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Combining Thio−Bromo "Click" Chemistry and RAFT Polymerization: A Powerful Tool for Preparing Functionalized Multiblock and Hyperbranched Polymers

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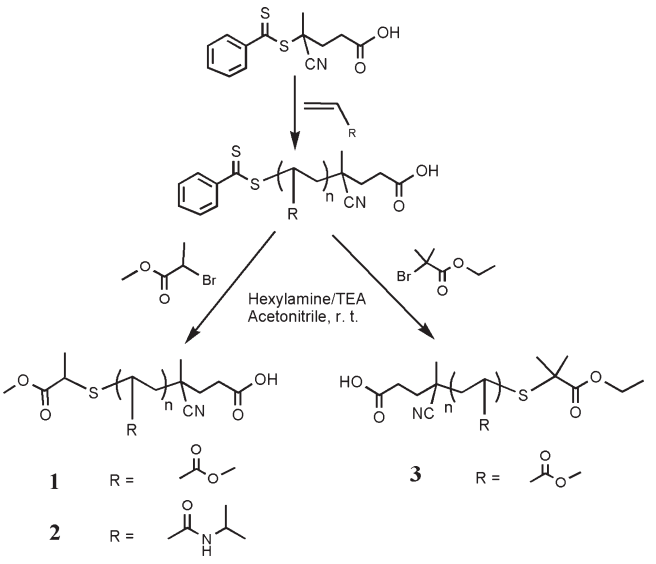
"Click" chemistry, first described in 2001 by Kolb, Finn, and Sharpless,[1] has been applied in a range of areas of chemistry, materials, and biology over the past decade.[2] An excellent example of such chemistry, the copper-catalyzed alkyne−azide cycloaddition (CuAAC),[3] has been employed in the synthesis of a broad diversity of functional materials, nanoparticles, and bioconjugates.[4] The orthogonality of CuAAC chemistry has also allowed the reaction to be combined with other efficient chemistries such as Diels−Alder cycloadditions[5] and the coupling of aldehydes and hydroxylamines (oxime bond formation).[6] In addition to CuAAC chemistry, a series of thiol-based reactions have recently been highlighted as powerful "click" chemistries and include the thiol−ene/yne[7−9] and thiol−isocyanate[10] reactions. A particularly attractive feature of such reactions is the large number of cheap, commercially available, thiols, enes, ynes, and isocyanates, including multifunctional species.

Controlled radical polymerization techniques, and especially reversible addition−fragmentation chain transfer (RAFT) polymerization,[11] have rapidly developed as facile and convenient approaches to controlled architecture and topology block, graft, star, hyperbranched, telechelic, multifunctional, and cyclic (co)polymers and as a simple route to new highly functional materials when combined with the above-mentioned "click" chemistries.[8,12] Recently, Percec and co-workers reported the nucleophilic thio−bromo "click" reaction and specifically highlighted the base-mediated thioetherification of thioglycerol with α-bromoesters to prepare a new class of poly(thioglycerol-2-propionate) (PTP) dendrimers[13] and dendritic macromolecules.[14] Such reactions were rapid and proceeded with near-quantitative conversion and were shown to be compatible with a range of functional thiols.

Herein we highlight that RAFT-prepared (co)polymers can serve as convenient masked macromolecular thiols suitable for thio−bromo reactions. The in situ aminolysis of thiocarbonylthio end groups in the presence of α-bromoesters serves as a convenient route to ω-thioether-functionalized homopolymers. We demonstrate that such chemistry can be extended to prepare functionalized multiblock and hyperbranched polymers. A model reaction (Scheme 1) was first examined to evaluate the general reaction rates and efficiencies.

For model polymeric studies we synthesized three short homopolymers: poly(methyl acrylate) (PMA) ($M_{n,GPC}$ = 560 Da, $M_{n,NMR}$ = 970 Da, PDI = 1.10, denoted PMA1000), PMA ($M_{n,GPC}$ = 4100 Da, $M_{n,NMR}$ = 4580 Da, PDI = 1.08, denoted PMA4500), and poly(*N*-isopropylacrylamide) (PNIPAAm) ($M_{n,GPC}$ = 1010 Da, $M_{n,NMR}$ = 1750 Da, PDI = 1.07, denoted PNIPAAm1750). Homopolymers were prepared by RAFT polymerization using 4-cyanopentanoic acid dithiobenzoate (CPADB) as the chain transfer agent, yielding homopolymers with dithiobenzoate groups at the ω-termini that can be readily cleaved to thiols via aminolysis. The generated thiol can subsequently react with many functionalities, including maleimide, pyridyl disulfide, and enes.[8,15] In our work, we utilized the in situ generated thiol for subsequent reaction with two model α-bromoesters: methyl 2-bromopropionate (MBP) and ethyl 2-bromoisobutyrate (EBiB) (Scheme 1).

