Ionic Liquids as Catalysts for the Radical Acrylate Polymerization Co-initiated by Imine Bases

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Abstract. The catalysis of the imine base acrylate (IBA) polymerization by Ionic Liquids (ILs) is reported. Addition of IL traces (~10–50 mM) to an imine base / acrylate mixture leads to both a significant decrease of the activation temperature (40 °C) required for the IBA polymerization process and an increase in the polymerization rate by a factor of 5–40 depending on the IL species. The radical character of the polymerization is proved by copolymerization experiments using methyl methacrylate (MMA) and methacrylonitrile (MAN) and comparison with literature known values of copolymerization parameters $r_{\text{MMA}}$ and $r_{\text{MAN}}$ of these co-monomers. The influence of the IL on the polymerization kinetics is quantified by the polymerization rate law; the order referring to the IL is 1 indicating its crucial impact on the monomer activation. The IBA activation properties are strongly dependent on the IL interaction strengths with the IBA components verified by the KAMELT-TAFT hydrogen bond donating ability $\alpha$. The stronger the interaction (higher $\alpha$) is, the less the IBA polymerization activation. The temperature dependence of four different IL catalysed IBA polymerization is investigated, allows a classification and anomalous non-Arrhenius regimes are discussed.

Activation energies $E_{\text{A,P}}$ span over 20 and 50 kJ mol$^{-1}$, which is between the values of thermal (~80 kJ mol$^{-1}$) and photo-initiation (~20 kJ mol$^{-1}$).

1. Introduction

Recently, we reported on a novel radical polymerization of acrylates such as methyl methacrylate (MMA), methacrylonitrile (MAN), and methyl acrylate which occurs in the presence of imine bases lacking a protic NH group such as 2-ethyl-2-oxazoline, 2-phenyl-2-oxazoline (POX) and 2-(methylthio)-2-thiazoline (MMT), respectively, at elevated temperatures. [1] A general scheme of the IBA polymerization is shown below (Scheme 1).

Scheme 1. Proposed multistep mechanism for the IBA polymerization.$^1$

Homo- and co-polymerizations of acrylates have been experimentally detected yielding high molecular weight polymers with dispersity around 1.90. We isolated the imine base after...
polymerization almost quantitatively and it can be multiply re-used. Either a six-membered ring or a zwitterion composed of the acrylate and the imine base is still hypothetically assumed to be an intermediate at the initiation process and, hence, this polymerization has been denoted as imine base / acrylate (IBA) polymerization. However, drawbacks of these systems are the high activation temperature of 100 °C and the high molar amounts of imine required for the polymerization.

Herein, we report on the impact of Ionic Liquids (IL) on the radical IBA polymerization. The use of room temperature Ionic Liquids have gained high interest in academia and industry in the last decades due to their use as co-reactants and catalysts in organic and inorganic chemistry as well as in polymer and material science. [2-13] In these works, most likely, ILs are used in high molar amounts or as solvents to gain notable effects on the reaction path. In the here reported systems, tremendous changes in the polymerization kinetics at IL concentrations even at catalytic amounts of 10–50 mM are detected. The use of Ionic Liquid traces at the IBA polymerization leads to both a decrease in activation temperature and an increase in reactivity of the IBA mixture; both effects are quantified in this work by measuring the polymerization kinetics. It is shown that the polymerization rate is a function of the hydrogen bond donating ability $\alpha$ of the Ionic Liquid and can be adjusted precisely in a range between 5- up to 40-fold the value of the non-IL containing IBA mixture. Scheme 2 shows the imine bases and Ionic Liquids classified by their $\alpha$-values that are used in this study.

### Scheme 2.

Imine Bases (IB) and Ionic Liquids (ILs) used in this study. The ILs are systematically arranged by their KAMLET-TAFT hydrogen bond donating abilities $\alpha$.

