Reversible Addition−Fragmentation Chain Transfer Polymerization Mediated by a Solid Supported Chain Transfer Agent

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The use of solid supports in living radical polymerization has attracted much attention in the past 6 years. All three main techniques of living radical polymerization (transition-metal-mediated living radical polymerization, also known as ATRP,[1] nitroxide-mediated polymerization (NMP),[2] and reversible addition−fragmentation chain transfer (RAFT) polymerization[3]) work well in the presence of a solid support. NMP was one of the first living techniques to use solid support for polymerization, by conversion of either silica or Merrifield resin into a solid-supported alkoxyamine to produce surface-grafted polymeric chains of controlled molecular weight, coined polymer brushes,[4] or to give larger resin beads via living free radical polymerization, which were called "Rasta resins" by their inventors.[5] ATRP also was used to surface-graft initiators in order to produce grafted polymeric chains of controlled molecular weight, either from silica[4] or from cross-linked poly(styrene) resins.[6,7] The ATRP catalyst was also attached to a support to ease the catalyst removal from the polymer and, to some degree, permit its recovery.[8−10] This system has attracted much interest in the past few years, although it does not deliver polymers with molecular weight as controlled as the equivalent homogeneous solution systems.[11−22]

Reversible addition−fragmentation chain transfer (RAFT) polymerization is among the most versatile of all the controlled/living radical polymerization techniques used to date due to its compatibility with a wide range of monomers and reaction conditions.[23,24] The RAFT process and the chain transfer agents (CTA's) utilized to mediate the polymerization have been extensively studied over the past few years. The main drawbacks of this system are the presence of impurities trapped in the final polymer product, including dead polymeric chains, monomer, and unrecoverable CTA. Furthermore, the RAFT process required the use of a free radical source that generates uncontrolled, dead polymeric chains. The use of solid supports in RAFT polymerization has already been reported,[25−32] but in all cases the chain transfer agent (CTA) is attached through its leaving and reinitiating group (R group), which results in the final polymer attached to the solid support, in a similar manner as what is observed in ATRP mediated by a supported initiator. Surprisingly, to date, there are no reports on the use of a CTA that is attached to a solid support through its Z group. The use of a functionalized Z group was first illustrated by the CSIRO group for the design of star polymers via RAFT[33] and has been further developed by the CAMD team.[30,34−36] One of the main disadvantages of the system is the difficulty of the addition of a growing polymeric chain to the thiocarbonyl−thio compound because of steric hindrance. However, the process is now well documented, and reasonably well-controlled polymeric architectures can be obtained. We report in this communication our initial findings on the use of a solid supported chain transfer agent that is attached to a surface through its Z group. Such CTA's offer the great advantage to allow separation between pure living polymeric chains, which are attached to the support, from nonliving chains, as well as nonreacted monomers and other side products from the reaction, which remain free in solution. The CTA's were synthesized from both organic and inorganic supports.

We have recently reported the synthesis of a versatile chain transfer agent, *S*-methoxycarbonylphenylmethyl dithiobenzoate (MCPDB), for the polymerization of a wide range of monomers.[37] This CTA is easily synthesized via reaction between the commercially available methyl-α-bromophenylacetate and a dithiobenzoic salt; we therefore chose this chain transfer agent as model for our supported syntheses.

Synthesis of Merrifield-Supported Chain Transfer Agent (Mer-MCPDB). The two-step synthesis involves the formation of a sodium dithiobenzoate salt on Merrifield resin via the reaction of the chlorobenzyl functional group from the resin with sodium methoxide and elemental sulfur. Methanol is usually the solvent of choice for this step, but as it is also a very poor swelling solvent for the poly(styrene)-based resins, we initially obtained a very low yield for the reaction (5% substitution after the final step). When replacing methanol by THF, a higher yield was obtained, although the use of sodium methoxide still reduced the swelling of the resins. Nevertheless, the sodium dithiobenzoate salt was subsequently converted to Mer-MCPDB by the addition of methyl-α-bromophenylacetate in THF. The resin was purified by washing with copious amounts of a range of solvents to remove any unreacted starting reagents, byproducts, and salts. The products were analyzed by FT-IR for the C═O in Mer-MCPDB and elemental analysis for the sulfur contents. The results indicated that Mer-MCPDB had been formed and gave a final loading in active sites of 0.320 mmol of CTA/g of solid (16.3% substitution). This low conversion was attributed to the difficulty for the reactants to diffuse to the reactive sites on the resin due to the differences in swelling of the unreacted resin, the dithiobenzoate salt resin, and the final product. Furthermore, sulfur analyses do not take into consideration that some dithiobenzoic salts may not have reacted with the methyl-α-bromophenylacetate and remain in the resin as dithiobenzoic acid. However, it has been shown that dithiobenzoic acid can form a chain transfer agent in situ following addition on a monomer;[38] in this case, the reaction of dithiobenzoic acid with methyl acrylate would lead to 1-methoxycarbonyl ethyl dithiobenzoate (MEDB).

