



Solution Polymerization of Methyl Methacrylate in an Ionic Liquid Employing Cyclic Multifunctional Initiators

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1-Butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]) was used as a solvent during the methyl methacrylate polymerization, in a temperature range of 110 to 130°C, employing two multifunctional cyclic peroxides as initiators, the pinacolone diperoxide and the diethylketone triperoxide, and results were compared with those obtained in N,N-dimethylformamide (DMF) as a solvent under the same reaction conditions. The polymerization rate was approximately four times faster in [BMIM][BF₄] than in DMF, and this behavior is supported by the higher decomposition rate constants calculated for both initiators in pure ionic liquid in comparison with those calculated in DMF. The average molecular weights values were nearly three times lower in DMF than in the ionic liquid, and this is explained by the reduction in the propagation activation energy in the presence of the ionic liquid.

1. Introduction

Volatile organic compounds (VOCs) are mostly employed as solvents in solution polymerizations due to their affinity with monomers/polymers, notwithstanding the environmental concerns of this fact.^[1,2] The study of alternative less harmful solvents to be used in solution polymerizations has gained attention in the last years, for example the use of water,^[3,4] supercritical carbon dioxide^[5,6] or ionic liquids (ILs).^[7,8] Last mentioned solvents have been explored in different chemical processes such as organic synthesis, catalysis and in oil extraction practices.^[9]

The presence of ILs as the solvents in radical polymerization reactions, has been scarcely studied due to several factors like their more elevated costs in comparison with typical VOCs,

however they present several advantages over VOCs such as their low volatility, negligible flammability, compatibility with many organic compounds and the fact that due to their immiscibility with a broad range of compounds they can be recovered after the reaction and re-used, such as reported by Guerrero-Sanchez *et al.* who compared the use of ILs with common organic solvents in the cationic ring opening polymerization of 2-ethyl-2-oxazoline^[10] and in the free radical polymerization of methyl methacrylate (MMA)^[11] in both cases, under microwave irradiation demonstrating that the ionic liquid was efficiently recovered and re-used in further reactions.

On the other hand, reported results evidenced some advantages when using ILs such as increments in polymerization

rates and molecular weights, where both behaviors are related with the increase in the k_p/k_t (propagation and termination rate constants) ratio due the presence of the ILs as the reaction media.^[12] In this sense, Benton and Brazel employed 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]) as a solvent during the MMA polymerization initiated with AIBN, and they reported a polymerization rate five times faster and an average molecular weight around four times greater in the presence of the ionic liquid than the corresponding results in benzene.^[13]

An increase in the k_p values has been also reported in radical polymerizations when ILs are used as solvents instead of bulk polymerizations. In this sense, Harrison *et al.* reported a k_p value 2.5 times higher in relation with the bulk reaction for the MMA polymerization initiated with AIBN in the presence of [BMIM][PF₆].^[14,15] Schmidt-Naake *et al.* studied several ILs; [BMIM][PF₆], 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]), 1-ethyl-3-methylimidazolium ethyl sulfate ([EMIM][EtSO₄]) and 1-ethyl-3-methylimidazolium hexylsulfate ([EMIM][HexSO₄]) during the MMA and glycidyl methacrylate (GMA) polymerizations using AIBN or BPO as the initiators.^[16] These authors reported higher k_p values (around 4 times higher for MMA and 2 times for GMA) when ILs were used, in comparison with the corresponding bulk polymerizations. In this kind of systems, the increase on the overall polymerization rates was explained by a decrease in the propagation activation energy (E_{ap}) by the presence of the ILs. The bulk polymerization requires an $E_{ap} = 22.4 \text{ kJ mol}^{-1}$, meanwhile it

