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First report of reversible addition–fragmentation chain transfer (RAFT) polymerisation in room temperature ionic liquids

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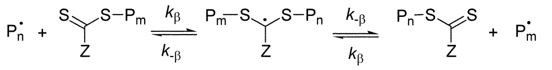
The Reversible Addition–Fragmentation chain Transfer (RAFT) polymerisation of acrylates, methacrylates and styrene is reported for the first time in room temperature ionic liquids; the acrylate and methacrylate polymerisations show a living character and lead to well-characterised polymers, with narrow polydispersity (< 1.3); in the case of styrene, the insolubility of the polymer in the ionic liquids stops the polymerisation at an early stage.

Living radical polymerisation has witnessed an impressive growth in the past few years, with the development of Nitroxide Mediated Polymerisation (NMP),[1] Transition Metal Mediated Polymerisation[2–4] and Reversible Addition-Fragmentation chain Transfer (RAFT) polymerisation.[5,6] RAFT is the youngest of these new methods, and is characterized by its application to a wide range of monomers. The polymerisation takes place in the presence of a thiocarbonylthio compound, which reacts reversibly with a propagating radical (addition) to form a radical intermediate. This intermediate can then fragment into a new thiocarbonylthio compound and a propagating radical. As the concentration of propagating chains is kept low by comparison to the thiocarbonylthio bearing polymer chains (dormant chains), the termination reactions are greatly reduced.[7,8] The principle of polymerisation is summarised in Scheme 1.

Room temperature ionic liquids have found extensive use as replacement solvents for many organic reactions.[9,10] However, apart from some early work on their use to prepare conducting polymer films their use in polymerisation studies has been limited in comparison.[11,12] There have been brief studies on Ziegler–Natta polymerisation in chloroaluminate(III) ionic liquids,[13,14] and more recently the neutral ionic liquids have been used in the examination of conventional free radical polymerisation[15–18] and transition metal mediated living radical polymerisation reactions.[18–20]



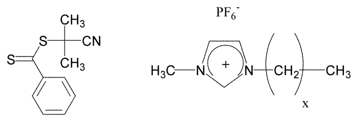
Scheme 1 Main equilibrium in the RAFT process.

The polymerisation of styrene, methyl methacrylate and methyl acrylate, mediated by 2-(2-cyanopropyl) dithiobenzoate (CPDB, **1**) was undertaken with 1-alkyl-3-methylimidazolium hexafluorophosphate ($[C_x][PF_6]$, where $x = 4$, 6 to 8, (**2**, Scheme 2) as the solvent. The alkyl chain length of $[C_x][PF_6]$ was varied to test its influence on the reactions. CPDB has already been reported as an efficient RAFT agent for methyl methacrylate, methyl acrylate and styrene.[21]

In order to compare the results, 'blank' samples were realised in bulk and in toluene. All polymerisations were undertaken at 60 °C in a 50% v/v ratio of monomer–solvent.†

In the case of styrene, precipitation in the ionic liquids was observed at an early stage of the polymerisation. This is explained by the insolubility of polystyrene in all the ionic liquids, resulting in very low molecular weight polymers. However, the polymerisation does take place in toluene and leads to a polymer with narrow molecular weight distribution (see Table 1).

In the case of methacrylate and acrylate monomers, the polymerisations reached high conversion, as both polymers are



1 2

Scheme 2 Structure of 2-(2-cyanopropyl) dithiobenzoate (CPDB, **1**) and 1-alkyl-3-methylimidazolium hexafluorophosphate (**2**).

Table 1 Final conversion, molecular weight and polydispersity data for the polymerisation of MMA, MA and styrene mediated by CPDB in bulk, room temperature ionic liquids and toluene

Reaction[a]	Monomer	Solvent	Conversion (%)[b]	M_n/g mol^{-1}[c]	$M_{n,theo}$/g mol^{-1}[d]	*PDI*[c]
1	MMA	—	89.7	49 100	43 800	1.19
2	MMA	Toluene	71.7	41 500	34 900	1.14
3	MMA	$[C_4][PF_6]$	84.3	59 700	41 000	1.15
4	MMA	$[C_6][PF_6]$	91.3	66 200	44 500	1.12
5	MMA	$[C_8][PF_6]$	90.1	67 400	43 900	1.11
6	MA	—	44.2	35 800	22 100	1.24
7	MA	Toluene	62.3	34 200	31 000	1.28
8	MA	$[C_4][PF_6]$	69.6	35 600	34 700	1.17
9	MA	$[C_6][PF_6]$	83.0	51 600	41 300	1.23
10	MA	$[C_8][PF_6]$	85.0	55 600	42 300	1.26
11	Sty	—	23.2	13 200	11 000	1.13
12	Sty	Toluene	15.0	7 900	7 100	1.07
13	Sty	$[C_x][PF_6]$, ($x = 4, 6, 8$)	< 2	—	—	—

[a] All polymerisations were carried out with a ratio [Monomer]/[CPDB] = 490, under nitrogen atmosphere at 60 °C for 24 h. [b] Determined ^{1}H NMR using d_8-DMSO as solvent. [c] Determined by SEC using THF as eluent and PMMA or PS standards. The molecular weights of the MA products were corrected using the Mark-Houwink constants available in the literature ($\alpha = 0.660$ and $K = 19.5$). [d] Calculated using the following formula: $M_{n,theo} = [\text{Monomer}]/[\text{CPDB}] \times M \times c$, where M is the monomer molecular mass and c, the fractional conversion.