Synthesis of Silica-Supported Chain Transfer Agents *S*-Methoxycarbonylphenylmethyl Dithiobenzoate (Si-MCPDB). The silica particles were pretreated in an aqueous solution of concentrated HCl at 90 °C to activate their surfaces. Activated silica particles

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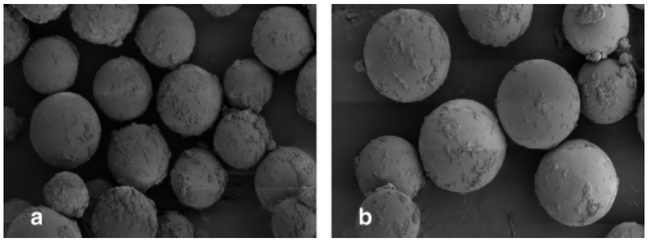


Figure 1. Scanning electron microscopy (×120) of (a) Merrifield resin prior to polymerization (98.5 μm) and (b) Mer-poly(methyl acrylate) (134.7 μm).

were then reacted with 4-(chloromethyl)phenyltrimethoxysilane in order to introduce a chlorobenzyl group at their surface. The chlorobenzyl group was then further reacted, following a similar procedure to that employed in the case of the Merrifield resin, by addition of sodium methoxide and elemental sulfur to a suspension of silica particles in methanol. Further addition of methyl-α-bromophenyl acetate led to the silica supported MCPDB chain transfer agent (Si-MCPDB). Elemental analyses revealed a loading in active sites of 0.328 mmol of CTA/g of solid, corresponding to a surface density of 0.39 molecules of CTA/nm^2.[42] However, scanning electron microscopy of the silica particles before and after reaction indicates that the particles were ground by the magnetic stirrer that was utilized during reaction. This led to an increase of the surface density of the particles, meaning that the real surface density is therefore very likely to be lower than that calculated.

Polymerization Mediated by Mer-MCPDB. In a typical polymerization, the resin-supported CTA (Mer-MCPDB) was added to a solution of methyl acrylate (MA) and 2,2-azobis(isobutyronitrile) (AIBN) in toluene, in a ratio monomer:Mer-MCPDB:AIBN = 250:1:0.1. The solution was then flushed for 5 min by nitrogen gas and immersed in an oil bath at 60 °C. The reaction was left for 24 h (conversion > 99%, as assessed by gravimetric analyses), then the solution was filtered, and the resin was submitted to a thorough wash to remove non-attached polymeric chains and side products. The non-attached polymeric chains were analyzed by size exclusion chromatography: $M_n = 256\,000$ g/mol and PDI = 1.44. Figure 1 shows the resin beads before (a) and after (b) polymerization and washing. Particle size analyses confirm an increase in diameter prior to (98.5 μm) and after polymerization (134.7 μm).

In a recent communication, we reported a straightforward technique to cleave the thiocarbonyl−thio end group of a polymer produced by RAFT polymerizations by mixing the polymeric chains with an excess of a source of radicals.[39] The in-situ addition of a radical to the reactive C=S bond of the thiocarbonyl−thio polymer end group leads to the formation of an intermediate radical, which can then fragment either back to the original attacking radical or toward the polymeric chain radical. In the presence of an excess of free radicals, the equilibrium is displaced toward the formation of the polymeric chain radical, which can then recombine irreversibly with one of the free radicals present in excess in solution, thus forming a dead polymeric chain. We applied the same principle to the supported polymeric chains. The addition of a solution of toluene with 20 equiv of AIBN to resin functionality followed by heating to 80 °C for 2.5 h led to the cleavage of the polymeric chain from the resin, and recovery of the supported CTA, showing a cyanoisopropyl group as R group. Simple filtration ensures the isolation of the polymeric chains and recovery of the resin. In the case of a supported CTA, the tetramethylsuccinonitrile resulting from combination reactions between cyanoisopropyl radicals could be removed by simple filtration. Size exclusion chromatography of the sample gave $M_n = 13\,950$ g/mol (PDI = 1.24), which is much lower than the expected molecular weight ($M_n = 21\,500$ g/mol, assuming all CTA's have reacted and neglecting the chains initiated by AIBN). Figure 2 shows the GPC trace of both attached and free polymeric chains, and it is noteworthy that the attached PMA chains do not show the hump at high molecular weights, due to termination by combination, usually observed in homogeneous RAFT polymerization. Particle size analysis gave a diameter of 103.0 μm after cleavage, which correlates well with the size of the beads before reaction (98.5 μm).