Scheme 1. Model Reactions Used To Evaluate the Combination of RAFT and Thio−Bromo "Click" Reaction



The aminolysis of PMA4500 in the presence of MBP was performed using hexylamine/triethylamine (TEA) as the cleavage agent and base, respectively, in a molar ratio PMA4500/hexylamine/TEA/MBP = 1/1/2/2 in acetonitrile at a concentration of 0.027 mol/L. The red color of the initial polymer solution faded completely within 30 min, after which an aliquot was withdrawn for GPC analysis. For comparison, the aminolysis of PMA4500 in the absence of MBP was performed as a control. The experimentally measured GPC traces are shown in Figure 1. A small shift to lower retention time was observed for the MBP-modified PMA4500 as well as the appearance of a small fraction of coupled products compared to the parent PMA4500 homopolymer. In contrast, a distinctive bimodal molecular weight distribution was observed for the control experiment with the large peak at lower retention time due to the presence of coupled PMA4500 chains. These model reactions indicate that the thio−bromo reaction is kinetically preferred over the competing reaction of disulfide formation. Such tandem reactions, i.e., aminolysis followed by thio−bromo substitution, proceed reasonably quickly and are essentially complete within ∼30 min. The aminolysis/thio−bromo sequence with PNIPAAm1750 gave similar results: uniform and unshifted GPC curves (Figure S1 in the Supporting Information) and rapid reaction time (∼30 min). However, a longer reaction time of ca. 3 h was required to obtain high yields of the thioether product from the aminolysis of PMA4500 in the presence of EBiB.

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To verify successful cleavage/thioether formation, PMA1000 was aminolyzed in the presence of MBP or EBiB and the products analyzed by ESI mass spectrometry (ESI MS). As shown in Figure 2, the main series of peaks in all three traces exhibits an interval of 86.01 mass units, which corresponds to the methyl acrylate (MA) repeat unit. The main peak, for example m/z = 904.39 in Figure 2A,D, can be attributed to PMA with a degree of polymerization of 7 and a ω-dithiobenzoate end-group cationized by Na^+. The absence of any other peaks indicates the high purity of the homopolymer. After aminolysis in the presence of MBP (Figure 2B,E) or EBiB (Figure 2C,F), the masses of the main series of peaks both matched with the predicted structures of polymer **1** or **3**, respectively, as indicated in Scheme 1. However, small amounts of impurities are observed as indicated by peaks P_1 in Figure 2F and P_3 in Figure 2E and are attributed to the presence of cyclic thiolactone[16] end-groups cationized by Na^+, while P_2 in Figure 2F is attributed to unreacted thiol end-groups cationized by Na^+. On the basis of these observations, the end-group functionality can be semiquantitatively calculated to be ~80% based on the intensities of the main peaks and impurities as seen in the ESI MS spectra. This value is supported by NMR (Figure S2 in the Supporting Information), in which the calculated degree of end-group modification from the aminolysis/thio−bromo reaction of PMA4500 and EBiB is ~73%. The aminolysis/thio−bromo sequence of PNIPAAm1750 with MBP gave better results (Figure S3 in the Supporting Information) with no detectable undesirable end-groups but was accompanied by the appearance of AIBN initiator-derived chain peaks[16a] cationized by Na^+ and main product cationized by H^+ (Figure S3D). Employing the semiquantitative calculation, the degree of ω-functionality was determined to be ≥95%.

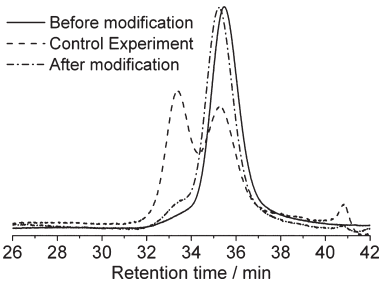


Figure 1. GPC traces for PMA4500 ($M_{n,GPC}$ = 4100 Da, $M_{n,NMR}$ = 4580 Da, PDI = 1.08) before (solid) and after (dashed and dash-dotted) aminolysis in the absence (dashed) and presence (dash-dotted) of methyl 2-bromopropionate (MBP). Aminolysis conditions: [PMA4500]/[hexylamine]/[TEA]/[MBP] = 1/1/2/2, [PMA4500] = 0.027 mol/L; room temperature; solvent: acetonitrile.