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decreases to 18.1 kJ mol^{-1} in the presence of 80% v/v of [BMIM][PF₆] or [BMIM][BF₄].^[17] However, the use of cyclic multifunctional initiators has not been reported in solution polymerizations carried out in ILs as solvents. As it was previously reported, the thermal decomposition of this kind of multifunctional initiators is strongly dependent of the solvent used.^[18–23] Moreover, when monomers such as MMA and styrene were employed as the reaction media, there was clear evidence of a strong dependence of the monomer nature^[24–27] on the initiators decomposition. In this sense, and taking the pinacolone diperoxide (PDP) at 140°C as an example, its decomposition rate constants (k_d) was $27.4 \times 10^{-5} \text{ s}^{-1}$ in benzene, $43.4 \times 10^{-5} \text{ s}^{-1}$ in acetic acid, $30.5 \times 10^{-5} \text{ s}^{-1}$ in acetonitrile, $23.2 \times 10^{-5} \text{ s}^{-1}$ in *n*-octane, $75.8 \times 10^{-5} \text{ s}^{-1}$ in 2-methoxyethanol and $29.6 \times 10^{-5} \text{ s}^{-1}$ in toluene.^[19] Thus, in this study it is reported the use of the cyclic multifunctional initiators PDP and diethylketone triperoxide (DEKTP) during MMA polymerizations, using [BMIM][BF₄] as a solvent and results are compared

with those obtained when *N,N*-dimethylformamide (DMF) is used as the reaction media.

2. Results and Discussion

The PDP and the DEKTP obtained were characterized by proton and carbon nuclear magnetic resonance. **Figure 1** a and b shows respectively the ¹H and the ¹³C spectra for the synthesized PDP, where the signal assignment is directly carried out in the spectra. Figure 1c and d shows respectively the ¹H and the ¹³C spectra for the synthesized DEKTP, and high purity of obtained compounds can be clearly evidenced in both cases. Complementary characterization of both synthesized molecules was achieved by Infrared Spectroscopy. Absorption bands around 944–970 cm^{-1} , characteristics of the O—O stretching vibrations, corroborate in both cases the presence of the cyclic peroxide instead of the precursor ketone. Most important absorption