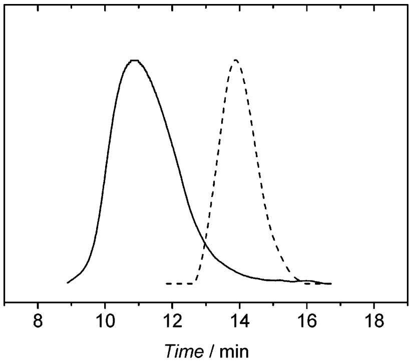


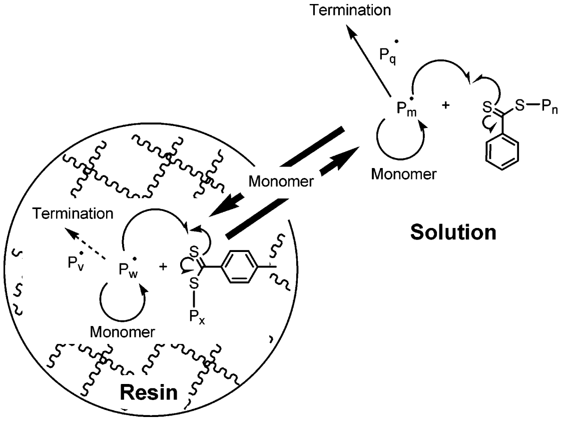
Figure 2. Size exclusion chromatograms of polymeric chains remaining free in solution (—) and polymeric chains attached to the support and cleaved via reaction with AIBN (- - -) analyzed by size exclusion chromatography using tetrahydrofuran as eluent (1 mL/min) and poly(methyl methacrylate) standards.

Using a radical technique to cleave the polymeric chains allows the recovery of the chain transfer agent, which can then be separated by filtration from the polymer product. To asses its activity, the recovered supported CTA was used to mediate a second polymerization, following the same experimental setup as that described above. After AIBN treatment, a polymer with M_n and PDI very close to that obtained previously was isolated ($M_n = 14\,600$ g/mol, PDI = 1.17), showing that the chain transfer agent seems to maintain its activity. We are currently testing the maximum number of cycles that allow retention of activity for solid supported CTA's.

We observed that the amount of dead polymeric chains (nonattached to the solid support) was noticeably higher than that observed in the case of homogeneous RAFT polymerizations. Quantification of the ratio attached:nonattached polymeric chains by gravimetric analyses[40] revealed a proportion of nonattached chains of 49%. The propagating polymeric chains in solution have the possibility either to undergo conventional free radical polymerization in solution (propagation, termination, and conventional chain transfer) or to add on the chain transfer agents, mainly present *inside* the resin. The difficult access of the propagating bulky polymeric chain to the chain transfer agent favors the former reactions, leading to a larger amount of side reactions (termination and conventional chain transfer) between the polymeric chains in solution, and justifies the high concentration of dead chains (see Scheme 1).

