Supported ATRP of fluorinated methacrylates in supercritical carbon dioxide: preparation of scCO$_2$ soluble polymers with low catalytic residues[†]

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Abstract

Synthesis of poly(2,2,2-trifluoroethyl methacrylate) by supported ATRP was investigated in supercritical carbon dioxide using a copper salt ligated to a polymeric ligand immobilised onto silica; after polymerisation, fluorinated polymers with well defined molecular weight and low polydispersity were obtained.

Atom transfer radical polymerisation is one of the most robust tool for the synthesis of polymers with well defined characteristics and architecture[1] but suffers from the major drawback that it relies on the use of transition metal catalysts that contaminate the final polymer. Recently, ARGET[2-5] and ICAR[6] ATRP have been proposed as very promising approaches to significantly decrease the amount of catalyst. In ARGET, a very low amount of catalyst (Cu(II)), as low as a few ppm, is continuously regenerated to the Cu(I) activator state by an excess of reducing species, *i.e.,* tin ethylhexanoate (Sn(EH)$_2$),[6] fructose[7] or ascorbic acid.[5] ICAR similarly regenerates Cu(I), but through the use of an organic radical initiator such as AIBN. Nevertheless, due to such a low content of catalyst, control of the polymerisation can be very difficult and is strongly dependent on the $-K_{ATRP}$ values.[8] Immobilising the catalyst onto an inorganic support is a second alternative to remove the catalyst.[9-11] Despite the requirement for use of a small amount of catalyst in its oxidated state[12-15] in order to increase the deactivation rate, synthesis of polymers with well defined molecular weight and low polydispersity has been reported by supported ATRP. In this work, we prepare poly(2,2,2-trifiuoroethyl methacrylate) (PFMA) in supercritical carbon dioxide (scCO$_2$) by supported ATRP which is a preliminary step for the synthesis of non-crystalline fluoro-polymers, known for high solubility in this medium, by a (semi)continuous ATRP process. Due to the unique properties of scCO$_2$ (high mass transport, low viscosity, high density), the use of a sacrificial initiator or deactivator is not required to obtain good control of the polymerisation when a macroligand is immobilised on the support.

Recently, we reported the successful synthesis of PMMA by dispersion ATRP using a CO$_2$-philic polymeric ligand bearing tetraethyldiethylenetriamine (TEDETA) pendant groups (Fig. 1) that had a dual role, *i.e.* complexation of a copper salt and stabilization of PMMA growing particles.[16] Whereas purification of PMMA by supercritical fluid extraction (SFE) of the fluorinated catalyst was easy, when a fluorinated polymer is considered (PFMA for instance), both the catalyst and the polymer exhibit high solubility in scCO$_2$. This could make the selective separation of the CO$_2$-soluble catalyst from the fiuoropolymer matrix by SFE rather difficult, which justifies the immobilisation of the ligand onto an inorganic support for the development of supported ATRP.

Homogeneous ATRP of FMA (10 ml) was first investigated in scCO$_2$. The polymerisation was initiated by α-methyl-bromophenyl acetate (MBPA) and catalyzed by CuBr ligated by a macroligand with $M_n = 5000$ g mol^{-1} and 2 TEDETA per chain. Polymerisation was conducted at 320 bar and 70 °C for 24 h in a 35 ml high pressure cell. FMA was chosen as a monomer because the resulting fluorinated polymer is soluble both in THF, which allows its easy characterization by size exclusion chromatography, and, more importantly, in scCO$_2$. Indeed, when polymerisation was realized in a view cell (Table 1, entry 3), the brownish polymerisation medium remained homogeneous during the whole polymerisation process, in agreement with the high solubility of the fluoropolymer in scCO$_2$. Different monomer to initiator molar ratios were investigated in order to target different molecular weights. In each case, the conversion, estimated by gravimetry, was high and the molecular weight was easily modulated by the monomer to initiator molar ratio, as expected for a controlled process. Moreover,

the molecular weight distribution was low ($1.1 \leq M_w/M_n \leq 1.15$) until high monomer conversions (Table 1). For comparison, the same experiment was repeated under the same conditions using free TEDETA instead of a macroligand to complex the copper salt. Under these conditions, the monomer conversion was low, the polymerisation was out of control and the polydispersity was high, resulting from the poor solubility of the catalyst in this medium.[16,17]

