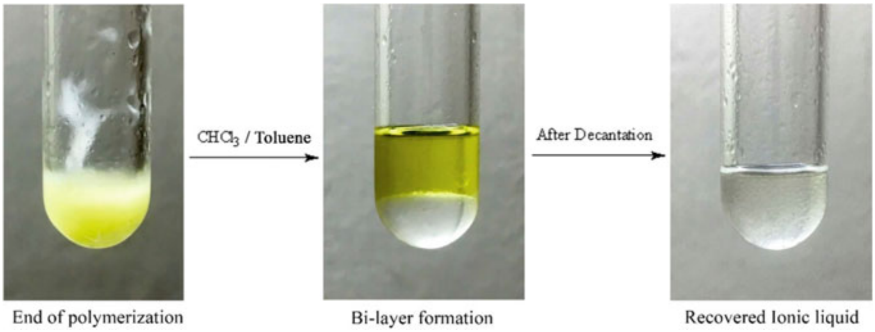


Fig. 6 Recovery of ionic liquid after BMA polymerization. Reproduced from Ref. [24] with permission from Elsevier

separated by decantation. We were able to recover more than 90% of the IL used in the polymerization. The purity of the recovered IL was checked with NMR [24]. The recovered IL was reused up to three times, and the results are tabulated in Table 3.

It can be seen that polymerization of BMA in pure IL and recycled IL produces similar results, and there is no change in the efficacy or efficiency of the IL after recycling. The ILs were recovered after every reaction, and the recovery% depends on the sophistication of the recovery technique. Also, we observed that toluene and hexane can also be employed to recover BMIM[PF_6] IL in methacrylate polymerization.

Table 3 RAFT polymerization of BMA in recycled IL[a]

Solvent	Conversion (%)	$M_{n(\text{theo})}$ (g/mol)	$M_{n(\text{GPC})}$ (g/mol)	Dispersity (Đ)	Ionic liquid recovered (%)
BMIM[PF_6]	96	15,300	14,600	1.20	94
BMIM[PF_6]—1st recycle	92	14,200	13,300	1.22	95
BMIM[PF_6]—2nd recycle	94	14,950	12,400	1.23	94
BMIM[PF_6]—3rd recycle	93.5	14,800	14,400	1.22	92

[a] [BMA]/[RAFT]/[AIBN] = 450:4:1. Reactions carried out at 70 °C under N-$_2$ atmosphere for 2 h. Reproduced from Ref. [24] with permission from Elsevier

3 Conclusion

In summary, the methacrylates such as FMA and BMA were successfully polymerized in ILs using RAFT polymerization technique. The CPDTC RAFT agent was found to act as a stabilizer for the FMA monomer in BMIM[PF_6] IL which can be used to control the particle size of the polymer. The rate of polymerization in IL was found to be higher than the same in organic solvents. The study on the polymerization kinetics shows that the IL accelerates the rate of polymerization irrespective of its miscibility with the monomer. The polarity of the IL affects the rate of polymerization. The study with binary solvent systems shows that the presence of even a small amount of IL would increase the rate of polymerization. The demonstration of the recycling of ILs shows that ILs are viable alternative ‘green’ solvents, to replace volatile organic solvents, which would improve the sustainability of the polymer synthesis.

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