The higher than expected molecular weight distributions of the attached (living) chains may arise from

Scheme 1. Proposed Reaction Mechanism of the Reversible Addition−Fragmentation Chain Transfer Polymerization in Presence of Merrifield Resin-Supported Chain Transfer Agents (CTA's) with the Addition of Free Chain Transfer Agents in Solution in a Ratio Supported CTA:Free CTA = 1:1



either the polymerizations or the cleavage reaction. During polymerizations, the growing chains are required to react back on the resin in order to add to the thiocarbonyl−thio moiety. Steric hindrance arising from such reaction may affect the rate of addition of the chains to the supported CTA by comparison to homogeneous RAFT polymerizations and would therefore affect the PDI of the final product. Furthermore, assuming all the dithiobenzoate salt on the resin has not been reacted with methyl-α-bromophenylacetate, there will be two types of chain transfer agents attached to the resin, MCPDB, and the CTA formed in situ by reaction of the dithiobenzoic acid with methyl acrylate (1-methoxycarbonyl ethyl dithiobenzoate, MEDB).[38] As the reinitiating groups of each CTA have a different reactivity toward MA, they will trigger the growth of the polymeric chains at different time, leading to broad polydispersities of the final product. The molecular weight distribution may also be affected by the technique used to recover the polymer from the resin. One of the disadvantages of using a radical process to separate the polymeric chains from the support is the potential for cleaved chains to react with each other (by termination reactions) and form species of higher molecular weight, which will affect the overall polydispersity of the recovered product (termination reactions occur mainly by combination in methyl acrylate polymerization[41]). Although termination reactions are very limited in homogeneous solution, they may be more preponderant in solid supported RAFT, as the steric hindrance of the resin would make it more difficult for the free radical to reach the polymeric chain end. Note that there are other, non-radical-based, techniques to detach the polymeric chains from the support, with the advantage of avoiding the potential termination reactions that may occur between polymeric chains during the cleavage radical reaction. Although such techniques do not regenerate the supported CTA, they can be used to recover the polymer from the solid support after reaction and filtration.

From our observations, we conclude that there are two competing polymerization reactions in the system. Free radical polymerization occurs in solution, leading to the formation of uncontrolled, high molecular weight polymers that remain free in solution. On the other hand, RAFT polymerization occurs in the presence of the resin (certainly *inside* the resin, where the concentration in CTA is the highest, fed by the monomer that swells the cross-linked network) and leads to attached living polymeric chains. The free radical chains in solution consume the monomer rapidly, therefore cutting the feed for the RAFT chains, which leads to chains of lower than anticipated molecular weight.

These observations are confirmed by studies undertaken on RAFT polymerization from solid support with a chain transfer agent linked to the support via its R group.[25−32] In this "grafting from" approach, it was observed that the free radicals generated in solution attack predominantly the chains in solution to produce a polymeric radical, some of which, before growing to the highest molecular weight limited by termination and conventional chain transfer reactions, add to the thiocarbonyl−thio unit grafted on the surface to generate a dormant polymeric chain in solution and a propagating radical at the solid surface—the RAFT agent is therefore transferred from the surface to the solution. Nevertheless, the concentration of thiocarbonyl−thio-capped chains in solution remains too low to control effectively the polymerization, and the system undergoes conventional free radical polymerization both at the solid surface and in solution.[32] However, the introduction of a free CTA in solution was shown to not only control the polymerization in solution but also maintain the concentration of dormant chains grafted to the surface by the exchange reaction of a graft radical with a dormant free chain.[32] In a system based on CTA linked via its Z group (we would coined such an approach "grafting to" approach), the RAFT agent is always attached to the surface; therefore, the chains attached to the support remain in the dormant state, and the radical always propagates in solution. As a result, the introduction of free CTA's in solution may slow down the propagation of free chains and favor the addition−fragmentation reactions on the support.

To improve the control over attached polymeric chains and reduce the amount of dead chains left in solution, we use a hydride reaction setup, by introducing a free chain transfer agent to the system (Scheme 1). In a typical polymerization of methyl acrylate, a ratio free CTA:supported CTA = 1:1 was used, keeping all other conditions the same. After cleavage, the attached polymeric chain showed a molecular weight of 8700 g/mol and PDI = 1.11, while the free polymeric chains had a M_n = 7400 g/mol and PDI = 1.20. It is noteworthy that the molecular weight for both attached and free polymeric chains is greatly reduced by comparison to a system without free chain transfer agent, as the polymerization is slowed down by the presence of a free CTA in solution. However, the molecular weight of both attached and free chains is very similar and is close to that expected for a polymerization reaching high conversion ($M_{n,theo}$ = 10 800 g/mol, assuming both attached and free chain transfer agents are fully reacted and neglecting the chains initiated by AIBN). Furthermore, quantification of the ratio of attached:nonattached polymeric chains revealed that the proportion of attached chains has increased to 62%.[40] Further work is currently being undertaken in our laboratories to investigate the kinetics of the reaction, follow the evolution of molecular weight of attached polymers in relation to conversion, and assess the maximum molecular weights achievable. At this stage, we anticipate that steric hindrance may stop high molecular weight polymers to react back onto the support, and for high ratios monomer:CTA, molecular weights may level off at high conversions.