Furthermore, we investigated the behavior of IL catalysed IBA polymerization at elevated temperatures. Four different polymerization mixtures were examined. Besides the detection of linear ARRHENIUS dependencies at the $\ln k$ versus $T^{-1}$ plots ([Emim]FAP) anomalous ‘volcano’ curves for [Cmim]NO$_3$ and [N$_{4441}$]Ntf$_2$ were observed and discussed. By knowing the factors that dominate the kinetics of this novel reaction type, we propose polymerization systems with tunable properties for applications in polymer and material science.

## 2. Results and Discussion

### 2.1 Qualitative observations

Polymerizations were carried out as described earlier.$^1$ MMA was distilled prior to use and the amine bases and ILs were used as received. A standard polymerization procedure is as follows; to a solution of 4.2 millimole (mmol) imine base in 2.65 mL (25 mmol) MMA, 10–100 mg of IL is added under inert conditions. The reaction mixture is heated to 65 °C for 4 h. Then, the viscous solution is cooled to room temperature, diluted with 10 mL of chloroform and gently dripped into 400 mL of methanol. After purification and drying of the precipitate, poly(methyl methacrylate) (PMMA) is obtained as a
colorless solid. Table 1 shows specific results of IL catalysed IBA polymerizations using MMT and POX.

### Table 1. Reaction conditions of IL catalysed IBA polymerizations as well as PMMA analysis results recorded by gel permeation chromatography. The MMA concentration is 4.7 M, the IB concentration is 0.8 M and that of the IL 50 mM.

| IB    | IL                  | α  | T [°C] | t [h] | M<sub>N</sub> [g mol⁻¹] | M<sub>W</sub> / M<sub>N</sub> | X<sub>MMA</sub> [%] |
|-------|---------------------|----|--------|------|--------------------------|-----------------------------|------------------|
| MMT   | [Emim]FAP           | 0.83| 65     | 3    | 46.700                   | 1.54                        | 25               |
|       |                     |    | 95     | 3    | 139.000                  | 1.85                        | 60               |
| POX   | [Emim]FAP           | 0.83| 65     | 10   | 62.400                   | 1.87                        | 61               |
|       | [Bmim]Ntf<sub>2</sub> | 0.55| 85     | 8    | 77.200                   | 1.60                        | 67               |
|       | [Bmim]PF<sub>6</sub> | 0.54| 85     | 10   | 60.000                   | 1.79                        | 99               |
|       | [Py<sub>6</sub>]Ntf<sub>2</sub> | 0.50| 85     | 5    | 266.800                  | 1.78                        | 99               |
|       | [C<sub>10</sub>mim]NO<sub>3</sub> | 0.36| 85     | 5    | 54.800                   | 1.52                        | 66               |

Both imine bases are suitable for the IL catalysed IBA polymerization; however, we detected significant differences in their reactivity, qualitatively. Thus, MMT has a higher reactivity and yields PMMA with a slightly reduced average molecular weight compared to the POX systems. We used a broad variety of Ionic Liquid species in the experiments and for each IL catalysis of the IBA polymerization was measured, considerably. More drastic changes in the reactivity of certain IBA systems were found while changing the IL type; a detailed quantification of this acceleration is given in chapter 2.2.

Interestingly, we re-obtained the imine base / IL mixture out of the methanol residue and it can be re-used for multiple times. No IL-groups were detected in the product PMMA, which was proven by <sup>1</sup>H and <sup>13</sup>C NMR (Figure one) studies underlining the fact that the Ionic Liquid acts as a catalyst in the IBA process.

![Figure 1.](image.png)  
### Figure 1.  
<sup>1</sup>H (a) and <sup>13</sup>C NMR of PMMA (250 MHz and 62.5 MHz, in CDCl₃). It was polymerized using the IBA combination POX / MMA and the IL [Emim]FAP. No Signals of the IL can be detected in neither of the spectra.