These model reactions suggested that the thio−bromo "click" reaction between an in situ generated thiol from RAFT-synthesized homopolymers and an α-bromoester can be rapid and efficient with appropriate substrates. Extending this modification approach, we applied the method to prepare functionalized hyperbranched polymers from AB_2 macromonomers. Two novel RAFT agents **6** and **7** (Scheme 2) bearing two bromoesters in the R group fragment were designed and synthesized by a similar procedure to one we have previously reported.[15a] After MA homopolymerization with **6** or **7**, novel AB_2 macromonomers **8** or **9**, bearing ω-dithiobenzoate and α-bis bromoester end-groups, were obtained. The ω-dithiobenzoate end-groups were cleaved, via aminolysis, to the corresponding thiol that then reacted intermolecularly with the α-bromoester terminal groups on other polymer chains yielding a hyperbranched structure via a step-growth polycondensation process.

The MA RAFT homopolymerizations were well controlled by the novel dithiobenzoates **6** and **7** as indicated by linear pseudo-first-order kinetic plots, the linear increase in the number-average molecular weights with conversion, and low polydispersity indices (M_w/M_n < 1.2) (see Figures S4 and S5 in the Supporting Information).

The aminolysis of the AB_2 macromonomers, **8** or **9**, was monitored by GPC. Multimodal GPC curves (Figure 3) consistent

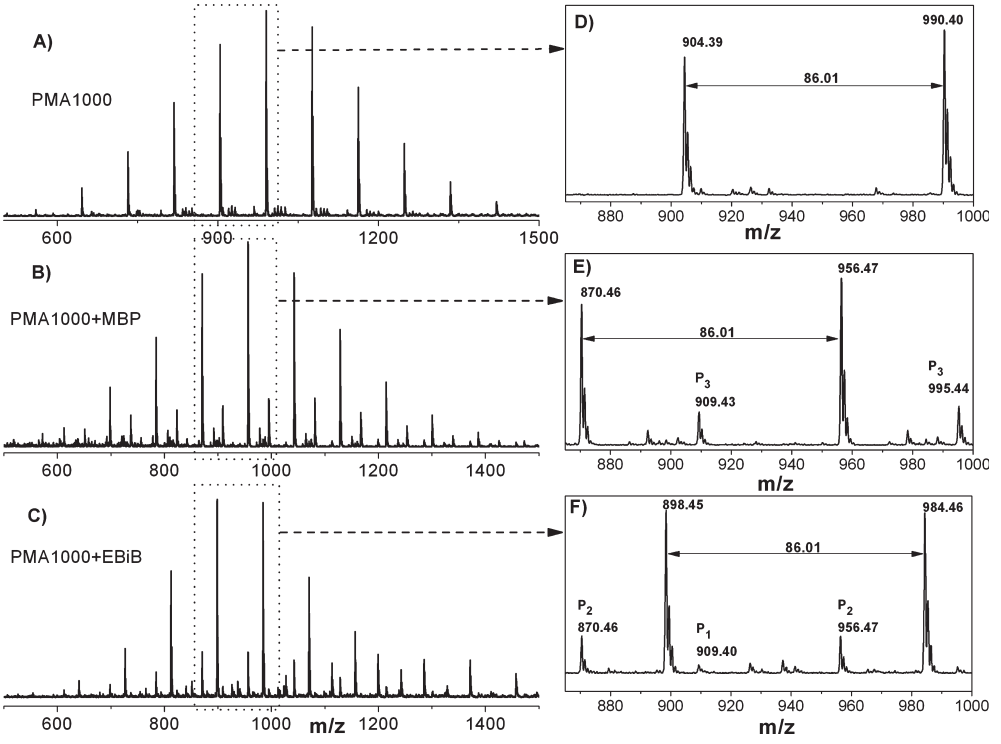
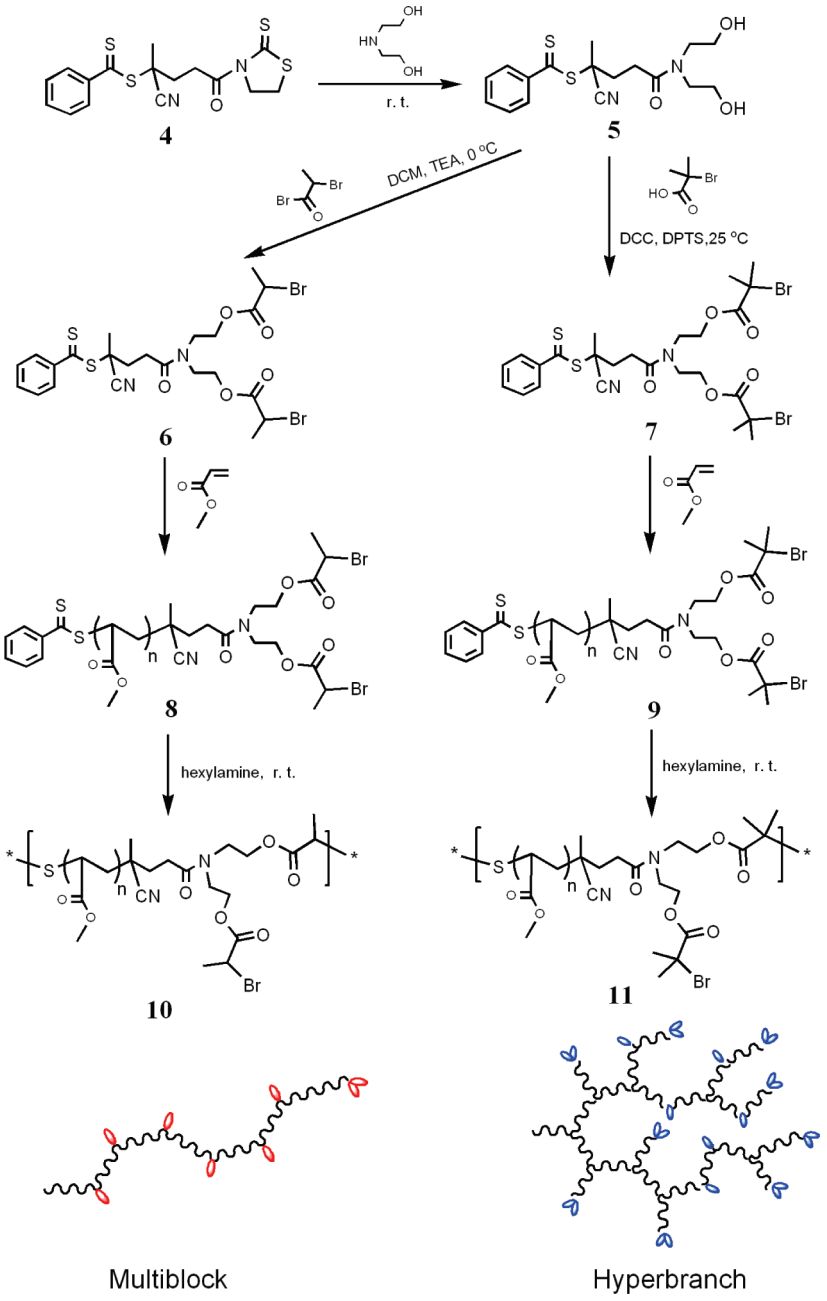