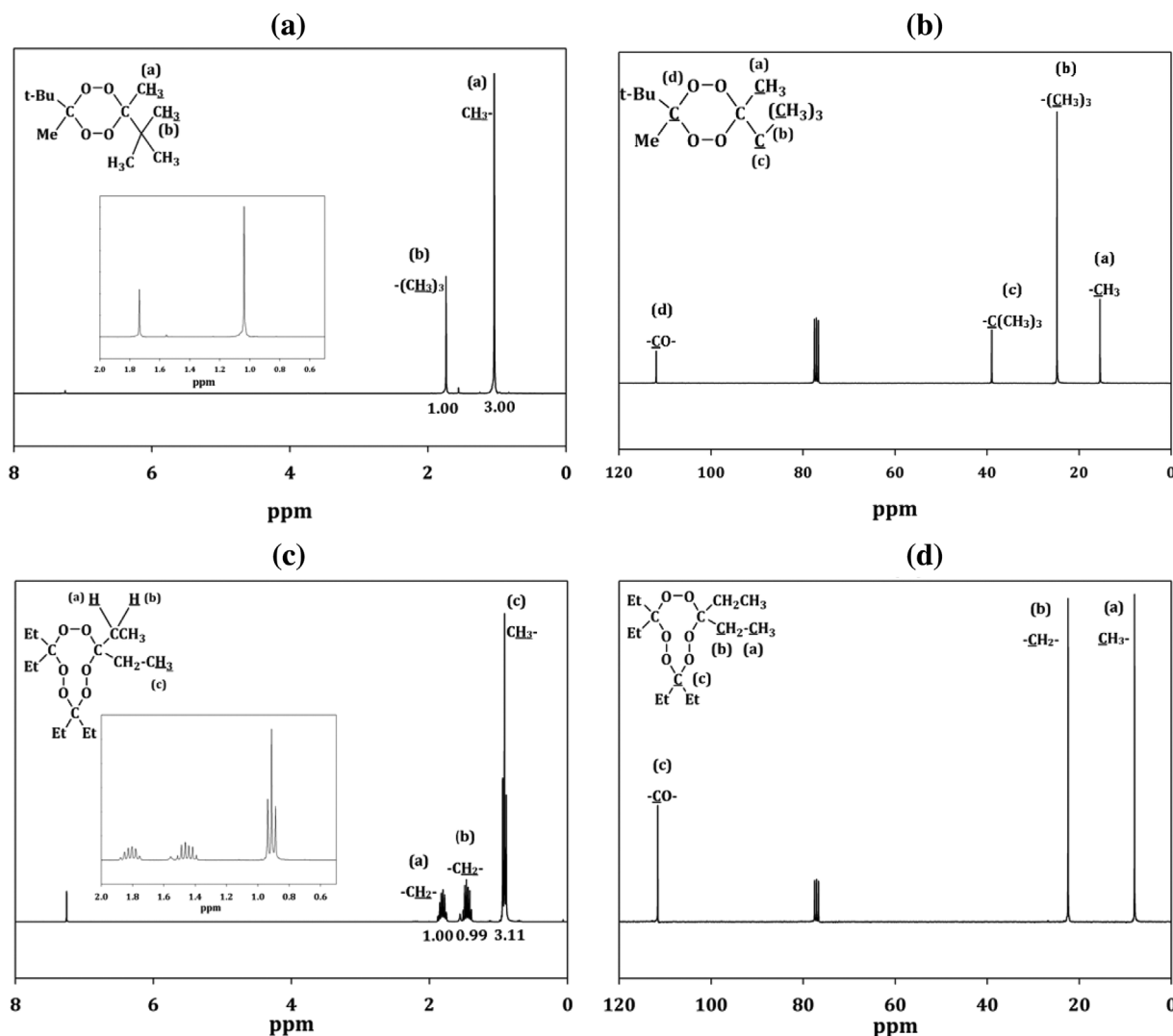


Figure 1. Spectra for PDP, a) ¹H NMR, b) ¹³C NMR; and for DEKTP, c) ¹H NMR, d) ¹³C NMR.

Table 1. DPP and DEKTP complementary characterization.

Multifunctional cyclic initiator	Infrared characterization	Melting point (°C)
PDP	(-CH ₃ , -CH-) 2969 (v), 2878 (v), 1458 (v), 1376 (v, δ), 1175 (δ), (O-O) 960 (δ)	124–125
DEKTP	(-CH ₃ , -CH ₂ -, -CH-) 2979 (v), 2946 (v), 2870 (v), 1475 (δ), (O-O) 974 (δ)	59–60

bands of both analyses are mentioned in **Table 1**. Determined values for melting points in both synthesized compounds are also shown in Table 1.

Solution polymerization reactions of MMA employing PDP and DEKTP as the initiators were carried out in [BMIM][BF₄] and DMF, in a temperature range of 110 to 130°C. **Figure 2** and **3** show the monomer conversion evolution as a function of the reaction time for polymerizations carried out in both studied solvents at the different temperatures. Figure 2a and b corresponds to the systems MMA-IL/PDP and MMA-IL/DEKTP, respectively. Figure 3a and b corresponds to equivalent systems but using DMF as a solvent instead of the ionic liquid.

For both initiators, and independently the temperature employed, the polymerization rate was approximately four times higher in [BMIM][BF₄] than in DMF as it was expected. The increase in the monomer conversion rate in those cases where [BMIM][BF₄] was involved, was attributed in part, to the higher viscosity of the IL relative to DMF. The high solution viscosity limited the diffusion rates of large polymer chains within the solution. This inability to manoeuvre limited the termination step, increasing the k_p/k_t ratio.

When [BMIM][BF₄] is used as the solvent, a maximum conversion value of 75% is reached, in 30 min for PDP and in 60 min for DEKTP, and then this value remains without changes throughout the polymerization. Directly comparison between both solvents, in the case of the system MMA-IL/PDP a conversion close to 78% was observed in only 15 minutes, meanwhile with DMF it was necessary 60 minutes to reach a similar conversion value. This last behavior is sustained not only by the explanation cited before associated to diffusion problems

of chains but also by the higher decomposition rate constants (k_d) recently reported by our team for both initiators in pure ionic liquid in comparison with those reported in DMF,^[28] as shown in **Table 2**.