The radical character of the IL catalysed IBA polymerization is proved by copolymerization experiments of MMA and MAN. Experiments yield the corresponding copolymerization parameters.
$r_{\text{MMA}}$ and $r_{\text{MAN}}$ that represent the molar ratios of the co-monomers in the copolymer as given by the MAYO-LEWIS equation. [14] Therefore, in an anionic polymerization the molar ratio of the stronger electrophile MAN is much higher than that of MMA (statistical non-azeotropic copolymerization) and in a radical copolymerization an azeotropic copolymerization is found. [15] The MMA/MAN copolymerization diagram using the combination POX / [Emim]FAP and literature known plots of an anionic and radical copolymerization of this co-monomer pair is shown in Figure 2 and the corresponding $r$-values are given in Table 2. Comparison of the results with literature known data of these co-monomers admits to confirm the propagating species at the IL catalysed IBA polymerization to be of a radical nature.

![Figure 2. Copolymerization diagrams of MMA / MAN using POX / [Emim]FAP (■) and fitted curve (---) as well as comparison with literature known plots for radical (----) and anionic (-----) copolymerizations of these co-monomers.][1]

![Figure 3. PMMA average number molecular weights $M_N$ (filled symbols) and polymer dispersity indices (hollow symbols) of IL catalysed IBA polymerizations using the combination POX (0.8 M) / MMA (4.7 M) as a function of the monomer conversion. It was catalysed with 50 mM [Emim]FAP (■) and [C$_{10}$mim]NO$_3$ (▲) at 85 °C.][2]

**Table 2.** Copolymerization parameters $r_{\text{MMA}}$ and $r_{\text{MAN}}$ using POX / [Emim]FAP as well as literature known $r$-values of radical and anionic copolymerizations of these co-monomers. [15]

| Initiation       | $r_{\text{MMA}}$ | $r_{\text{MAN}}$ |
|------------------|------------------|------------------|
| POX/[Emim]FAP   | 0.57             | 0.58             |
| MMT/[Emim]FAP   | 0.54             | 0.53             |
| Radically        | 0.67             | 0.65             |
| Anionic         | 0.67             | 5.20             |

At the IL catalysed IBA homopolymerization of acrylates, we found that with increasing monomer conversion the macromolecule chain length increased. The results of MMA polymerizations using POX and Ionic Liquids [Emim]FAP and [C$_{10}$mim]NO$_3$ are shown in Figure 3. Besides the increase in $M_N$ a slight increase in the polymer chain length dispersity (PDI) is notable. In common living polymerizations the PDI value decreases with increasing conversion; [16] the character of the IL catalysed IBA polymerization, hence, cannot be classified as a purely living polymerization. As found earlier for the non-IL containing IBA polymerization in bulk the measured behavior belongs to a quasi-living process. The observations manifest the fact that the Ionic Liquid dominantly influences the initiation process via an activation of the monomer and co-initiator; quantification of the effects by means of the polymerization kinetics is the next step for a detailed description of the IL catalysis.
2.2 **Kinetic studies**

We used standard approaches of polymer physics for determining the polymerization rate law.\(^\text{16}\) In a previous study we quantified the shape of the IBA polymerization rate law that reads\(^4\)

\[ v_{P,0} = k_{P,0} \cdot [\text{POX}]^{0.5} \cdot [\text{MMA}]^{1.5}, \]

where, \(v_{P,0}\) is the net polymerization rate, \(k_{P,0}\) the polymerization rate constant and [POX] and [MMA] the concentrations of POX and MMA. Inclusion of the Ionic Liquid in the polymerization rate law gives

\[ v_{P,0} = k_{P,0}^* \cdot [\text{POX}]^{0.5} \cdot [\text{MMA}]^{1.5}, \]

\[ k_{P,0}^* = k_{P,0} \cdot [\text{IL}]^x, \]

where \([\text{IL}]\) is the Ionic Liquid concentration and \(x\) equals the order referring to the IL. For an entire description of \(v_{P,0}\), in the next step the order \(x\) referring to the IL is defined. Therefore, we transferred equation 2 into a logarithmic straight line equation

\[ \ln v_{P,0} = \ln k_{K,0} + x \ln [\text{IL}] + 0.5 \ln [\text{POX}] + 1.5 \ln [\text{MMA}]. \]

A set of IL catalysed IBA polymerizations was performed; \(v_{Br,0}\) was determined from the initial slopes of the [MMA] versus time plots and concentrations of POX and MMA were held constant whereas [IL] was modified.\(^{16}\) The slope of the correlation \(\ln v_{P,0}\) over \(\ln [\text{IL}]\) yields \(x\). In Figure 4 the experimental data set as well as the \(x\)-determination of the IL catalysed IBA polymerization using the combination POX / [Emim]FAP / MMA are shown. The experiments yield a value of one for the order referring to the Ionic Liquid that indicates a crucial impact of the IL on the whole kinetics of the IBA polymerization. A full description of the IBA polymerization rate law allows for a detailed quantification of the influence of ILs on the polymerization kinetics.