Figure 2. ESI-MS spectra of polymer PMA1000 (A), aminolysis products of PMA1000 in the presence of MBP (B) and EBiB (C), and their respective partial enlargements (D, E, and F). Aminolysis conditions: [PMA4500]/[hexylamine]/[TEA]/[MBP] = 1/1/2/2, [PMA4500] = 0.027 mol/L; room temperature; solvent: acetonitrile.

Scheme 2. One-Pot Preparation of Multiblock and Hyperbranched Polymers



with growth toward high molecular weight were observed as aminolysis progressed. Obviously, the increase of molecular weight in the macromonomer **8** system was much quicker than in the case of macromonomer **9**. After 30 min, the reaction involving macromonomer **8** was essentially complete, as evidenced by the near-constant molecular weight at subsequent sampling times, whereas the molecular weight in the macromonomer **9** system steadily increased. Static light scattering (SLS) was employed to measure the absolute weight-average molecular weight (M_w), yielding $M_w \sim 72\,230$ for **10**, derived from macromonomer **8**, and $M_w \sim 64\,360$ for **11**, formed from macromonomer **9**. The M_w values as determined by GPC, calibrated with narrow molecular weight distribution polystyrene standards, were 30 300 ($M_w/M_n = 2.01$) for **11**, which is much lower than the value determined by SLS (64 360), indicating that the final product structure is hyperbranched. It is interesting to note that the GPC-measured M_w for **10** was 68 760 ($M_w/M_n = 1.83$), which is close to the value measured by SLS, suggesting that **10** is not hyperbranched, but a linear multiblock or lightly branched species. This supposition is borne out qualitatively when the viscosities of aqueous solutions of **10** and **11**, at identical concentrations, are compared. Visually, the solution of **10** is noticeably more viscous than that of **11**, which is consistent with a linear vs hyperbranched species of similar molecular weight and concentration in aqueous solution.