The differences in k_d values reported in Table 2 can be explained, taking as an example the case of the system MMA-DMF/DEKTP, due to a higher solvation of the *initial initiator molecular state* (at room temperature) conducting to its stabilization and requiring a higher energetic barrier in order to generate the intermediate bi-radical (transition state). On the contrary, in the case of MMA-IL/DEKTP, the *transition state* is mostly solvated as a consequence of a rapid orientation of solvent molecules, stabilizing the transition state (due to greater interactions initiators-solvent), that causes a reduction in the activation enthalpy and consequently, the products formation is favored. This explanation is supported by the reaction coordinate diagram (shown in **Figure 4**) where a lower activation energy (E_a) value for [BMIM][BF₄] (22.2 kcal mol⁻¹) can be observed when it is compared with the corresponding value in DMF (34.4 kcal mol⁻¹).

Figure 5 and **6** show the evolution of the molecular weight as a function of reaction conversion for the corresponding MMA solution polymerizations aforementioned. First at all, the temperature effect on the molecular weights in both solvents (independently of the initiator) shows an expected behavior for a radical polymerization, where an increase in the reaction temperature directly yields a reduction of molecular weights.

On the other hand, in the temperature range evaluated, the molecular weights are greater for those polymers synthesized in the presence of [BMIM][BF₄] as a solvent than those obtained in

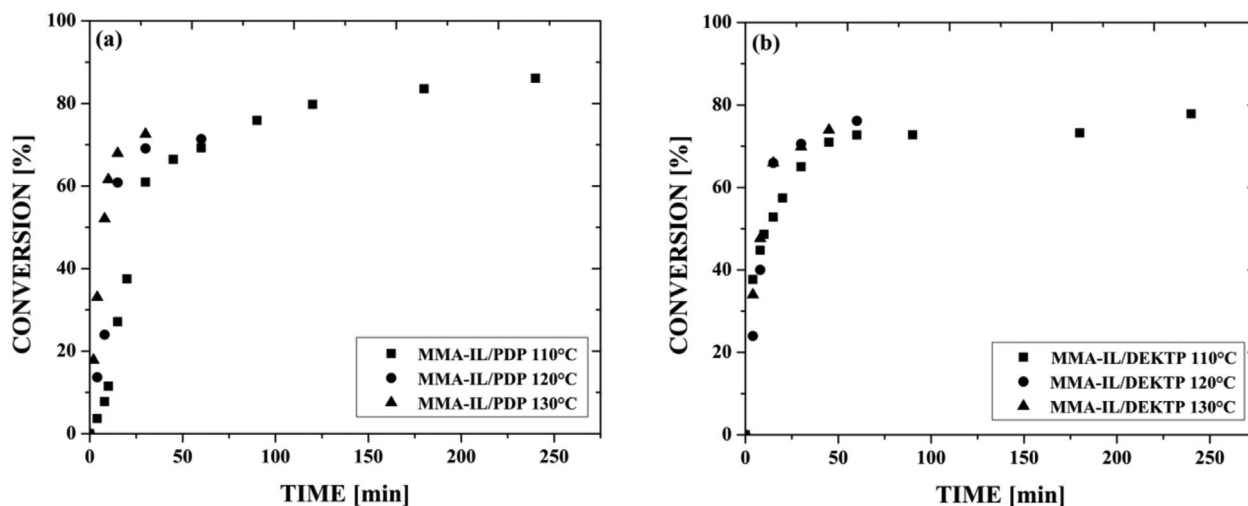


Figure 2. Monomer conversion evolution as a function of reaction time for MMA polymerizations in [BMIM][BF₄] in the temperature range of 110 to 130°C, initiated with a) PDP, and b) DEKTP.

