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Copper bromide complexed by fluorinated macroligands: towards microspheres by ATRP of vinyl monomers in $scCO_2$†

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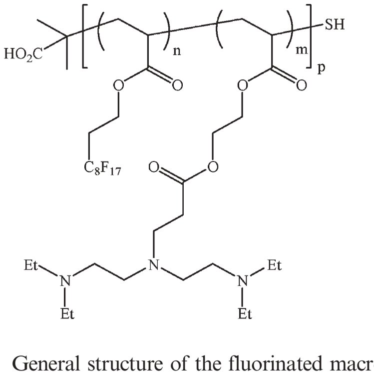
We report the successful synthesis of poly(methyl methacrylate) (PMMA) by atom transfer radical polymerization using a catalyst ligated to a polymeric ligand having a dual role, *i.e.*, the complexation of the copper salt and the stabilization of the growing PMMA particles; at the end of the polymerization, the catalyst is removed by supercritical fluid extraction leading to PMMA microspheres with low residual catalyst content.

Controlled radical polymerization is a powerful technique for the preparation of (co)polymers with well-defined molecular parameters such as molecular weight, architecture, composition and end functional groups. Various methods have been developed for the controlled polymerization of vinyl monomers. Atom transfer radical polymerization (ATRP) has emerged as a powerful tool for the synthesis of well-defined polymers under relatively mild conditions.[1] Nevertheless, purification of the polymers at the end of the polymerization is required to eliminate the metal catalyst which can be environmentally and toxicologically problematic. Some progress has been made to decrease the amount of catalyst in the product polymers by using supported catalysts.[2] However, the polymerization medium still must be diluted by organic solvents (volatile organic compounds, VOCs) after polymerization in order to isolate the catalyst. More recently, activators regenerated by electron transfer (ARGET)[3] have been developed using a new initiating/catalytic method and dramatically decrease the catalyst requirement. For all processes, the use of VOCs must be restricted, and this makes the search for environmentally acceptable polymerization media very important. Supercritical carbon dioxide ($scCO_2$) (p_c = 73.8 bar, T_c = 31.1 °C), is one such alternative and exhibits low cost, low toxicity, non-flammability, easy recyclability.[4] Moreover, the density of CO_2 can be finely tuned by adjusting the pressure and temperature, which has shown utility for numerous applications such as supercritical fluid extraction, organic synthesis, homogeneous and supported catalysis, and polymerization.[5] ATRP has been demonstrated in $scCO_2$ for the homogeneous ATRP of fluorinated (meth)acrylates using copper(I) bromide ligated by bipyridine.[6] Others also showed that poly(dimethylsiloxane)-*b*-poly(methyl methacrylate) (PDMS-*b*-PMMA) and poly(methyl methacrylate)-*b*-poly(ε-caprolactone) (PMMA-*b*-PCL) diblock copolymers could be prepared in $scCO_2$.[7,8] However, the ATRP catalytic systems used for these syntheses are generally poorly soluble in $scCO_2$ and most vinyl polymers are insoluble, with the exception of those that are fluorinated,[9] which generally leads to polymer precipitation during polymerization, and this strongly affects control of macromolecular parameters and introduces catalyst residues which may lead to environmental and toxicological problems.

In this paper we report the efficient controlled dispersion ATRP of methyl methacrylate (MMA) in $scCO_2$ using a CO_2-philic ATRP catalyst which also acts as a stabilizer for the heterogeneous polymerization. A key advantage of this process is the production of PMMA microspheres with controlled molecular weight, and the CO_2-philic catalyst that acts as both ATRP catalyst and stabilizer can be recycled. The CO_2-philic ATRP catalyst is based on copper(I) bromide ligated by an amino-based fluorinated macroligand of the general structure shown in Scheme 1. The synthesis of this macroligand was reported elsewhere[10] and relies on a three-step strategy that first consists of the synthesis of a well-defined random copolymer of heptadecafluorodecyl acrylate (AC8) and 2-hydroxyethyl acrylate[11] (HEA), followed by esterification of the pendant hydroxyl groups with an excess of acryloyl chloride. A Michael-type addition of tetraethyldiethylenetriamine (TEDETA) onto the acrylate groups leads to the macroligand.[11] In the first step of the process, poly(heptadecafluorodecyl acrylate)-*co*-poly(2-hydroxyethyl acrylate) (PAC8-*co*-PHEA) copolymer with predictable molecular weight ($M_{n,NMR}$= 15000 g mol^{-1}), well-defined composition (AC8–HEA = 85 : 15), and low polydispersity index (PDI) ($M_w/M_n \sim 1.1$) was formed by reversible addition–fragmentation chain transfer (RAFT) polymerization in the presence of *S*-1-dodecyl-*S*-(α,α′-dimethyl-α″-acetic acid)trithiocarbonate as a chain transfer agent in benzotrifluoride at 80 °C.[10]