Polymerization Mediated by Si-MCPDB. A reference polymerization was undertaken in the presence of nonmodified silica particles. A PMA of M_n = 57 300 g/mol (PDI = 1.61) was obtained from the solution, but no polymer was found attached to the support.

The polymerization mediated by the silica-supported RAFT agents was undertaken in the same conditions as those described for the Mer-MCPDB-mediated polymerization. The ratio monomer:Si-MCPDB:AIBN was kept to 250:1:0.1, and the polymerization was left at 60 °C for 24 h (conversion >99%, as assessed by gravimetric analyses). After polymerization, the nonattached polymeric chains were analyzed by size exclusion chromatography (M_n = 263 000, PDI = 1.80), and we found that nearly 90% of the polymeric chains were present in solution.[40] A similar treatment with AIBN was used to cleave the polymeric chains from the silica support, and the resulting product was analyzed by SEC (M_n = 820, PDI = 1.07). The recovered CTA was reused in a polymerization with the same concentration in reactants as before, and the cleaved polymer was analyzed by SEC, which revealed a M_n = 840 and PDI = 1.06. In similar conditions, the silica supported CTA leads to oligomers of PMA, by opposition to the higher molecular weight PMA obtained from Merrifield supported CTA, and only few chains are attached to the support. In the case of silica, all of the CTA functionalities are present at the surface, and all the polymeric chains grow in solution. Both free radical and RAFT polymerization are therefore in direct competition, and the conventional free radical propagation in solution is favored by comparison to the addition−fragmentation reaction occurring only at the silica surface. As a result, the monomer is rapidly consumed through the free radical process. Furthermore, growing chains have more opportunities to cross-terminate, which also justifies the higher PDI obtain for the free chains in the case of silica supported polymerization by comparison to Merrifield-supported polymerization.

By introducing a free CTA in the reaction solution, following the same ratio as that described above (MA:Si-CTA:CTA:AIBN = 250:1:1:0.1), and performing the polymerization in the exact same conditions as previously, we obtained a free polymer of M_n = 10 400 g/mol (PDI = 1.34) and an attached polymer of M_n = 9200 g/mol and PDI = 1.13. The presence of the free CTA in solution mediates the MA polymerization and slows down the overall polymerization rate, allowing chains to react with the support more often. Such reaction leads to a higher molecular weight polymer, close to the theoretical M_n ($M_{n,theo}$ = 10 800 g/mol, see above), and permits a dramatic increase in the amount of chains attached to the support (52%).[40] The close correlation between the molecular weight of the attached chains and the expected molecular weight confirms that most of the CTA's are active and sufficiently spaced to avoid steric hindrance of growing polymeric chains. This confirms that the calculated surface density (0.39 molecules of CTA/nm^2) is likely to be overestimated, certainly due to the grounding of particles during reaction, which leads to an increase in active surface and decrease in surface density.

By comparing the “grafting from” (R approach[25−32]) and “grafting to” (Z approach, this work) techniques, we can conclude that the latter system does not allow the formation of high-density polymer brushes achievable by the former technique, but it permits to isolate “true” living chains (100% of the chain isolated retain their chain-end functionality) from dead material. We anticipate this process to be very powerful for the design of end-functional and block (co)polymers and are currently investigating further its development.

Conclusion. In conclusion, we are reporting in this communication a novel concept in RAFT polymerization—the use of a chain transfer agent attached to a solid support (Merrifield resin or silica) by its Z group to control the polymerization of methyl acrylate. Preliminary results have revealed that the reaction leads to well-controlled polymers, and the supported nature of the CTA allows its easy recovery after reaction. The use of free chain transfer agents in solution helps to increase the control over the molecular weight and polydispersity of the product. In this technology, nonreactive (dead) polymeric chains can be separated from the “true” living polymeric chains by simple filtration. We anticipate this technique will allow the production of very well-defined block copolymers, free of homopolymers impurities, and we are currently developing further the process.

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Supporting Information Available: All experimental procedures and analyses data. This material is available free of charge via the Internet at http://pubs.acs.org.

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