Fig. 1: *Grafting of TEDETA and macroligands by the "grafting onto" approach.*
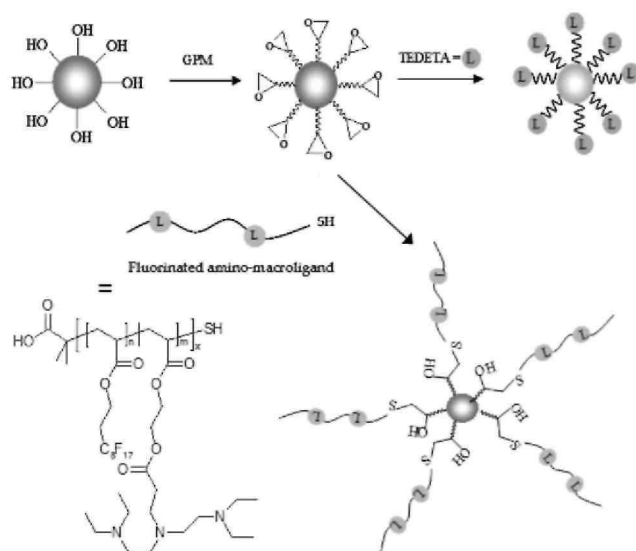
Table 1: *Experimental conditions for ATRP of FMA in scCO₂*

	Macroligand							
Entry	M_n/g mol^{-1}	**No. TEDETA per chain**	**[Cu]/[MBPA]**	**[FMA]/[MBPA]**	**Conv. (%)**[a]	$M_{n,theor}$/g mol^{-1b}	$M_{n,exp}$/g mol^{-1c}	**PDI**
1	5000	2	0.5	130	78	17 400	19 000	1.11
2	5000	2	0.5	240	78	31 200	32 000	1.14
3	5000	2	0.5	360	72	43 000	45 000	1.13
4	15 000	4	0.5	165	90	27 000	31 000	1.15
5	—	Free TEDETA	0.5	240	15	6000	9200	5.60

[a] Gravimetrically determined. [b] $M_{n,theor}$ = (weight of monomer/n initiator) x monomer conversion. [c] Estimated by SEC with PMMA calibration.

In a second step, the macroligands, which are end-capped by a thiol group,[18] were immobilised by the "grafting onto" approach onto Cab-O-Sil EH5 (specific surface area: 380 m^2 g^{-1}; ~4.5 Si-OH nm^{-2}) (Fig. 1). The silanol groups at the surface of silica were first reacted with 3-glycidoxypropyltrimethoxysilane (GPM) in order to convert them into epoxy groups *via* a stable Si-C bond. In order to prevent the methoxy groups of GPM from condensing in the presence of water, the silica particles were previously dried at 120 °C for 24 h *in vacuo,* before being dispersed in dry toluene and added to an excess of GPM (20 eq. GPM compared to Si-OH). After 24 h at 100 °C, the excess of GPM was removed by repeated cycles of centrifugation (5000 rpm, 20 min)/redispersion in toluene. After drying *in vacuo,* the grafting yield of the particles was determined by thermogravimetric analysis. The TGA curves showed two weight losses, at 120 °C for the adsorbed GPM and at 350 °C for the covalently bonded GPM, respectively (*cf.* ESI, [†] Scheme S1). Therefore, the non-grafted GPM was eliminated by thermal post-treatment of the silica particles until the first weight loss in the thermogram completely disappeared. TGA of the so-purified silica showed a weight loss of 11% which corresponds to 1.5 epoxy group nm^{-2}. The grafting of GPM was confirmed by ^{13}C and ^{29}Si solid state NMR spectroscopy (*cf.* ESI, [†] Schemes S2 and S3, respectively). The solid state ^{29}Si CP-MAS NMR spectrum of silica grafted by GPM shows the typical silicon resonances of the particle core between -100 and -130 ppm. Three distinct peaks are also visible at -49, -57 and -99 ppm, which correspond to the bonding of GPM to the surface by reaction of 1, 2 or 3 methoxy groups, respectively.[19] Macroligands with a ω-thiol end group were finally grafted onto silica by reaction with the surface epoxy groups at room temperature for 5 days in trifluorotoluene (TFT). After reaction, silica was purified by repeated centrifugation (5000 rpm, 20 min)/redispersion (in TFT) cycles before characterization by TGA in order to estimate the amount of grafted macroligand (0.06 macroligand nm^{-2}) (*cf.* ESI, [†] Table S1). The same

procedure was used to graft a macroligand with a higher molecular weight (M_n = 15 000 g mol^{-1}).

