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Short communication:

Removal of copper-based catalyst in atom transfer radical polymerization using different extraction techniques

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Abstract: Several methods allowing the removal of copper-based ATRP active complexes from crude amino-functionalized polymethacrylate chains are compared. Among them, precipitation in basic medium is one of the most efficient techniques since it allows high recovery yields (above 90%) with a residual metal content as low as 5 ppm. Extraction methods such as liquid-liquid phase separation and dialysis but also selective adsorption on acidic macroporous ion exchange resin constitute other attractive alternatives. As far as water-insoluble polymers are concerned, catalyst adsorption on alumina remains the most universal method and provides acceptable recovery efficiency. However, we want to stress the key-importance of the experimental adsorption conditions and above all the relative content of alumina used for catalyst extraction.

Introduction

Atom transfer radical polymerization (ATRP) is one of the most robust controlled/ 'living' radical polymerization methods since it can be applied to a wide variety of monomers and provides well-defined polymers [1-7]. The basis of ATRP is the reversible transfer of a radically transferable atom, typically a halogen, from a monomeric or polymeric alkyl halide (macro)initiator to a transition metal complex in a lower oxidation state, forming an organic radical and a transition metal complex in a higher oxidation state. During the early stages of the development of ATRP, equivalent amounts of transition metal complex and initiator were typically employed in order to achieve reasonable polymerization rates. While more active catalysts have now been developed allowing the reduction of the content in transition metal complex with regard to the initiator, one of the main limitations of ATRP remains the contamination of the formed polymer with rather high amounts of residual coloured metal/ ligand complex. Therefore, it is of key-interest to identify methods that eliminate or at least significantly reduce the content in catalyst complex poisoning the recovered polymer chains right after the polymerization procedure. Another interesting approach consists in immobilizing the catalyst complex on a solid support without losing its activity for promoting controlled ATRP, with the possibility to potentially recycle it for any further polymerization reactions [8-12]. Polyethylene-bound ATRP ligands have

been also investigated since they enable homogeneous reaction conditions to be combined with a facile method for removal of the catalyst. Indeed, polyethylene (PE) is soluble under reaction conditions but precipitates from solution at room temperature due to the crystallization of PE chains [13]. Similarly, some precipitation ligands have been developed [14], however, although they have proved to be very efficient in removal of copper catalyst, they cannot be recycled, which might mitigate the performance [15].

Up to now, the removal of residual metal complex in ATRP has been achieved with variable success by using methods such as adsorption on alumina columns, selective precipitation of polymer in a non-solvent, treatment with an ion-exchange resin or liquid-liquid phase separation [5-8,10-12,16]. Because all these purification methods have been reported separately, i.e., for different monomers, catalytic complexes, solvents and polymerization conditions, there is no data available allowing to compare them to each other in terms of catalyst removal efficiency. The aim of this note is to report on the ATRP catalyst complex extraction by use of different methods carried out under very similar and practical operating conditions. Purposely, we studied an amino-functionalized polymethacrylate known for entrapping most of the catalyst complex, i.e., poly[2-(*N,N'*-dimethylamino)ethyl methacrylate] (PDMAEMA). Indeed, PDMAEMA strongly interacts with transition metal complexes via its pending tertiary amine functions [17-19]. PDMAEMA was prepared by ATRP of *N,N'*-dimethylaminoethyl methacrylate (DMAEMA) in tetrahydrofuran (THF, 50/50 v/v) using CuBr/1,1,4,7,10,10-hexamethyltriethylenetetramine (CuBr/HMTETA) as catalytic complex and 2-ethylbromoisobutyrate (EBⁱB) as initiator, at 60°C for 16 h ($[\text{DMAEMA}]_0/[\text{EB}^i\text{B}]_0/[\text{CuBr}]_0/[\text{HMTETA}]_0 = 100/1/1/2$). Under these conditions, the DMAEMA polymerization has proved to be controlled with the possibility to predetermine the number-average molecular weight (M_n) [17-19]. In this experiment, an M_n value of 15 700 is expected at 100% monomer conversion. The green-coloured polymer was first recovered by precipitation in an excess of heptane (yield = 95%, copper content = 3970 ppm as determined by inductively coupled plasma (ICP)), then dissolved in selected solvents (see hereafter) and submitted to different catalyst extraction methods. The efficiency of the catalyst removal method has been assessed by measuring the residual catalyst content by ICP while checking the PDMAEMA recovery yield and molecular parameters (M_n and M_w/M_n).