Scheme 1 General structure of the fluorinated macroligand.

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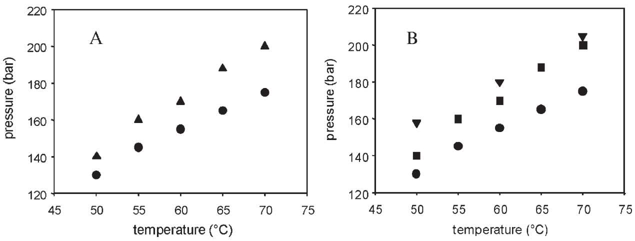

Fig. 1 (**A**) Effect of the macroligand composition: (▲) macroligand (15000 g mol^{-1}, 2.7 L/chain), 1 g/130 ml; (●) PAC8 (15000 g mol^{-1}), 1 g/130 ml; and (**B**) effect of copper bromide complexation on the cloud point measurements: (▼) macroligand (15000 g mol^{-1}, 2.7 L/chain), 1 g/130 ml, CuBr; (■) macroligand (15000 g mol^{-1}, 2.7 L/chain), 1 g/130 ml; (●) PAC8 (15000 g mol^{-1}), 1 g/130 ml.

Esterification of the pendant hydroxyl groups of the copolymer was then carried out with an excess of acryloyl chloride in dry benzotrifluoride in the presence of *N*-methylmorpholine.[11] Finally, an excess of tetraethyldiethylenetriamine (TEDETA) was added onto the acrylate double bonds by a Michael-type addition,[11] so making the well-defined macroligand with binding sites available to copper complexation ($M_{n,NMR}$= 15000 g mol^{-1}; TEDETA/chain = 2.7). It must be noted that the trithiocarbonate end-group of the original PAC8-*co*-PHEA copolymer was released during the Michael addition, leading to thiol terminated macroligand.[10]

The solubility of the fluorinated macroligands (M_n = 15000 g mol^{-1}) containing 2.7 TEDETA moieties per chain was investigated by cloud point measurements in scCO$_2$ over a range of temperatures and pressures. The macroligand solubility in scCO$_2$ was compared to a reference poly(heptadecafluorodecyl acrylate) (PAC8) of the same molecular weight (15000 g mol^{-1}). Fig. 1A clearly shows that the pressure required to dissolve the fluorinated macroligand increases with the grafting of the TEDETA moieties and this is attributed to the incorporation of CO$_2$-phobic amino groups along the fluorinated CO$_2$-philic chains. Complexation of copper bromide by the macroligands also further decreases slightly the solubility in scCO$_2$ (Fig. 1B). From these measurements, it is clear that working pressures higher than 220 bar are sufficient for dissolving the copper catalyst ligated by the amine-containing fluorinated macroligand at 70 °C.

The ATRP of MMA in scCO$_2$ was initiated by methyl α-bromophenylacetate (MBPA) at 70 °C and 320 bar in the presence of copper bromide ligated by the fluorinated macroligand (M_n = 15000 g mol^{-1}; 2.7 TEDETA units/chain; [MBPA]/[TEDETA] = 2; [CuBr]/[TEDETA] = 1, see ESI†). After 24 h of reaction at 1000 rpm, the reactor was cooled and vented. The molecular weight of the product was estimated by size exclusion chromatography with PMMA standards, and monomer conversion was determined gravimetrically. The monomer to initiator molar ratios were varied to target different molecular weights. Thus, at higher ratios M_n increased and the PDI was narrow ($1.15 \leqslant M_w/M_n \leqslant 1.25$) (Table 1, entries 1 to 4), demonstrating a controlled process. The initiator efficiency ($f = M_{n,theo}/M_{n,SEC}$) is however limited to about 0.65, indicating that only 65% of MBPA initiated MMA polymerization (Table 1). This compares favourably with supported ATRP in organic solvents where initiator efficiencies of around 0.6 were observed.[12]