Supported ATRP of FMA (10 ml) was initiated by methyl-α-bromophenylacetate (MBPA) at 70 °C and 320 bar in the presence of CuBr ligated by the two different supported fluorinated macroligands (M_n = 15 000 g mol^{-1}; 4 TEDETA units per chain; weight loss = 39%, and M_n = 5000 g mol^{-1}, 2 TEDETA per chain, weight loss = 20%) without the addition of free Cu(II)/TEDETA catalyst. ATRP was conducted in a 35 ml high pressure cell thermostated in a preheated oil bath and equipped with a stirring bar. After 24 h at 1000 rpm, the reactor was cooled below room temperature, so that the fluorinated polymer precipitated in the high pressure cell, and CO_2 was rapidly vented in order to avoid the extrusion of CO_2-plasticised PFMA through the releasing valves during venting. A liquid was however extracted during CO_2 venting and ^{1}H NMR characterization demonstrated that it was the residual monomer. After complete depressurisation, the cell was opened and a few mg of PFMA were dissolved in THF in order to determine the apparent molecular weight and the polydispersity of the final product by size exclusion chromatography in THF calibrated by PMMA standards. After drying of the polymer under vacuum overnight at 40 °C, the monomer conversion was gravimetrically determined. CuBr supported on Cab-O-Sil is an effective catalyst for the ATRP of FMA. Indeed, the molecular weight of PFMA is close to the value observed in homogeneous ATRP (Table 2, entries 3-8). It should be noted that the molecular weight of the PFMA chains was too high to be estimated by ^{1}H NMR spectroscopy. Nevertheless, the molecular weight of the supported macroligand has an impact on the molecular weight distribution of PFMA formed. Indeed, when a short macroligand is immobilised, the polydispersity is low (M_w/M_n = 1.10, Table 2, entry 4) and is similar to the value obtained for homogeneous ATRP of FMA in scCO$_2$.

For comparison, the same experiment was repeated using copper catalyst ligated by TEDETA immobilised onto silica (Table 2, entry 2) or a higher molecular weight macroligand grafted onto the support (Table 2, entry 8). Whereas the polymerisation rate is not affected by the length of the spacer, higher polydispersity values (1.35 < M_w/M_n < 1.45, Table 2, entries 2, 6, 8) were obtained. These results are quite different from those reported by Shen *et al.* who investigated the effect of a polyethylene glycol spacer on the polymerisation rate in the supported ATRP of MMA in organic solvent.[20] Moreover, low polydispersity was obtained even in the absence of free Cu(II) deactivator whereas supported catalyst/free oxidized catalyst hybrid systems were proposed in order to improve the control of the polymerisation in case of supported ATRP in organic medium.[12,13] These results are the consequence of the unique properties of scCO$_2$, *i.e.,* high mass transport properties, low viscosity and high density, so increasing the diffusivity of the active species (gas-like properties of scCO$_2$) combined with the small size of the support (~0.3 µm). These statements are in line with Zhu *et al.* who demonstrated that surface-mediated deactivation was not feasible when large supporting particles (~100 µm) were used due to the geographic isolation of the catalytic sites.[21,22] The deactivation rate was however improved when small supporting particles were used. The high efficiency of our supported catalyst might also be explained by the presence of leached catalyst that also increases the deactivation rate.[21,22]

Table 2: *Homogeneous and supported ATRP of FMA in scCO$_2$: [MBPA]/[TEDETA] = 2, [CuBr]/[TEDETA] = 1, [Cu]$_0$ = 4314 ppm*

Entry		Macroligand characteristics		Polymerisation characteristics				
		M_n/g mol^{-1}	No. TEDETA per chain	[FMA]/[MBPA]	Conv. (%)^a	$M_{n,app.}$/g mol^{-1} ^{b}	PDI	Residual catalyst (ppm)
1	Free TEDETA	—	—	240	20	9200	5.6	n.d.
2	Supported TEDETA	—	0.25 TEDETA nm^{-2}	240	82	36 000	1.4	321
3	Homogeneous ATRP	5000	2	240	78	32 000	1.14	n.d.
4	Supported ATRP	5000	2	240	77	33 000	1.10	117
5	Homogeneous ATRP	15 000	4	150	90	31 000	1.15	n.d.
6	Supported ATRP	15 000	4	150	76	26 000	1.45	63
7	Homogeneous ATRP	15 000	4	240	90	34 000	1.15	n.d.
8	Supported ATRP	15 000	4	240	80	30 000	1.35	138

^{a} Gravimetrically determined. ^{b} Determined by SEC with a PMMA calibration.

Finally, the removal of the catalyst was investigated. In practice, after depressurisation of the high pressure cell, PFMA was dissolved in THF before removal of the supported catalyst by centrifugation (5000 rpm, 5 min) and the residual amount of copper was estimated by ICP measurements (Table 2). From the ICP results, in the best case, more than 98.5% of the catalyst were extracted (Table 2, entry 6), which leads to PFMA with catalytic residues as low as 63 ppm compared to $[Cu]_0 = 4314$ ppm.

In conclusion, a copper-based catalyst ligated by silica supported fluorinated macroligands is very active in ATRP of FMA to high conversions in $scCO_2$. Indeed, due to the unique properties of $scCO_2$, the use of a sacrificial initiator or Cu(II) deactivator is not required to obtain PFMA with controlled molecular weight and polydispersity as low as 1.1. Finally, after removal of the catalyst the residual copper content was as low as 63 ppm. Optimization of the recycling conditions (extraction and reuse of the catalyst) is in progress. These preliminary results are a step to the semi-continuous synthesis of fluoropolymers by ATRP in $scCO_2$.

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