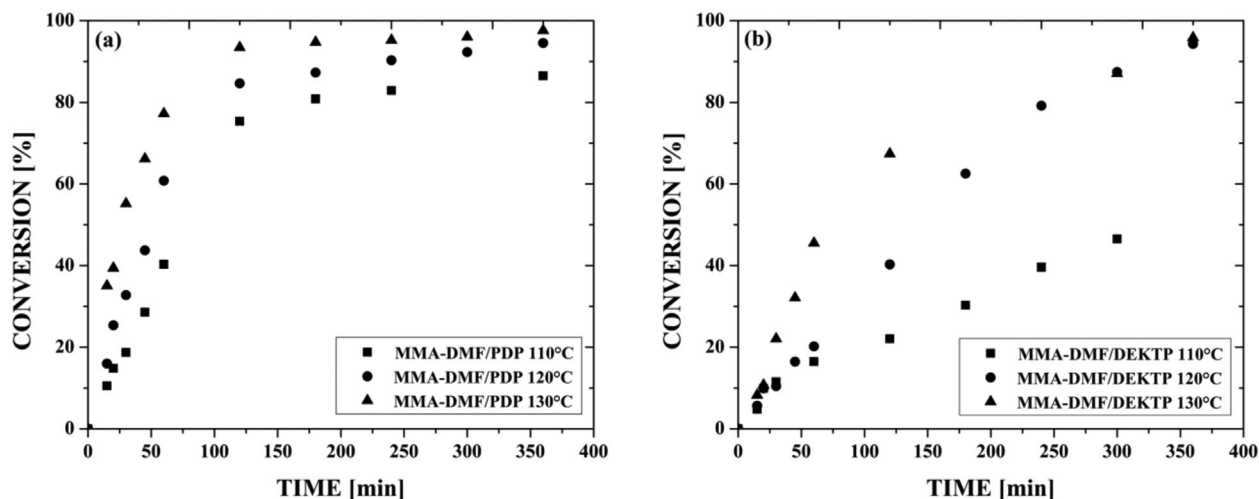


Figure 3. Monomer conversion evolution as a function of reaction time for MMA polymerizations in DMF in the temperature range of 110 to 130°C, initiated with a) PDP, and b) DEKTP.

DMF. This behavior can be justified, as a consequence of the observed reduction in the propagation activation energy in the presence of [BMIM][BF₄] ($E_{ap} = 11.08 \text{ kcal mol}^{-1}$), where this reduction allows a simultaneous increase in the propagation rate, as well as in the molecular weights. On the contrary, when DMF is used as a solvent, an increment in the propagation activation energy ($E_{ap} = 26.63 \text{ kcal mol}^{-1}$) instigates a slower propagation rate and lower molecular weights, simultaneously.

In the case of DMF two opposite effects must be considered: (1) the increase in radical concentration as the temperature increases, and (2) the decrease in the concentration of polymeric radicals due to the increase in the termination rate. Thus, the polymer chains are shortened by the increase in the concentration of radicals (reason: increasing temperature), and the increase in the probability of the termination reactions (reason: increase of k_t with a decrease in viscosity).

Comparing both initiators in [BMIM][BF₄] as a solvent, greater molecular weights (around two times greater) were produced with PDP than with DEKTP. This can be justified considering the E_a of DEKTP ($22.2 \text{ kcal mol}^{-1}$) once the initiator has decomposed, which is lower than that calculated for PDP ($28.3 \text{ kcal mol}^{-1}$), making the O—O bonds more susceptible to cleavage. This situation in conjunction with a lower value of (ΔH^\ddagger), yields a higher radical concentration, higher polymerization rates (as it was previously demonstrated) and lower molecular weights.

On the contrary, in the case of DMF as a solvent, greater molecular weights were obtained with DEKTP than with PDP, which can also be justified with the E_a values calculated in this solvent, which were estimated in $32.6 \text{ kcal mol}^{-1}$ for PDP and $34.4 \text{ kcal mol}^{-1}$ for DEKTP. Independently of the initiator employed, the polydispersity values ranged from 1.7 to 2.2.

