“One-pot” dispersion ATRP and alkyne-azide Huisgen’s 1,3-dipolar cycloaddition in supercritical carbon dioxide: towards the formation of functional microspheres

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Abstract: Functional polymers were successfully prepared in $scCO_2$ by combining alkyne-azide 1,3-dipolar Huisgen’s cycloaddition and dispersion ATRP in a “one pot” process using new perfluorinated polymeric amino-based ligands that had a dual role, i.e. the complexation of the copper catalyst and the stabilization of growing particles.

Introduction

Atom Transfer Radical polymerization (ATRP) has emerged as a robust tool for the preparation of polymers with well-defined molecular weight, architecture and chain-end functionality[1-4]. Recently, attention has been paid to the combination of ATRP and alkyne-azide 1,3-dipolar cycloaddition of Huisgen (CuAAC) [5,6], or click reaction, for the preparation of well-defined telechelic or block copolymers, functional polymers or polymer architectures[7-16]. Indeed, polymers prepared by ATRP are end capped by a C-Br bond that can be easily transformed in a carbon-azide group by nucleophilic substitution with NaN_3 and subsequently reacted with functional alkynes. Moreover, well-defined “clickable” polymers were also prepared by ATRP using azide or alkyne functional initiators or monomers[17-19]. Despite a huge number of works dealing with combination of ATRP and click reaction, examples of simultaneous ATRP and click reaction is quite limited. Because both ATRP and click reaction rely on the use of a Cu(I) catalyst and are tolerant towards non protected functional groups, combination of these two techniques in a “one-pot” process showed to be an attractive approach for preparing functional materials. For instance, Haddelton et al. reported on the use of a Cu(I)/iminopyridine catalytic system for the preparation of functional polymers by simultaneous CuAAC and ATRP in homogeneous organic medium[20-22]. Matyjaszewski et al. described with moderate success the coupling by a one-pot ATRP-nucleophilic substitution-click reaction strategy of homo and heterotelechelic polystyrene oligomers in DMF using a CuBr catalyst[23]. Dubois et al. reported on the synthesis of well-defined amphiphilic Poly(ε-caprolactone)-*b*-poly(dimethylaminoethyl methacrylate) block copolymers by a combination of ATRP and click chemistry following either a two-step procedure or a straightforward one-pot process using CuBr ligated by bipyridines as the sole catalyst[24].

Recently the use of $scCO_2$ as a green medium for polymer synthesis by Atom Transfer Radical Polymerization has gained increasing interest in academic laboratories and was recently reviewed [25,26]. In 1999, DeSimone et al. were the first to report on the copper-mediated synthesis of poly(1,1-dihydroperfluorooctyl methacrylate) (PFOMA) and poly(1,1-dihydroperfluorooctyl acrylate) (PFOA) by homogeneous ATRP in $scCO_2$ as well as the synthesis of PFOA based diblock copolymers [27]. Howdle et al. reported their initial work on ATRP carried out in $scCO_2$ for the synthesis of semifluorinated homopolymers[28] or non fluorinated polymers[29]. Instead of using a fluorinated catalyst in $scCO_2$, a much simpler cosolvent approach was adopted for creating a homogeneous system. The same group also published results on the “one-pot” synthesis of poly(ε-caprolactone)-b-poly(methyl methacrylate) diblock copolymers by combining the ring-opening polymerization of ε-caprolactone and the copper mediated ATRP of methyl methacrylate (MMA)[30]. Okubo et al. investigated the possibility to prepare PMMA-based diblock microparticles starting from a CO_2-soluble PDMS macroinitiator [31]. Recently, Detrembleur et al. reported on the synthesis of PMMA by dispersion ATRP in $scCO_2$ using a macroligand that had a dual role, i.e. the complexation of the copper salt and the stabilisation of the PMMA growing chains[32-34]. The concept of dispersion ATRP was extended to the preparation of polystyrene or poly(methyl methacrylate-b-poly(2,2,2trifluoroethyl methacrylate) (PMMA-b-PFMA) diblock copolymers starting from PMMA beads as macroinitiators[32] and to the synthesis of PMMA particles by Activator Generated by electron Transfer (AGET) ATRP[32]. Finally, by immobilizing the macroligand onto an inorganic support, the synthesis of perfluorinated polymers by supported ATRP was described and depending on the molecular weight and the composition of the macroligand, results obtained by homogeneous ATRP were identical to those obtained by supported ATRP even in the absence of Cu(II) as deactivator[35].

