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Communications to the Editor

Multiblock Copolymers Synthesized by Miniemulsion Polymerization Using Multifunctional RAFT Agents

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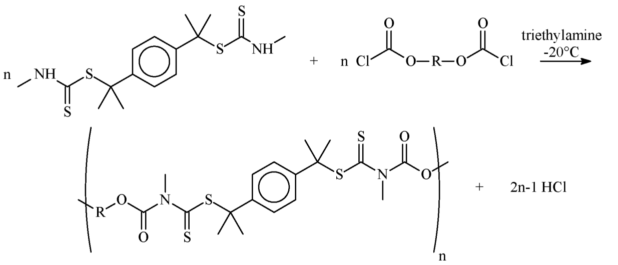
Of the currently known controlled or "living" radical polymerization techniques, reversible addition fragmentation chain transfer (RAFT) radical polymerization is the most versatile, the most robust, and accordingly the most promising mechanism.[1,2] This technique allows the living polymerization of both polar and nonpolar monomers, and polymerization can be performed using a broad range of reaction conditions, both in solution and in aqueous dispersions.[1-8]

The living character of the RAFT polymerization allows the synthesis of (multi)block copolymers,[9] even in aqueous dispersions.[10,11] However, if a multiblock copolymer consisting of n polar and m nonpolar blocks is the target molecule, $(n + m)$ separate monomer additions or polymerization steps are required if a standard monofunctional RAFT agent is used, even if superb amphipathic monofunctional macro RAFT agents are used, as recently described by Pham et al.[12]

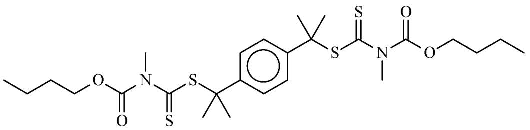
In this paper multifunctional *S-tert*-alkyl-*N,N*-alkoxycarbonylmethyldithiocarbamate RAFT agents are introduced. If the nitrogen atoms are part of an aromatic system, or substituted with electron-withdrawing groups, dithiocarbamates are effective RAFT agents.[13-15] In Scheme 1 the chemistry resulting in a multifunctional RAFT agent containing $2n$ RAFT groups is depicted.

Scheme 1. Synthesis of a Multifunctional RAFT Agent by Polymerizing a Difunctional Dithiocarbamate with a Difunctional Chloroformate[a]



[a] Conditions: equimolar quantities of the dithiocarbamate and the difunctional chloroformate are mixed in THF, and after addition of 5 equiv of the proton trap TEA, polymerization is performed for 48 h at −20 °C.

Scheme 2. *N,N*-Butoxycarbonylmethyldithiocarbamate, the Difunctional "Butyl-RAFT" Agent Used in This Paper[a]



[a] Synthesis conditions: similar to those given with Scheme 1, except a *n*-butyl chloroformate/dithiocarbamate ratio of 2 is used.

If instead of a difunctional chloroformate *N*-butyl chloroformate is used for the coupling reaction with the dithiocarbamate, (*N,N*-butoxycarbonylmethyldithiocarbamate) is generated, which is the difunctional RAFT agent used in this paper. With these novel multifunctional RAFT agents, tri- or multiblock copolymers can be formed in merely two sequential polymerization steps. We realize that other researchers have published excellent papers on the concept of monomer insertion into polymer chains by controlled radical polymerization,[16-18] but the route described in the present work is different and novel.

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For the synthesis of (*N*,*N*-butoxycarbonylmethyldithiocarbamate), thiourea (17.2 g, 0.23 mol) and α,α,α′,α′-tetramethyl-1,4-benzenedimethanol (20.0 g, 0.10 mol) were mixed and added slowly with stirring to 48% HBr (41.7 g, 0.25 mol). The slurry was heated to 50 °C, after which the slurry solidified. The white solid was cooled, filtered, washed with 0.1 mol/L aqueous HBr solution, and dried under vacuum. The resulting white powder was stirred for 2 h in aqueous NaOH (containing 0.62 mol of NaOH) at 40 °C. The resulting clear and red solution was filtered, the red filtrate was cooled to 5 °C, and under an Ar atmosphere a methyl isothiocyanate (15.8 g, 0.22 mol) solution in methanol was added dropwise. *S*-(1,4-Phenylenebis(propane-2,2-diyl)) bis(*N*-methyldithiocarbamate) readily precipitated out as a white solid. After filtration and washing with cold water, the white solid was recrystallized twice from ethanol and dried under vacuum. The overall yield was 60%. Purity was confirmed with ^{1}H and ^{13}C NMR spectroscopy and with LC-MS (MNa$^+$ experimental: 395.01; theoretical: 395.07).