Results and discussion

As aforementioned, selective adsorption of the crude polymerization product over alumina or silica columns is undoubtedly the most widely reported method to reduce the content in residual catalyst complex, however, it has to be pointed out that most often the actual experimental conditions are barely defined. In a first series of experiments, this selective adsorption technique has been approached by using different adsorbents under well-selected experimental conditions. It has been chosen to elute 1 g of crude polymer dissolved in 10 ml of THF through a linear column (30 mm diameter) filled with 10 g of various adsorbents, followed by precipitation of the polymer from heptane. More concentrated polymer solutions triggered excessive viscosity whereas the use of larger relative contents in adsorbent made the selective filtration of the polymer chains highly difficult. Results are gathered in Tab. 1. Interestingly, acidic alumina (activated alumina type 504C, from Aldrich) proved to be an excellent compromise taking into account both the residual copper content (14 ppm Cu) as determined by ICP and the weight loss in PDMAEMA as measured by gravimetry

(recovery yield higher than 90%). In contrast, adsorption of cupric and cuprous catalyst complexes is not satisfying using silica (silica gel grade 12, from Aldrich). The residual content in copper catalyst is by far too high for performing any SEC analysis on the so-isolated coloured PDMAEMA chains. It is also worth noting that no effect of the alumina adsorbent, i.e., acidic or basic alumina (aluminium oxide type 5016A, from Fluka), could be detected on PDMAEMA molecular parameters as determined by size exclusion chromatography using buffered aqueous solution at pH 4.8 as eluent (conc. = 0.5 mol/L) at 30°C. However and as aforementioned, the relative content in alumina is of key-importance. For instance, a simple twofold increase in the alumina relative content while keeping all other conditions unchanged triggers a loss of polymer materials of more than 50 wt.-%, which results in higher M_n (lower M_w/M_n of c. 1.3) values as determined by SEC on the isolated PDMAEMA chains. Finally, other adsorbents such as Celite (Celite 521, from Aldrich) or active carbon (active carbon DarcoG-60, from Aldrich) have also been tested in THF under equivalent experimental conditions, however, leading to much higher contents in residual metal catalyst (227 and 630 ppm of Cu, respectively) and limited recovery yields (83 and 91%). Such high copper content actually prevents any SEC analysis from being carried out on the recovered polymethacrylate chains.

Tab. 1. Purification of PDMAEMA chains by selective adsorption of the copper catalyst. Elution of 1 g of as-recovered crude PDMAEMA (dissolved in 10 ml THF) through a column filled with 10 g of adsorbent

Entry	Adsorbent	Recovery yield in %	Copper content in ppm	M_n	M_w/M_n
1	basic Al ₂ O ₃	77	10	15 100	1.41
2	acidic Al ₂ O ₃	92	14	14 800	1.41
3	silica	95	177	ND ^a	ND ^a
4 ^b	Celite 521	83	227	ND ^a	ND ^a
5 ^c	active carbon	91	630	ND ^a	ND ^a

^a Not determined by SEC due to a too high contamination by residual metal complex.

^b 5 g of adsorbent instead of 10 g. ^c A few mg of adsorbent instead of 10 g.

Another tested method for the removal of Cu(I) and Cu(II) catalytic complexes consists in using recyclable macroporous ion exchange resins bearing acidic groups. Most commercially available cationic ion exchange resins are based on sulfonated or carboxylated cross-linked polystyrene-divinylbenzene beads, e.g., Dowex MSC-1 (cPS- ϕ -SO₃H, from Aldrich) and Chelex 20 (cPS- ϕ -CH₂-NH⁺-[CH₂-COO-Na⁺]₂, from Fluka), respectively. The exchange of the copper complexes with resin cations takes place without release of the ligand but rather formation of hydrogen or sodium halides. To be effective the removal of Cu(I) and Cu(II) catalysts requires the use of an excess of ion exchange resin, i.e., excess of accessible H⁺ or Na⁺ sites (> 5 equiv.), as well as at least a couple of hours to remove more than 95% of the metal complex from the solution at room temperature [16]. This is the main reason why separation experiments were carried out by either passing the crude PDMAEMA solution through a column filled with the selected ion exchange resin ('column' method) or by contacting the solution with ion exchange resin for one night before filtration (batch process). Tab. 2 shows the extraction efficiency of Dowex MSC-1 (D,