In this communication, we report on the synthesis of functional microspheres by combining 1,3-dipolar Huisgen's cycloaddition and dispersion Atom Transfer Radical Polymerization in a "one-pot" process using supercritical carbon dioxide as a green reaction medium.

Results

Recently, we reported on the successful implementation of dispersion ATRP of vinyl monomers in $scCO_2$. Using a α-methyl-bromophenyl acetate/Cu(I)Br/perfluorinated aminomacroligand (Scheme 1) catalytic system, the ATRP of MMA or styrene was controlled and polymers were collected as microspheres (PMMA) or quasi spherical microparticules (PS) demonstrating a dual role of the macroligands, i.e. the complexation and solubilization of the transition metal salt in $scCO_2$ and the stabilization of the growing polymers chains[32,33].

Due to an increasing demand on functional materials, including colloidal microspheres that are of special interest in various applications such as coating[36], biological assays[37] and fillers[38,39], functional PMMA beads were prepared in $scCO_2$ by combining dispersion ATRP and alkyne-azide 1,3-dipolar Huisgen's cycloaddition in a one-pot process according to the general strategy shown in Scheme 2.

In order to prepare such functional PMMA beads, the synthesis of a N_3-functional initiator was first realized according to the procedure reported in the literature[40]. In a first step, bromoethanol was reacted with a slight excess of NaN_3 and the hydroxyl group were subsequently derivatized into ATRP initiator by esterification with bromoisobutyrylbromide. In a second step, ATRP of MMA was initiated by the azido-functional initiator and catalyzed by Cu(I)Br ligated to a macroligand exhibiting a Mn of 10000 g/mol and bearing 3 TEDETA moieties per chain (cf scheme 1) ([MMA]/[initiator]/Cu(I)] = 400/1/0.5) at a CO_2 pressure of 300 bar. When it was first conducted at 75°C, for 24h, the monomer conversion gravimetrically determined was high (> 90%) and the experimental molecular weight determined by size exclusion chromatography was in good agreement with the theoretical value. However, the molecular weight distribution was high (Mw/Mn = 1.59) as a result of a strong tailing towards the lower molecular weight side (Table 1, entry 1). By adding 10 mol% of Cu(II)Br, the polymerization control was improved as evidenced by the good agreement between Mn theo and Mn exp and the lower molecular weight distribution (Mw/Mn = 1.31, Table 1, entry 2). Significant improvement of the ATRP of MMA was achieved by decreasing the temperature to 60°C without Cu(II). Indeed, at this temperature, whatever the monomer to initiator molar ratio (Table 1, entries 3-5), the monomer conversion was high after 36h (> 90%), the theoretical Mn was in good agreement with the experimental value and the polydispersity was narrow (Mw/Mn < 1.2). Finally, after depressurization of the cell, αN_3-

PMMA was collected as a free flowing powder consisting of microspheres with a mean diameter of 42 +/- 14 µm (Mn = 39000 g/mol, table 1, entry 3, Figure 1A) or smaller spherical particles (diameter = 13.5 +/- 5.3 µm) for PMMA of lower Mn (10000 g/mol, Table 1, entry 5, Figure 1B). The decrease of the particles size with the decrease of the molecular weight of the PMMA chains is explained by the fact that the macroligand had a dual role, i.e. the complexation of the copper salt and the stabilization of the growing chains. When lower PMMA molecular weights are targeted, the amount of initiator, CuBr and macroligand are increased compared to the monomer. Consequently, stabilization of the growing chain by the macroligand is enhanced and smaller microspheres are thus formed