n-Butyl chloroformate (3.1 g, 23 mmol) was dissolved in THF (10 mL) and brought under an Ar atmosphere. The mixture was cooled to −20 °C. *S*-(1,4-Phenylenebis-(propane-2,2-diyl) bis(*N*-methyldithiocarbamate) (4.0 g, 11 mmol) and triethylamine (5.4 g, 54 mmol) were dissolved in THF. This solution was added drop-by-drop to the cold *n*-butyl chloroformate. The mixture was stirred for 48 h, after which it was brought back to room temperature. Triethylamine hydrochloride was filtered off, and THF was removed under reduced pressure. The resulting yellow oil was purified by column chromatography using dichloromethane as the eluent and yielded *N*,*N*-butoxycarbonylmethyldithiocarbamate as a yellow liquid. Yield: 85%. Purity was confirmed with ^{1}H and ^{13}C NMR spectroscopy and with LC-MS (MNa$^+$ experimental: 595.76; theoretical: 595.84).

For the miniemulsion polymerizations, *N*,*N*-butoxycarbonylmethyldithiocarbamate (the "butyl-RAFT" agent) was dissolved under stirring in a mixture of monomer and hexadecane, comprising the organic phase. Sodium dodecyl sulfate (SDS) was dissolved in water, and the organic phase was added dropwise to the aqueous phase under vigorous stirring. The preemulsion was sonicated for 30 min. After emulsification, the miniemulsion was transferred into an emulsion reactor under an argon atmosphere, equipped with a reflux cooler and a thermocouple. The miniemulsion was heated to 70 °C under stirring, and potassium peroxodisulfate (KPS), dissolved in water, was added, after which polymerization was performed for 3 h. At regular time intervals, samples were taken for gravimetric conversion measurement and GPC analysis, using PS standards. The seed latexes, obtained after the described polymerization (= formation first block), were swollen overnight at room temperature with a fresh amount of monomer, after which the second polymerization step was performed under argon, as described for the first step, using fresh KPS.

In one miniemulsion polymerization experiment, 8.0 g of *n*-butyl acrylate (BA) was polymerized, using 2 wt % hexadecane with respect to the monomer and using 0.044 mol of difunctional butyl-RAFT agent/L. In the aqueous phase (30 g), 0.0023 mol/L SDS and 0.0030 mol/L KPS were present. Figure 1 shows the linear increase of $\bar{M}_n$ with conversion, which is a good indication that the addition of the butyl-RAFT agent resulted in a good control of the radical polymerization. The measured values for $\bar{M}_n$ are somewhat higher than the calculated values, which might be explained by the fact that the measured molecular weights are expressed in polystyrene equivalents.

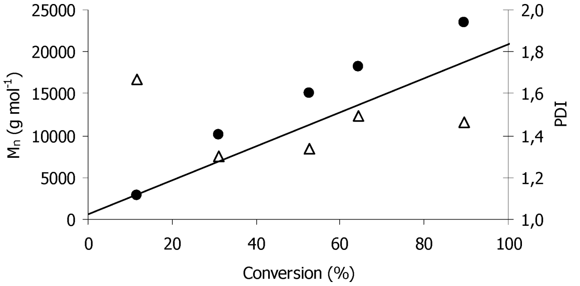

Figure 1. Number-average molar mass ($\bar{M}_n$, ●) and polydispersity index (PDI, Δ) vs conversion of the mimiemulsion polymerization of *n*-butyl acrylate (BA), using the "butyl-RAFT" agent. Drawn line is theoretical $\bar{M}_n$. Conditions: 3 h, 70 °C; organic phase: 8.0 g of BA, 2 wt % hexadecane with respect to BA, 4.4×10^{-2} mol of "butyl-RAFT" per L$_{\text{organic phase}}$; aqueous phase: 30 g of water, 2.3×10^{-3} mol of sodium dodecyl sulfate (SDS) per L$_{\text{water}}$, 3.0×10^{-3} mol of potassium peroxodisulfate per L$_{\text{water}}$.

In another miniemulsion polymerization experiment, 10 wt % of the BA monomer was successfully substituted by methacrylic acid (MA), leaving the rest of the variables exactly the same. For this polymerization, the theoretical and experimental $\bar{M}_n$ were 20 100 and 22 500 g/mol, respectively, and the polydispersity index after 92% conversion was 1.48. So, relatively polar blocks with a controlled length can be synthesized using this new concept.

The poly(butyl acrylate) latex described above was applied as a seed latex for the polymerization of the second monomer isooctyl acrylate (iOA). This seed latex had a $\bar{M}_n$ of 23 500 g/mol after 90% monomer conversion (see Figure 1). The amount of iOA used was 3.0 g, whereas 15 g of BA seed latex was used. The amount of water was 12.0 g, and the (fresh) KPS concentration was 0.003 mol/L. For this seeded emulsion polymerization, yielding a triblock copolymer, $\bar{M}_n$ increases linearly with iOA conversion.