It is important to mention that in MMA polymerizations in the presence of [BMIM][BF₄] (Figure 5a and b) the dissociation mechanism of the initiators seems to change in the temperature range evaluated, from a predominantly sequential decomposition mechanism (MMA-IL/PDP 110°C system) to a predominantly total or concerted decomposition mechanism for the rest of the evaluated systems. This change in the decomposition mechanism could be in principle ascribed to an increase in the reaction media polarity that directly affects the reactivity of the initiators. On the other hand, the polydispersity values in the case of the polymerizations in the presence of IL are higher (ranging from 4 to 7) probably due to the presence of different species associated to the change in the initiation mechanism. The behavior observed herein for the evolution of molecular weights is opposite to the previously reported in bulk conditions for MMA polymerizations employing these multifunctional initiators, where the DEKTP behaves as a multifunctional initiator, with an increase in molecular weight as the reaction takes place, from 110 to 130°C while PDP decomposes in a sequential manner in the temperature range of 110 to 120°C.^[26]

Table 2. k_d values for PDP and DEKTP, in DMF and [BMIM][BF₄] in the temperature range of 120 to 150°C.

Temperature [°C]	$k_{d,PDP} \times 10^{-4} \text{ [s}^{-1}\text{] DMF}$	$k_{d,PDP} \times 10^{-4} \text{ [s}^{-1}\text{] [BMIM] [BF}_4\text{]}$	$k_{d,DEKTP} \times 10^{-4} \text{ [s}^{-1}\text{] DMF}$	$k_{d,DEKTP} \times 10^{-4} \text{ [s}^{-1}\text{] [BMIM] [BF}_4\text{]}$
120	0.54	3.05	0.15	1.66
130	1.44	8.94	0.42	3.11
140	4.26	20.74	1.29	6.85
150	10.12	39.66	3.32	12.67

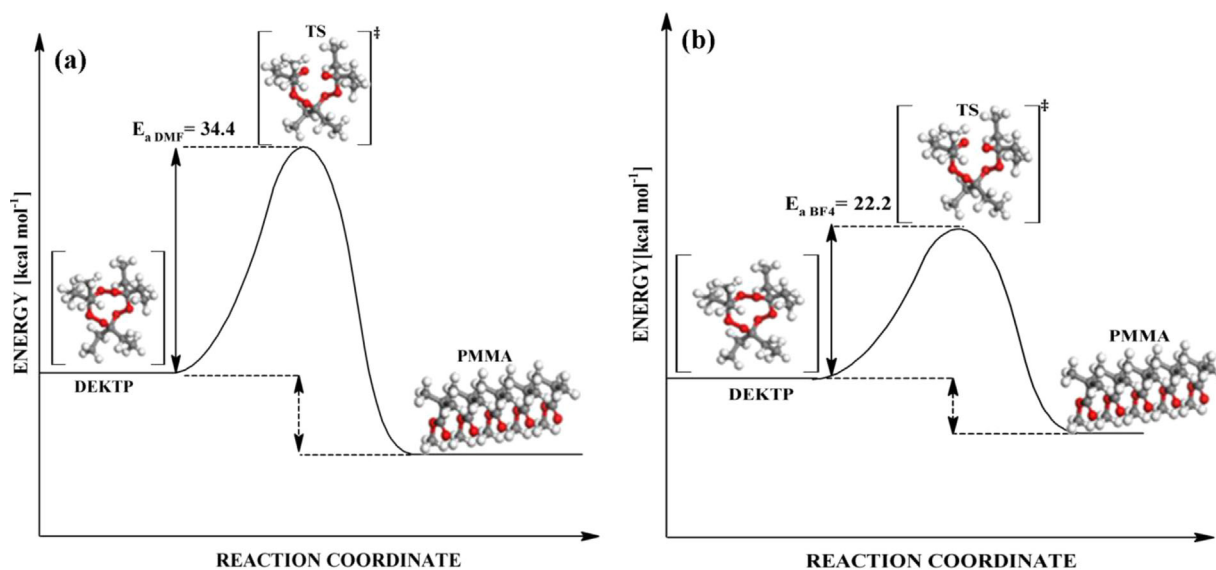


Figure 4. Scheme of energy as a function of reaction coordinate for DEKTP initiator in a) DMF and b) [BMIM][BF₄].