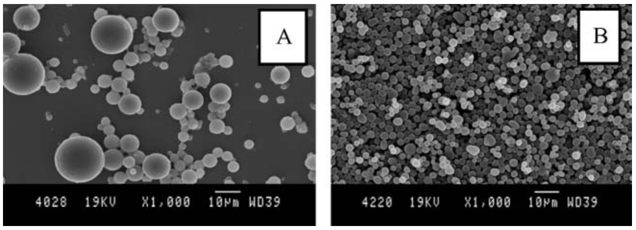

Fig. 2 SEM pictures at same magnifications for the dispersion ATRP of MMA using a macroligand (2.7 TEDETA/chain, 15000 g mol^{-1}, [MMA]/[MBPA] = 400, entry 4, Table 1) (A); and the free radical dispersion polymerization of MMA using a macroligand (3 TEDETA/chain, 15000 g mol^{-1}, 12.5 wt% compared to the monomer, entry 6, Table 1) as a stabilizer (B).

Most importantly, PMMA microspheres with diameter of 5–20 μm were collected as a free flowing white powder in the reactor (Fig. 2). It is clear that the macroligand containing amino CO$_2$-phobic and fluorinated CO$_2$-philic groups must have a dual role of ligand for copper bromide and stabilizer of the polymer particles by formation of a steric barrier around the growing PMMA particles. The macroligand should thus be located at the surface of the microspheres. In order to support this hypothesis, XPS analysis was carried out on the microspheres. Prior to analysis, the PMMA particles were purified by supercritical fluid extraction (P_{CO_2} = 300 bar, flow rate = 5 ml min^{-1}, T = 70 °C, time = 80 min) in order to remove the excess of free macroligand highly soluble in scCO$_2$ and not localized at the particle surfaces. The XPS spectrum (see ESI†) clearly evidenced the presence of a high concentration of fluorine atoms (36 atomic%) at the surface of the particles, which supports our hypothesis. For sake of comparison, when the same MMA polymerization was carried out with non-supported TEDETA (Table 1, entry 5) under the same conditions, the polymerization is uncontrolled, giving a broad and

Table 1 ATRP polymerization of MMA in scCO$_2$ at 320 bar and 70 °C for 16 h[a]

Entry	[MMA]/[MBPA]	*n* TEDETA[b]	Conv. (%)[c]	$M_{n,theo}$/g mol^{-1} [d]	$M_{n,SEC}$/g mol^{-1} [e]	M_w/M_n	f[f]
1	200	2.7	94	19000	29000	1.15	0.65
2	300	2.7	90	27000	40000	1.20	0.67
3	400	2.7	93	37000	59000	1.20	0.63
4	700	2.7	80	56000	85000	1.20	0.65
5	400	TEDETA	67	27000	33000	1.90	0.8
6[g]	—	3	95	—	77000	1.8	—

[a] Polymerization conditions: M_n of the macroligand = 15000 g mol^{-1}; 2.7 TEDETA units/chain; [MBPA]/[TEDETA] = 2; [CuBr]/[TEDETA] = 1; 70 °C; 320 bar; 1000 rpm; 24 h. [b] Number of TEDETA moieties per macroligand. [c] Determined gravimetrically. [d] $M_{n,theo}$ = ([MMA]0/[MBPA]0) × M_{MMA} × conv. [e] Determined by size exclusion chromatography (SEC) with poly(methyl methacrylate) standards. [f] $f = M_{n,theo}/M_{n,SEC}$. [g] Conventional radical polymerization of MMA initiated by AIBN in the presence of the macroligand (15000 g mol^{-1}, 2.7 TEDETA/chain, 65 °C, 7 h, 280 bar, 1 wt% AIBN compared to MMA).