The formation of a hyperbranched vs linear/lightly branched species from **9** and **8** respectively can be rationalized as follows:

While the α-bromoester functional groups in both **8** and **9** are initially equally reactive, they become potentially disparate after a couple of condensation reactions with α-bromoester functionality now, potentially, located at a chain termini and pendant along the chain with the later suffering from steric crowding effects. As such, the formation of a linear vs hyperbranched structure is a direct reflection of the relative rates of reaction of the α-bromoester functional groups, as these different locations, toward substitution. In the case of macromonomer **8**, the high

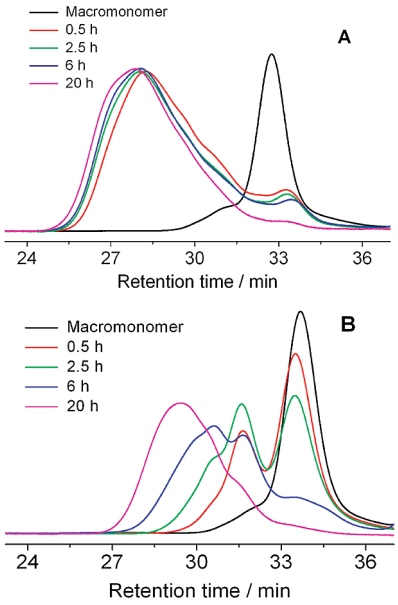


Figure 3. GPC traces (RI signal) monitoring aminolysis of AB_2 macromonomers: (A) AB_2 macromonomer **8** ($M_{n,GPC}$ = 7830 Da, $M_{n,NMR}$ = 9100 Da, PDI = 1.10); (B) AB_2 macromonomer **9** ($M_{n,GPC}$ = 5390 Da, $M_{n,NMR}$ = 6050 Da, PDI = 1.10) at different time points. Aminolysis conditions: $[macromonomers]_0/[hexylamine]_0/[TEA]_0$ = 1/1/2; room temperature; solvent: acetonitrile.

reactivity of the secondary α-bromoester functionality, as evidenced in the model reaction, favors reaction at the chain termini, and hence formation of a linear/lightly branched species, with steric effects due to the polymer backbone significantly, reducing the reactivity of pendent α-bromoester functionality. However, with macromonomer **9**, the difference in reactivity between chain-end and pendant α-bromoester groups is not as dramatic. From the model reaction with EBiB it is clear that the thio−bromo reaction is slow, at least relative to MBP, requiring >20 h of reaction time to reach high yields. Clearly, the reactivity of the already sterically hindered tertiary α-bromoester is little affected by being located at a chain terminus or as a pendant functional group. As such, it appears that if the spacer between the polymer backbone and the pendant functionality is short, then in an AB_2 macromonomer with an inherent high reactivity between A and B that the formation of a linear/lightly branched polymer is favored whereas a low reactivity between A and B tends to favor the formation of a hyperbranched species.[15a,17]

It should also be noted that in any typical AB_n polymerization intramolecular cyclization is always a potential, undesirable side reaction. However, in this present work, provided optimized conditions are used, no cyclic structures could be identified from the GPC curves (Figure 3).

The excess bromoester functionality in the multiblock/lightly branched or hyperbranched structures can be proven by ^{1}H NMR spectroscopy (Figure S6). After aminolysis, the protons (1, 2, 3) associated with the dithiobenzoate disappeared completely, while the methine proton (6) in the monomer repeat unit close to the thiocarbonylthio group moved to a lower chemical shift, and the integration of overlapped peaks 4 and 5 decreased. After post-treatment of the aminolysis product **10** with excess benzyl mercaptam (Figure S6C in the Supporting Information), a further decrease in the integration of peaks 4 and 5 verified the presence of bromoester functionality after aminolysis.

In conclusion, thio−bromo "click" reactions between in situ generated thiols obtained by the aminolysis of RAFT-synthesized polymers and α-bromoesters was simulated by a model reaction and the products characterized by GPC, NMR spectroscopy, and ESI MS. Two novel AB_2 macromonomers bearing ω-dithiobenzoate and α-double bromoester end-groups were utilized to prepare functionalized and defined multiblock/lightly branched and hyperbranched polymers. Excess α-bromoester functionalities could be modified easily to other functionalities on the periphery of these multiblock/lightly branched and hyperbranched structures and provide potential anchoring points for graft polymerizations via ATRP/SET-LRP or other metal-catalyzed living radical processes.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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