In previous studies, investigations on the interaction of ILs with acrylates and imine bases by means of near field attenuated total reflection infrared spectroscopy and correlation with KAMLET-Taft parameters have been done.\(^{[17, 18]}\) There, we detected a significant shift of the MMA \(\nu(\text{C=O})\) stretching vibrational mode to lower wavenumbers in the presence of ILs. This observation indicates an increase in the electrophilicity of the monomer that contributes to the nucleophilic imine addition rate. Consequently, an increase in the IBA reactivity results (Scheme 3). The outcomes of this study encourages us to use the hydrogen bond donating ability \(\alpha\) of Ionic Liquids as an indicator for the interplay strengths of ILs with the IBA components. In this work, we used Ionic Liquids that drastically vary in their hydrogen bond donating abilities; \(\alpha\)-values span over the range between 0.36 (weak H-bond donor) and 0.83 (strong H-bond donor).

IL catalysed IBA polymerizations were carried out using the combination POX / MMA; the IL species was changed. Polymerization rate constants \(k_{P,0}\) were determined and brought into correlation to the corresponding hydrogen bond donating ability of the Ionic Liquid; the results are given in Figure 5.
Figure 4. a) Concentration of MMA as a function of time for IL catalysed IBA polymerizations using the combination POX / [Emim]FAP / MMA at 65 °C at [Emim]FAP concentrations of 20 mM (■), 40 mM(▲), 75 mM (●), 110 mM (■). The linear fits of the initial stages are [MMA]_{20mM} = −7.2 \times 10^{-4} \cdot t + 4.77; [MMA]_{40mM} = −15.2 \times 10^{-4} \cdot t + 4.77; [MMA]_{75mM} = −24.2 \times 10^{-4} \cdot t + 4.78; [MMA]_{110mM} = −40.9 \times 10^{-4} \cdot t + 4.76. b) Double-logarithmic plot of the polymerization rate $v_{P,0}$ as a function of the [Emim]FAP concentration. The linear fit is $\ln v_{P,0} = 1.02 \ln ([\text{Emim}]\text{FAP}) + 5.9$, $R^2 = 0.99$.

Scheme 3. Interactions of [Emim]FAP with MMA and POX.\textsuperscript{17,18}

Figure 5. IBA polymerization rate constants $k_{P,0}$ at IL catalysis as a function of the IL hydrogen bond donating abilities $\alpha$. The power law fit is $k_{P,0} \times 10^5 = 3.7 \cdot \alpha^{-3}$, $R^2 = 0.83$. The dotted black line indicates the $k_{P,0}$ value at the non-IL containing IBA polymerization.
Each $k_{P,0}$ value of the IL catalysed IBA polymerization is higher than that of the non-IL containing IBA polymerization ($1.72 \times 10^{-5}$, Fig. 4, dotted black line). We observed that with increasing IL hydrogen bond donating ability the $k_{P,0}$ values decreased. Besides the MMA activation by the IL as described above, a complexation of the imine bases has to be taken into consideration, which is the dominating equilibrium, obviously. With increasing hydrogen bond donating ability of the IL the imine bases is stronger complexed which results in a reduction in $k_{P,0}$. The IBA polymerization kinetics can be fine-tuned facilely in a range between $9.5 \times 10^{-5}$ and $76.5 \times 10^{-5} \, L^2 \cdot mol^{-2} \cdot s^{-1}$ by varying the catalyst IL. Hence, we are able to control the monomer conversion, enabling the potential use of these systems in various fields of material fabrication.