4.5 mmol H⁺/g) and Chelex 20 (C, 1.6 mmol Na⁺/g) as ion exchange resins under different operating conditions. The initial concentration of crude polymer solution was kept at 1 g in 5 ml of solvent, which thus contains 0.062 mmol of Cu(I) and Cu(II) based ATRP active complexes. Confirming previous observations [16], the rate of catalyst complex removal is rather slow so that a batch process is the preferred procedure compared to the elution of the polymer solution through a filled column (entries 1 and 2, Tab. 2). Higher efficiency was obtained when substituting water for THF and by using sulfonated resin rather than a carboxylated one (entries 2, 3, and 5, 6). Such behaviour is consistent with an ion exchange capacity increasing with solvent polarity, acidic strength of the exchanging groups as well as a decrease of the exchanged cation size. From entries 3 and 4, it comes out that the use of a too large excess of ion exchange resin reduces the recovery yield, at least in the case of PDMAEMA, which is prone to interact with the ion exchange resin through favourable coordinative bonding between the sulfonic acid groups and tertiary amine functions.

Tab. 2. Purification of PDMAEMA chains by using cation-exchange resins: Dowex MSC-1 (D) and Chelex 20 (C) containing, respectively, 4.5 mmol H⁺/g and 1.6 mmol Na⁺/g. Effect of operating procedure, i.e., batch mode or column elution, on copper catalyst extraction (1 g of as-recovered crude PDMAEMA dissolved in 5 ml THF or H₂O)

Entry	Type of resin (g)	Procedure	Solvent	Recovery yield in %	Copper content in ppm	<i>M_n</i>	<i>M_w/M_n</i>
1	D (2.5)	column	H ₂ O	85	161	ND ^a	ND ^a
2	D (2.5)	batch	H ₂ O	83	1	15 300	1.41
3	D (2.5)	batch	THF	71	16	14 800	1.39
4	D (1.0)	batch	THF	80	17	14 700	1.44
5	C (0.25)	batch	THF	86	34	14 300	1.40
6	C (0.25)	batch	H₂O	94	9	14 200	1.42

^a Not determined by SEC due to a too high contamination by residual metal complex.

As additional alternatives, removal of Cu(I) and Cu(II) ATRP active complexes from the crude PDMAEMA solution was also attempted by liquid-liquid phase separation (LLPS, see Tab. 3). Purposely, 2 g of crude PDMAEMA were solubilized in 50 ml CHCl₃ and treated with 50 ml of an aqueous solution of diethylenetriaminepentaacetic acid (DTPA, 0.015 mol/L) buffered at pH 8.3 by NaHCO₃. Furthermore, cellulose membranes with molecular weight cut-off (MWCO) of 500 (Spectra/Pro CE, from Spectrum Laboratories) and 1000 (Cellu Sep H1, from Membrane Filtration Products) were also used to dialyze the aqueous solution of crude PDMAEMA chains against Millipore water for 24 h (Dialysis method). Finally, crude PDMAEMA chains were also separated from residual catalyst complexes by selective precipitation (SP method), by taking advantage of the pH-dependence and thermo-responsive behaviour of this polymer in H₂O [17]. In practice, a crude polymer solution (1 g in 5 ml H₂O) was added drop by drop into 100 ml of an aqueous NaOH solution and the mixture was heated up to 65°C, and colourless precipitated PDMAEMA was readily recovered by filtration. Tab. 3 gathers the copper catalyst extraction efficiency for

these different procedures. First of all and whatever the investigated method, it came out that high recovery yields were reached (>90 %). The lowest content in residual catalyst complex was obtained by selective precipitation of PDMAEMA in an aqueous basic medium at 65°C, i.e., 5 ppm in residual Cu meaning that more than 99.85% of the initial copper catalyst have been eliminated. Liquid-liquid phase separation is also an efficient technique (recovery yield almost quantitative and 9 ppm in residual Cu) though it is rather time-consuming and can rapidly become cost prohibitive for larger-scale polymer purification. As far as the dialysis method is concerned, the choice of the dialysis membrane is of the utmost importance as the molecular weight cut-off must be high enough to enable catalyst complex diffusion through the membrane while preventing undesirable polymer weight loss. Again, it is worth pointing out that extraction conditions have no influence on the recovered PDMAEMA molecular parameters, at least within the experimental error of SEC performed in buffered aqueous solution at pH 4.8 as eluent (conc. = 0.5 mol/L) at 30°C.