Table 2 Catalyst extraction. Conditions, $[\mathrm{Cu}]_0$ = 4300 ppm, P = 300 bar, CO_2 flow rate = 5 ml $\min^{-1}$, extraction time = 80 min

Macroligand characteristics			PMMA characteristics			Catalyst extraction	
Entry	M_n/ g mol^{-1}	n^a	M_n/ g mol^{-1}	M_w/ M_n	Conv (%)	T/°C	Residual catalyst^b/ppm
1	10000	2.7	23000	1.25	92	50	158
2	10000	2.7	24000	1.2	90	70	250
3	15000	4	29000	1.15	90	50	430
4	15000	4	25000	1.25	85	70	1650

^{a} Number of TEDETA/chain. ^{b} Determined by ICP.

multimodal distribution (M_w/M_n = 1.9). This loss of control might result from poor solubility of the non-fluorinated catalyst in $scCO_2$. Moreover, the PMMA chains rapidly precipitate, without formation of microspheres. The beneficial effect of the fluorinated macroligand on both polymerization control and stabilization of PMMA is thus clear. In order to confirm further the role of the macroligand, polymerization of MMA was initiated by a conventional free radical initiator, azobis(isobutyronitrile) (AIBN), in the presence of the macroligand but without addition of copper salt. After 7 h of reaction at 280 bar and 65 °C, PMMA was recovered with 95% monomer conversion (M_n = 77000 g mol^{-1}; M_w/M_n = 1.8; Table 1, entry 6). The morphology, microspheres with a narrow size distribution and a diameter ranging from 2–3 μm, confirms that the macroligand acts as an effective steric stabilizer for MMA polymerization (Fig. 2b), that is consistent with the extensive published studies[5] of dispersion polymerization in $scCO_2$.

Finally, for a commercially viable process it will be necessary to demonstrate the potential for recycling of the catalyst. To do this, polymerization of MMA was first initiated by methyl-α-bromophenylacetate at 320 bar and 70 °C in the presence of copper bromide ligated by a macroligand with 2.7 TEDETA per chain (M_n = 10000 g mol^{-1}; [MMA]/[TEDETA] = 200) for 24 h (92% monomer conversion). At the end of polymerization, the stirrer was stopped and the PMMA microspheres rapidly settled but the CO_2-philic macroligand remained in solution. The catalyst was then recovered by venting the reactor with a continuous flow of CO_2 (5 ml $\min^{-1}$ at 300 bar) into a second high pressure vessel held at 1 bar of CO_2. This ensured that the catalyst rapidly precipitated and was collected as a green polymeric complex in the second reactor. The effect of temperature on the yield of extraction (Table 2) demonstrated that at lower temperature the extraction was more efficient. This clearly shows the dependence of macroligand solubility on temperature and pressure of $scCO_2$ and reinforces the cloud point data (Fig. 1). As a consequence, conducting the catalyst extraction at lower temperature while keeping the pressure constant should favour recovery. The effect of macroligand molecular weight on the catalyst extraction was also analyzed by conducting the MMA polymerization with copper bromide complexed to macroligands of the same composition but different molecular weights. A decrease in the ligand molecular weight increased the extraction yield because of the higher solubility of the low molecular weight chains. Inductively coupled plasma (ICP) analysis of the recovered polymer showed that more than 95% of the copper catalyst was separated from the polymer by $scCO_2$ extraction at 50 °C and 300 bar (residual copper determined by ICP = 160 ppm, $[\mathrm{Cu}]_0$ = 4300 ppm). Further research will be focussed upon the reuse of the catalyst.

In conclusion, a copper-based catalyst ligated by fluorinated macroligands is very active in the ATRP of MMA up to high conversions in supercritical carbon dioxide, yielding microspheres of PMMA with predictable molecular weight and low polydispersity. Due to the non-solubility of the PMMA chains in this medium, removal of the highly soluble fluorinated catalyst could be easily performed by supercritical extraction. Study of the influence of the macroligand composition and molecular weight on the polymerization control is under current investigation. Optimization of the recycling conditions (extraction and reuse of the catalyst), and studies into understanding the mechanism of particle stabilization are in progress. This new ATRP catalytic system has a high potential for macromolecular engineering in $scCO_2$, and for the production of metal-free tailored (co)polymers.

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