2.3 Behavior at varying thermal treatment

It is practicable to determine the thermal properties of the system described in this work for its establishment in the field of material science. To quantify the behavior of the IBA polymerization with IL catalysis at varying thermal treatment we use the Arrhenius approach:

$$k_{P,0} = A \cdot \exp(-E_{A,P} \cdot (R \cdot T)^{-1}),$$

$$\ln k_{P,0} = \ln A - E_{A,P} \cdot (R \cdot T)^{-1},$$

where $A$ is the pre-exponential factor, $R$ the ideal gas constant, $T$ the absolute temperature and $E_{A,P}$ the activation energy of the polymerization rate constant. The activation energy $E_{A,P}$ is taken as a measure for the activation barrier for the net polymerization process including the initiation, propagation and termination. The double logarithmic form of equation five given in equation 6 enables the verification of $-E_{A,P} \cdot R^{-1}$ by determining the slope of the plot $\ln k_{P,0}$ over $T^{-1}$. In Figure 6, experimental results of [Emim]FAP catalysed MMA IBA polymerizations using the imine bases POX and MMT are shown.

![Figure 6. Arrhenius plots of IL catalysed IBA polymerizations using MMT / [Emim]FAP / MMA (■) and POX / [Emim]FAP / MMA (▲). The linear fits are $\ln k_{P,0}$(MMT) = 2683.1 $\cdot T^{-1}$–0.48; $R^2 = 0.97$ and $\ln k_{P,0}$(POX) = 5955.3 $\cdot T^{-1}$+7.81; $R^2 = 0.88$ and the corresponding activation energies are 22.3 kJ mol$^{-1}$ (MMT) and 49.5 kJ mol$^{-1}$ (POX).]
A detailed look on the POX-mediated IBA polymerizations catalysed by \([\text{C}_{10}\text{mim}]\text{NO}_3\) and \([\text{N}_{4441}]\text{Ntf}_2\) under thermal treatment reveals an anomaly; the appropriate correlations \(\ln k_{P,0}\) over \(T^{-1}\) more rather equal ‘volcano’-like curves (Figure seven).

Experimental data cannot be fitted linearly. The system reaches a certain optimum temperature with a maximum \(k_{P,0}\); above that temperature the polymerization rate decreases. A drastic increase in the IL–POX interaction for \([\text{N}_{4441}]\text{Ntf}_2\) and \([\text{C}_{10}\text{mim}]\text{NO}_3\) at higher temperatures is most probably to be responsible for this trend. Thereof, at a certain threshold temperature the POX–IL interaction exceeds the sum of interactions that lead to the formation of the initiating species which, consequently, because the initiation is the rate determining step, results in a reduction in \(k_{P,0}\). The data manifest the versatility of interactions at the IL catalysis of IBA polymerizations.

3. Conclusion

The addition of Ionic Liquid traces to the binary imine base / acrylate (IBA) polymerization mixture has notable effects on the whole polymerization process. Most considerably, IBA polymerization activation temperatures are decreased and kinetics is accelerated in the presence of ILs. The activation properties are strongly dependent on the IL–IBA component interplay strengths that are elucidated here by the hydrogen bond donating ability \(\alpha\) of the IL. Therefore, the stronger the IL–IBA component interaction (the higher \(\alpha\)) is, the less are the IL activation properties. The quasi-living behaviour of the IL catalysed IBA polymerization is indicated by the molecular weight increase of acrylate polymers at increasing monomer conversions, which is achieved solely by catalytic IL amounts. The form of the polymerization law of the IL catalysed IBA polymerization is determined allowing a formal classification of the catalysis effect of particular IL / imine base / acrylate mixtures. The reaction rate at IL catalysis can be precisely controlled and reach values up to 40-fold the reactivity of the non-IL IBA mixture. Our investigations of IL catalysed IBA polymerization at thermal treatment yield the specific polymerization activation energies. The polymerization is ranged between thermal- and photo-initiation. The results reveal novel approaches on the way to designing acrylate coatings based on IBA polymerization mixtures.

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