Although the experimental part only describes the detailed synthesis of a difunctional butyl-RAFT agent, a multifunctional RAFT agent containing on average 12 RAFT groups ("poly(decyl-RAFT)" with R = decyl and $n_{\text{average}} = 6$ in Scheme 1) was synthesized using a difunctional chloroformate (for conditions, see Scheme 1). The yield was 70%. Figure 2 shows $\bar{M}_n$ and PDI vs BA conversion for this multifunctional RAFT agent.

For this homopolymerization of BA, for which the conditions were comparable to those applied using the difunctional butyl-RAFT agent, $\bar{M}_n$ increases linearly with conversion, indicating that also for this multifunctional RAFT agent the radical polymerization occurs in a controlled way. This polymer shows a good match of the measured and calculated $\bar{M}_n$ value after 85% BA conversion ($\bar{M}_{n,\text{exp}} = 97\,000$ g/mol, $\bar{M}_{n,\text{calc}} = 99\,500$ g/mol, PDI = 3.1, average latex particle size = 207 nm). On the other hand, the molar mass distribution is relatively broad, which is related to the high PDI of the "poly(decyl-RAFT)" itself, being 1.59. This high PDI is inherent in the step-growth polymerization technique, used to synthesize the multifunctional RAFT agent (see Scheme 1).

The BA latex, obtained in the miniemulsion polymerization with the multifunctional RAFT agent de-

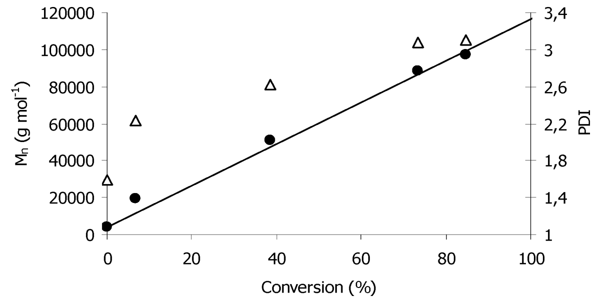

Figure 2. Number-average molar mass ($\bar{M}_n$, ●) and polydispersity index (PDI, Δ) vs conversion for the miniemulsion polymerization of *n*-butyl acrylate (BA), using a multifunctional "poly(decyl-RAFT)" agent (with R = decyl, $\bar{M}_{n,\mathrm{poly(decyl-RAFT)}}$ = 3700 g/mol in PS equivalents, $\mathrm{PDI}_{\mathrm{poly(decyl-RAFT)}} = 1.59$, on average 12 RAFT moieties present per molecule, so $n = 6$ in Scheme 1). Drawn line is calculated $\bar{M}_n$. Conditions: 3 h, 70 °C; organic phase: 8.0 g of BA, 2 wt % hexadecane with respect to BA, 8.0×10^{-3} mol of "poly(decyl-RAFT)" per $L_{\mathrm{organic\ phase}}$; aqueous phase: 30 g of water, 2.3×10^{-3} mol of sodium dodecyl sulfate (SDS) per L_{water}, 2.5×10^{-3} mol of potassium peroxodisulfate per L_{water}.

scribed above, was used as a seed for the emulsion polymerization of isooctyl acrylate (iOA). For this seeded emulsion polymerization the conditions were comparable to those used for the seeded emulsion polymerization described for the "butyl-RAFT" agent. Also for this second step the experimentally determined $\bar{M}_n$ increased linearly with conversion, from 97 000 g/mol ($\bar{M}_{n,\mathrm{seed}}$) to 152 000 g/mol for 90% iOA conversion. The calculated $\bar{M}_n$ was 178 000 mol. After the second polymerization step, the average particle size of the latex had increased from 207 to 302 nm.

After complete basic hydrolysis of the RAFT residues in the main chain, by a treatment with triethylamine in a water/DMF mixture at 90 °C for 48 h and after careful analysis of the hydrolysis products by SEC and gradient polymer elution chromatography, using a solvent gradient from 85/15 water/THF to pure THF in 20 min, it could be concluded that the synthesized multiblock copolymer had consisted of four poly(BA) blocks and three poly(iOA) blocks. The reason that the number of blocks is significantly lower than the initial number of RAFT groups in the multifunctional RAFT agent is that not all chain scissions, occurring during the fragmentation step, are restored later on. This phenomenon, also causing a broadening of the molar mass distribution, in addition to the already mentioned broadening effect of the high PDI of the multifunctional RAFT agent (see earlier), can probably be optimized by further raising the RAFT agent/free radical initiator ratio. This work is in progress.

In summary we have demonstrated that multifunctional RAFT agents can be synthesized in a relatively easy way. These multifunctional RAFT agents, depending on the number of RAFT groups they contain, yield triblock or even multiblock copolymers in merely two polymerization steps. The number of blocks generated in the multiblock copolymers is lower than expected in view of the number of RAFT groups in the multifunctional RAFT agent. This problem can probably be solved by optimizing the flux of radicals into the latex particles.

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