However, in the case of polymerizations using DMF as a solvent (Figure 6a and b), the molecular weights present the typical behavior of a classic radical initiator, associated with the mostly total or concerted dissociation of initiators. In this case, the polarity of the solvent is higher causing a greater solvation, increasing in this way the reactivity of PDP and DEKTP.

3. Conclusions

The MMA polymerization initiated with PDP and DEKTP using [BMIM][BF₄] as a solvent presented a polymerization rate around 4 times faster in comparison with that in DMF, attributed to differences in their decomposition rate constants values calculated in both solvents. The elevated temperatures, the structure of the multifunctional initiator and the nature of the solvent used during the polymerization process affected the

molecular weights of resulting poly(methyl methacrylate) samples. Higher molecular weights were obtained in the presence of [BMIM][BF₄] in comparison with DMF attributed to a decrease in the initiator efficiency and/or a decrease in the propagation activation energy. Molecular weights were also higher when PDP was used as the initiators instead of DEKTP which was also explained in terms of the activation energy values.

4. Experimental Section

Reactants: Sulfuric acid (98%) and hydrogen peroxide (50%) purchased from J. T. Baker were used as received. [BMIM][BF₄], ammonium chloride (≥99.5%), 3-pentanone (≥99%), 3,3-dimethyl-2-butanone (98%), anhydrous sodium sulfate (≥99%), DMF (99.8%), petroleum ether (ACS reagent), methanol (99.8%), and tetrahydrofuran

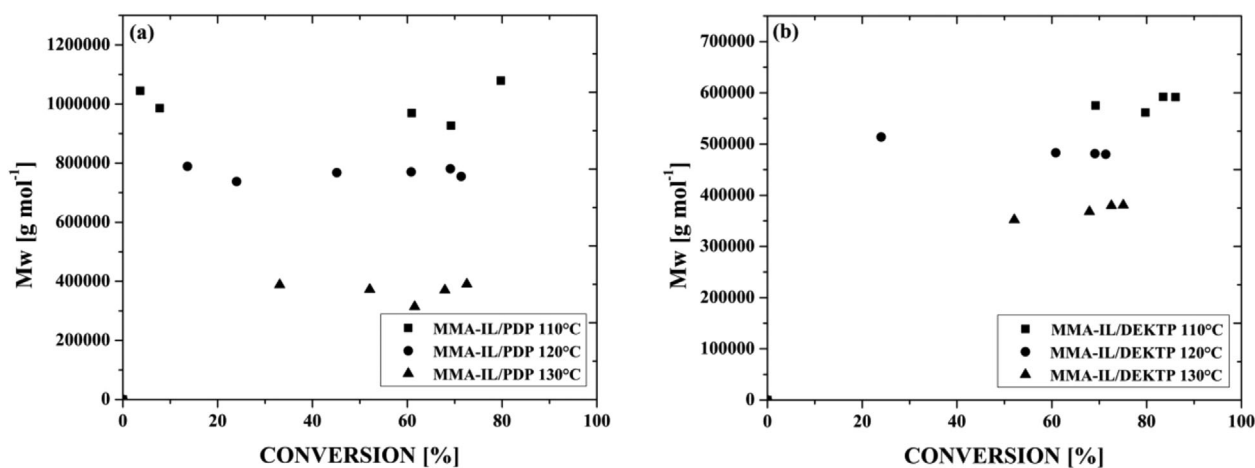


Figure 5. Molecular weight evolution as a function of reaction conversion for MMA polymerizations in [BMIM][BF₄] in the temperature range of 110 to 130°C, initiated with a) PDP, and b) DEKTP.