In a second step, because both ATRP and Huisgen's cycloaddition rely on the use of a Cu(I) catalyst, functionalization of the PMMA chains by combining click reaction and dispersion ATRP in a one-pot process was investigated (Scheme 3). As a proof of the concept, ethynylpyrene was chosen as an alkyne model because it allows the easy characterization of pyrene end-capped PMMA chains either by size exclusion chromatography using UV detection and by ^{1}H NMR spectroscopy.

In practice, ATRP of MMA was initiated by the N_3-ATRP initiator and catalyzed by Cu(I)Br ligated to a macroligand of Mn = 10000 g/mol bearing 3 TEDETA groups per chain in the presence of ethynylpyrene. The reactions were conducted at 300 bar using a Cu(I)/N_3-initiator/alkyne molar ratio of 0.5/1/1. Different monomer to initiator molar ratios were investigated in order to target different molecular weights (Table 2). After 36h at 60°C, the pressure was released and the monomer conversion, gravimetrically determined, was high (> 90%) and the pyrene end-functionalized PMMA chains (αPy-PMMA) were characterized by size exclusion chromatography using refractive index and UV detection (λ = 366 nm). From these results, it is shown that the SEC traces are narrow ($Mw/Mn < 1.2$, Table 2, entry 3) and all the PMMA chains strongly absorb in UV (Figure 2), confirming the grafting of the alkyne onto the polymer.

For each case, the experimental molecular weight of the PMMA chains determined by SEC using a PMMA calibration is quite different from the theoretical value. This discrepancy is not understood yet. However, experimental molecular weight determined by SEC is identical to the Mn estimated by ^{1}H NMR spectroscopy ($M_{n,\ 1H\ NMR}$) determined by comparison of the relative intensity of the peaks corresponding to the pyrene protons and the proton of the triazole ring (10H, 7,8 ppm, m) and the peak characteristic of the methyl group of the repeating units of MMA (CH_3, 3.6 ppm, s) (Figure3). This excellent fit between $M_{n,\ SEC}$ and $M_{n,\ 1H\ NMR}$ confirms the presence of one pyrene group per polymer chain and therefore attests for the efficient simultaneous click reaction/dispersion ATRP under green conditions. More interestingly, after depressurisation of the cell, pyrene end-functionalized PMMA was collected as microspheres (mean diameter ~16 +/- 7 µm for αPy-PMMA of Mn = 27000 g/mol) that were characterized by fluorescence microscopy. From the results, it appears that particles consisting of PMMA chains end-capped by pyrene units show strong fluorescence (Figure 4) whereas αN_3-PMMA doesn’t fluoresce.

Conclusions

Preparation of functional microspheres by combination, in a “one-pot” process, of alkyne/azide 1,3-dipolar Huisgen’s cycloaddition and dispersion ATRP in $scCO_2$ was successfully reported using Cu(I)Br as a catalyst ligated to perfluorinated polymeric amino-based ligand that had a dual role, i.e. the complexation of the copper salt and the stabilization of growing polymer chains. For ease of characterization, the proof of concept was first demonstrated for the functionalization of PMMA by pyrene groups. Actually, this system is extended to the functionalization of PMMA by others functional groups such as alcohols, amines and epoxides.

Experimental part

Materials. N_3-ATRP initiator[40] and the perfluorinated macroligands[34] were prepared according to the procedure reported in the literature. Ethynylpyrene (Fluka, 96%), MMA (Aldrich, 99%) and CO_2 (N48, Air liquide) were used as received. CuBr (Aldrich, 99%) was purified by dispersion within glacial acetic acid and washed with methanol.