Tab. 3. Purification of PDMAEMA chains by liquid-liquid phase separation (LLPS), dialysis (D) and selective precipitation (SP) (for conditions, see text)

Entry	Extraction method	Recovery yield in %	Copper content in ppm	M_n	M_w/M_n
1	LLPS	99	9	14 800	1.44
2	D MWCO500	>99	3310	ND ^a	ND ^a
3	D MWCO1000	95	29	15 000	1.41
4	SP	91	5	14 700	1.39

^a Not determined by SEC due to a too high contamination by residual metal complex.

Conclusion

In this note we have compared several methods allowing the removal of Cu(I) and Cu(II) ATRP active complexes from crude amino-functionalized polymethacrylate chains (PDMAEMA). Among them, precipitation in basic medium is one of the most efficient and economically viable, at least for polymers such as PDMAEMA, which are pH- and thermo-sensitive. Actually, the polymer chains can be readily isolated within high recovery yields (above 90%) while the residual metal content is found as low as 5 ppm as measured by ICP. It is worth recalling that such a purification method has already been reported by some of us to prepare well-defined PDMAEMA homopolymers and copolymers (with poly(ethylene glycol) blocks) by ATRP according to a totally solvent-free procedure [20]. Extraction methods like liquid-liquid phase separation and dialysis have proved to be quite efficient with almost quantitative recovery yields and a reduction of the metal content higher than 99% compared to the initial amount in copper catalyst. Use of strong acidic macroporous ion exchange resin constitutes an attractive alternative even though the slow rate of catalyst removal may represent a main drawback. As far as polymers are insoluble in water, adsorption on alumina remains the most universal method and provides acceptable efficiency. However the key-importance of the experimental adsorption conditions and above all the relative content of alumina used for the catalyst extraction have to be stressed out. Indeed, the adsorbent content has to be correctly adjusted to the amount of crude polymer materials in order to avoid any substantial loss of materials

and erroneous measurement of the actual molecular parameters of the polymer chains formed by controlled ATRP.

Experimental part

Materials

2-Ethylbromoisobutyrate (EBⁱB), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) and CuBr were purchased from Aldrich and used as received. Tetrahydrofuran (THF, 99+%, from Chem-Lab) and 2-dimethylaminoethyl methacrylate (DMAEMA, from Aldrich) were purified through a column of basic alumina in order to remove the stabilizing agents. The monomer was then stored under N₂ at -20°C.

Synthesis of PDMAEMA homopolymer

CuBr (3.0 mmol) and a magnetic bar were introduced in open air into a dry glass-tube, which was then closed by a three-way stopcock capped by a rubber septum and purged by three repeated vacuum/nitrogen cycles. In a 100 ml dry flask, DMAEMA (296.7 mmol), HMTETA (6.0 mmol) and THF (50 ml) were introduced and bubbled with nitrogen during 10 min before transferring the mixture into the glass-tube placed in a oil bath maintained at 60°C. Degassed EBⁱB (3.0 mmol) was added to the tube with a degassed syringe. After 16 h, the glass-tube was cooled down to room temperature and its content was dissolved in THF. The polymer was selectively recovered by precipitation from heptane. The conversion in polymer was determined gravimetrically after drying at 80°C for one night under reduced pressure.

Inductively coupled plasma (ICP) analyses

Residual copper was determined using a Jobin Yvon 35+ inductively coupled plasma atomic emission spectrophotometer. Samples were prepared by mineralization at 500°C, followed by digesting approximately 6 mg of polymer in 2.5 ml H₂SO₄ conc./ 1 ml HNO₃ conc. and then diluting the solutions up to 50.0 ml with deionized water.

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