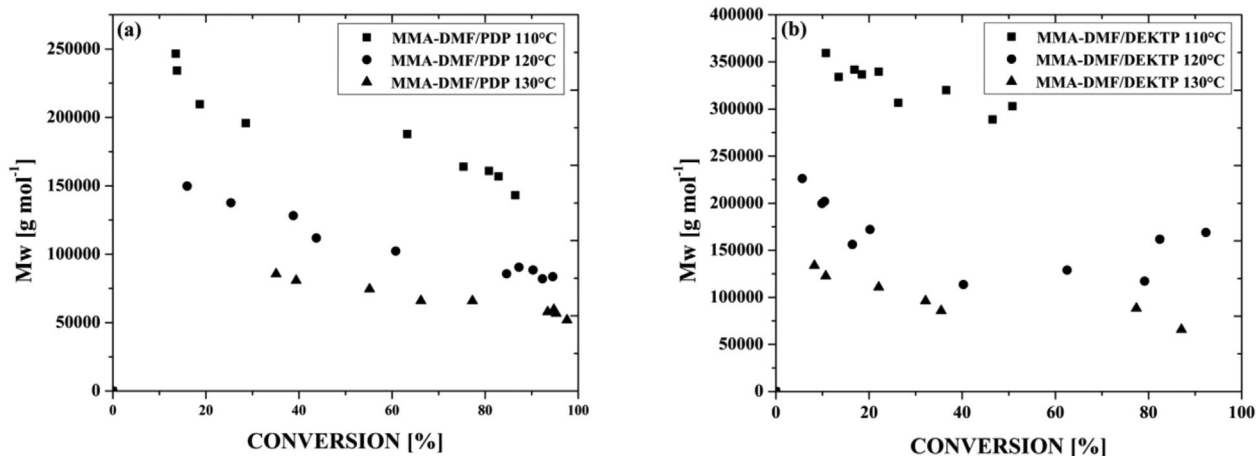


Figure 6. Molecular weight evolution as a function of reaction conversion for MMA polymerizations in DMF in the temperature range of 110 to 130°C, initiated with a) PDP, and b) DEKTP.

(THF, $\geq 99\%$) were supplied by Sigma-Aldrich, and used without further purification. MMA (99%) provided by Sigma-Aldrich, was purified before use by vacuum distillation over calcium hydride.

Synthesis of PDP and DEKTP: PDP and DEKTP were synthesized according to methods reported in the literature.^[19,29] PDP synthesis involves the reaction between 3,3-dimethyl-2-butanone and hydrogen peroxide (30% v/v) in sulfuric acid (70% v/v) at -15 to -20°C . DEKTP was obtained by the reaction between 3-pentanone and hydrogen peroxide at the same reaction conditions mentioned for PDP.

Polymerization Reactions: A stock solution of PDP (or DEKTP) 0.01 mol L^{-1} in MMA was prepared followed by the addition of [BMIM][BF₄] or DMF with an established monomer/solvent ratio of 20/80% v/v. The solution thus prepared was distributed in glass ampoules to be thoroughly degassed by three freeze-pump-thaw cycles and then sealed with a flame torch. The ampoules were immersed in a thermostatic oil bath stabilized at the selected temperature and they were withdrawn after predetermined times. The polymeric products were dissolved in THF, and precipitated adding drop-wise over methanol, filtered and dried under vacuum at room temperature until constant weight. The elimination of the ionic liquid residues from the polymeric sample after the filtration step was achieved by 3 cycles of dissolution-precipitation, taking advantage the high solubility of the ionic liquid in polar solvents, methanol in this case. After these cycles, the dried polymer was weighted to determine conversion taking into account the mass of monomer employed in the reaction.

Characterization: Purity of PDP and DEKTP was confirmed by proton and carbon nuclear magnetic resonance (¹H and ¹³C NMR) at room temperature on a Jeol 300 MHz NMR spectrometer, deuterated chloroform (CDCl₃) was used as the solvent. Monomer conversion was determined by gravimetric procedures and the molecular weights of polymer samples were determined by size exclusion chromatography at 40°C using a Hewlett-Packard instrument (HPLC series 1100) equipped with a refractive index detector. A series of three PLGel columns with porosities of 10³, 10⁵, and 10⁶ Å was used. Calibration was carried out with poly(methyl methacrylate) standards and THF (HPLC grade) was used as the eluent at a flow rate of 1 mL min^{-1} .

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Keywords

ionic liquid, methyl methacrylate, multifunctional initiators, solution polymerization

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