Characterization techniques. Size exclusion chromatography (SEC) was carried out in THF at 45°C at a flow rate of 1 mL/min with a SFD S5200 autosampler liquid chromatograph equipped with a SFD refractometer index detector 2000. PL gel 5µm (10^5 Å, 10^4 Å, 10^3 Å and 100 Å). Waters gel 5µm (10^5 Å, 10^4 Å, 500 Å and 100 Å) columns were calibrated with PMMA standards. ^{1}H NMR spectra were recorded in $CDCl_3$ at 400 MHz in the FT mode with a Brucker AN 400 apparatus at 25°C.

One-pot dispersion ATRP and click reaction. In a typical experiment, ethynylpyrene (0.127g, 5.61 10^{-4} mol), N_3-initiator (0.1325g, 5.61 10^{-4} mol) were introduced in a glass tube in the presence of 12 ml of MMA. The reaction mixture was deoxygenated by N_2 bubbling for 5 minutes and transferred with the help of a syringe into a 35 ml high pressure, under CO_2, containing the Cu(I)Br catalyst (0.0402 g, 2.81 10^{-4} mol) and the macroligand (0.936 g, Mn =

10000 g/mol, 3 TEDETA/chain). The high pressure cell was then equilibrated at 60°C for 36h at 300 bar.

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References and notes

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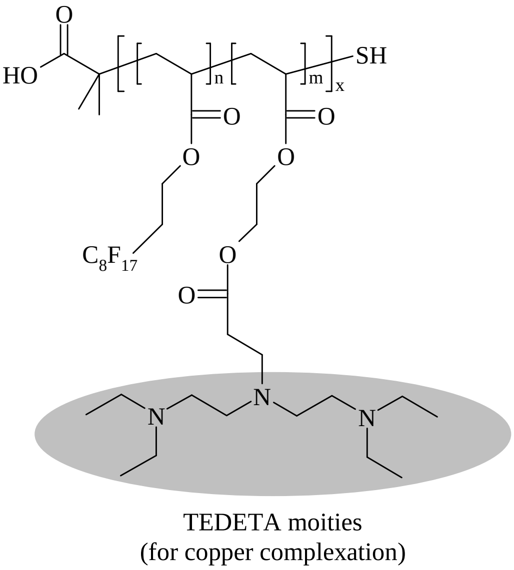
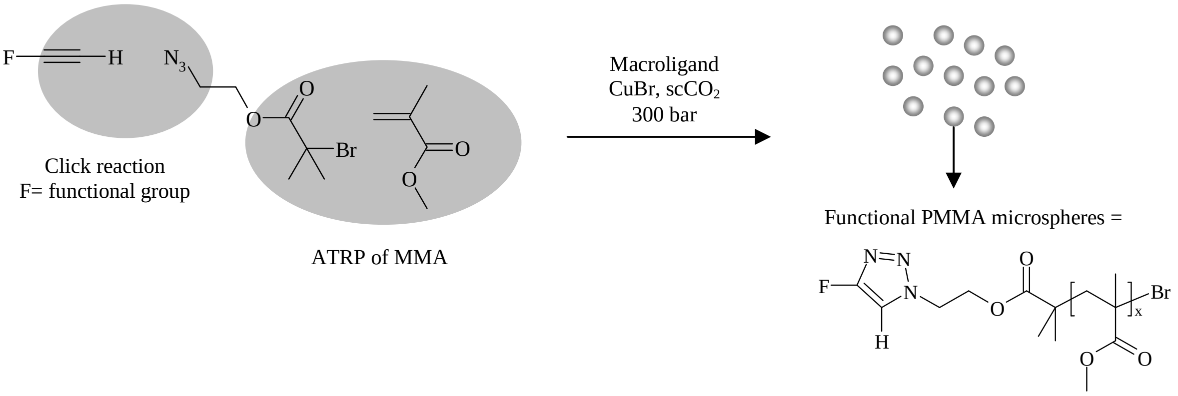
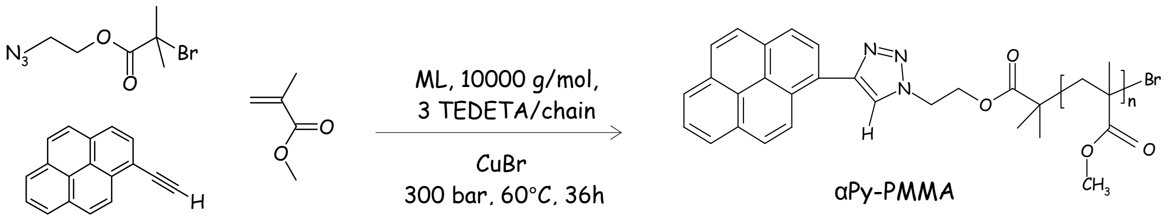