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fully soluble in the ionic liquids. Table 1 summarises the results of the polymerisations. For both monomers, the polymerisation rate seems to be faster in ionic liquids than in toluene. This is consistent with previous studies, which showed that free radical polymerisations occur at a faster rate when performed in ionic liquids.[16–18] For instance, at 60 °C, a conversion of 25% is reached in 20 min when polymerising MMA free radically in $[C_4][PF_6]$, while the polymerisation in toluene, keeping the other conditions constant, leads to 3% conversion.[18] In the present case, however, the effect on the rate is less pronounced, as the CPDB mediated polymerisation of MMA in $[C_4][PF_6]$, leads to 84.3% conversion against 71.7% in toluene. Moreover, the polymerisation in $[C_4][PF_6]$ (84.3%) seems slightly slower than in $[C_6][PF_6]$ and $[C_8][PF_6]$ (91.3% and 90.1%, respectively). The MMA polymerisations in ionic liquids lead to final products with polydispersities as low as 1.11, which are close to the ones obtained when reacting in bulk or in toluene (1.19 and 1.14, respectively). In the case of the MA polymerisations, the polydispersity was slightly higher than with MMA, but still smaller than 1.30. It is remarkable that both polymerisations present similar rates, in contrast to what is observed in classic free radical polymerisation. This can be explained by the equilibrium between active and dormant species being more favoured towards the dormant species in the case of MA polymerisation than in the case of MMA polymerisation (Indeed, the active PMA chain has a terminal secondary carbon radical which is less stable than the terminal tertiary carbon radical of PMMA).

Another interesting observation is the difference between the experimental and theoretical molecular weights in both polymerisations. A poor efficiency of the RAFT agent in the presence of the solvent (only part of the CPDB present in solution participates to the RAFT equilibrium) is a possible explanation for this effect. We are currently undertaking further experiments to investigate this original behaviour.

In order to prove the living character of the polymerisation, products from the reactions in ionic liquids were isolated and further reacted. The polymers were dissolved in their own monomers, and used as macroRAFT agents. The resulting products were analysed by SEC, and compared to the original macroRAFT agent. While more than 90% of the chains reinitiate the polymerisation in the case of PMA, we found a higher proportion of dead polymeric chains for PMMA. However, these dead chains seemed to have been formed *during the purification* of the polymers, and not *during polymerisation*. Indeed, if the chain extension is performed without purification, by simply adding a new batch of monomer toward the end of the polymerisation, products with narrow molecular weight distribution are obtained (no peak due to dead polymer chains is observed). Furthermore, in the case of the chain extension on a purified PMMA, the deconvolution of the bimolecular SEC signal leads to two peaks, both showing very narrow molecular weight distribution. If the dead materials were formed by termination reactions during polymerisation, one would not expect such narrow PDI. Fig. 1 shows the SEC traces for the chain extension of PMA. The polymer was initially formed in $[C_4][PF_6]$ (M_w = 69 500 g mol^{-1} *PDI* = 1.16), then fully reacted into a new polymer of molecular weight (M_w) 94 500 g mol^{-1} with *PDI* = 1.19. The high molecular weight shoulder observed in Fig. 1 is due to the few unavoidable reactions of termination by combination occurring during polymerisation, classically observed in any RAFT polymerisation of acrylates and styrene.

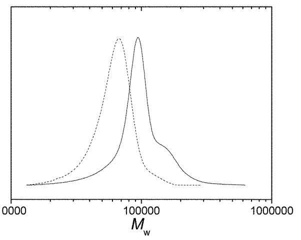

Fig. 1 SEC curves for the chain extension of PMA utilised as macroRAFT agents.

As a conclusion, we have shown for the first time that the RAFT poymerisation of MA and MMA in ionic liquids presents a living character and leads to polymers with narrow molecular weight distributions. We are currently extending our investigations.

Notes and references

† The polymerisations were performed as follows. 2 mL of ionic liquid were placed in an ampoule, and left under vacuum for 30 min in order to remove the oxygen. Stock solution of CPDB (42.5 10^{-3} g, 19.2 10^{-5} mol), 2,2-azobisisobutyronitrile (AIBN, 5.6 10^{-3} g, 3.4 10^{-5} mol) and monomer (10 mL, 11.1 10^{-2} mol (MA), 9.4 10^{-2} (MMA), 8.7 10^{-2} mol (Sty)) was prepared and submitted to 3 freeze–pump–thaw cycles. 2 mL of this solution were transferred to the ampoule containing the ionic liquid under inert atmosphere. In the case of the use of toluene as solvent, 2 mL of toluene were added to the 2 mL of stock solution and a further 3 freeze–pump–thaw cycles were performed. The sealed ampoules were then placed in a constant temperature oil bath at 60 °C, and each ampoule was removed after a pre-determined time interval. The reactions were stopped by the cooling of the solutions in an ice bath. Final conversions were measured by ^{1}H NMR using d_8-DMSO as solvent. SEC analysis was carried out on the bulk of the reaction media by dissolving the ionic liquid solution directly in the THF eluent. The polymer was isolated by evaporating off the residual monomer and extraction into toluene.

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