Scheme 1: Structure of the perfluorinated amino-macroligand



Scheme 2: Synthesis of functional PMMA microspheres by combining click reaction and dispersion ATRP in $scCO_2$ in a one-pot process



Scheme 3: Synthesis of functional PMMA chains by combination of click reaction and dispersion ATRP in $scCO_2$ in a “one-pot” process (ML = perfluorinated macroligand)

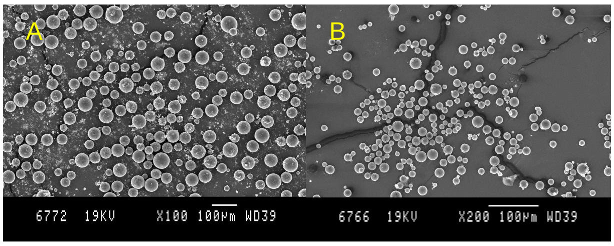


Figure 1: SEM characterization of PMMA micropsheres prepared by dispersion ATRP using N_3-ATRP initiator

A: αN_3-PMMA of Mn = 39000 g/mol

B: αN_3-PMMA of Mn = 10000 g/mol

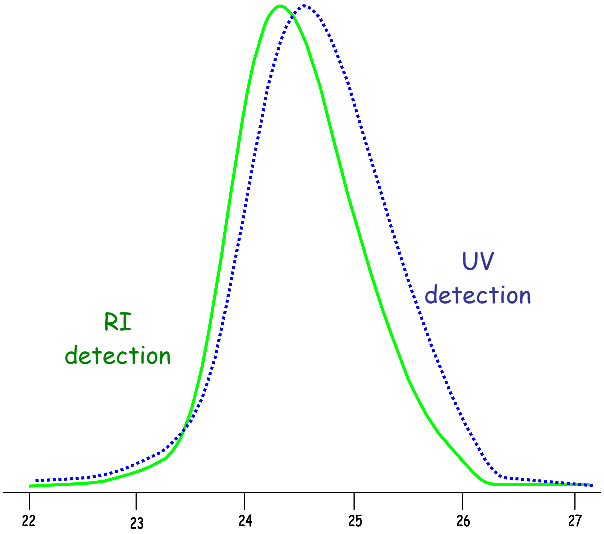


Figure 2: SEC characterization of pyrene end-capped PMMA chains using refraction of UV detection.

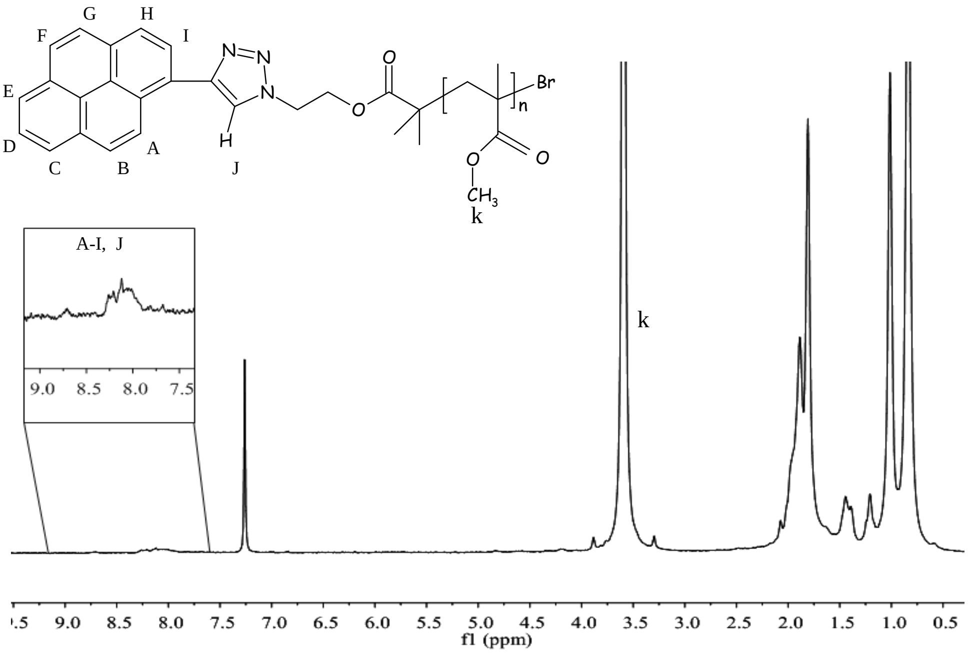


Figure 3: ^{1}H NMR spectrum of αPy-PMMA (Mn = 29000 g/mol, table 2, entry 1)

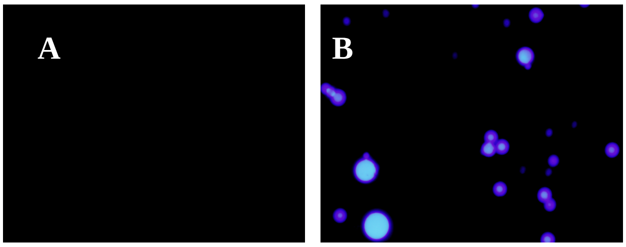


Figure 4: Characterization of α-functional PMMA microspheres by fluorescence microscopy: A: αN_3-PMMA (Mn = 19000 g/mol, table 1, entry 4) and B: αPy-PMMA (Mn = 29000 g/mol (table 2, entry 1)

entry	MMA/ initiator	T° (°C)	Time (h)	Cu(II) (%)	Conv (%)[a]	Mn, theo[b]	Mn, exp[c]	PDI
1	400	75	24	/	90	36000	37000	1.59
2	400	75	24	10	92	37000	36000	1.31
3	400	60	36	/	95	38000	39000	1.17
4	200	60	36	/	92	18400	19000	1.20
5	100	60	36	/	93	9600	10000	1.19
6	400	60	36	10	92	37000	37000	1.19

Table 1: Dispersion ATRP of MMA using the N_3-ATRP initiator/macroligand/Cu(I)Br catalytic system: P=300 bar, n CuBr/n initiator = 0.5

a gravimetrically determined

b Mn, theo = (Weight of MMA/n initiator) x conv

c determined by SEC using PMMA calibration

Entry	MMA/ initiator	Conv (%)[a]	Mn, theo (g/mol)[b]	Mn, SEC (g/mol)[c]	Mn, ^{1}H NMR (g/mol)[a]	PDI
1	100	94	9400	27000	29000	1.18
2	200	94	19000	43000	44000	1.19
3	400	96	38000	62000	65000	1.16

Table 2: One-pot Huisgen's cycloaddition and dispersion ATRP: T = 60°C, P = 300bar, t = 36h, initiator/alkyne/Cu(I)Br = 1/1/0.5

a gravimetrically determined

b Mn, theo = (Weight of MMA/n initiator) x conv

c determined by SEC using PMMA calibration

d determined by ^{1}H NMR spectroscopy on the base on the pyrene chain end