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Dual Concurrent ATRP/RAFT of Methyl Acrylate Co-initiated by Alkyl Halides

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INTRODUCTION

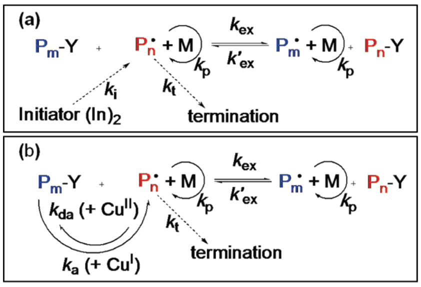
Atom transfer radical polymerization (ATRP) is a valuable and robust system for the preparation of functional materials, as it is able to polymerize a wide variety of monomers into many complex, yet well-controlled architectures.[1−5] ATRP proceeds by an activation/deactivation mechanism through which dormant species, alkyl (pseudo)halides, are activated to propagating radicals by a transition metal complex. While ATRP proved to be very successful in the polymerizations of many monomers under a variety of conditions, the amount of transition metal salts, frequently copper halides, in the initially studied systems was quite high. Thus, recently a new system, activators regenerated by electron transfer (ARGET) ATRP, was introduced in order to reduce the amount of copper and decreased the amount of catalyst to parts per million (ppm), while still retaining control of the polymerization.[6,7] The mechanism of ARGET ATRP is similar to traditional ATRP except that a reducing agent is present in excess to reduce copper(II) to copper(I), thereby regenerating the activating species lost in radical termination. Ascorbic acid, Sn(II)EH_2, copper wire, and other reducing agents were successfully used for ARGET ATRP.[8−19]

Reversible addition−fragmentation chain transfer (RAFT) polymerization is another versatile and robust controlled radical polymerization technique which proceeds through a degenerative transfer process.[20−23] Control in RAFT polymerization relies on fast and reversible transfer reactions between dormant species, dithiocarbonyl compounds, i.e., chain transfer agents (CTA), and radicals propagating with rate constant k_p (Scheme 1a). This system, however, requires a constant supply of radicals through decomposing radical initiators such as AIBN (with the rate constant k_i), to compensate for radical termination (with the rate constant k_t).[24] Recently, it was shown that the presence of appropriate ATRP catalysts, including CuBr/*N*,*N*,*N*′,*N*′′,*N*′′-pentamethyldiethylenetriamine (PMDETA), CuBr/2,2′-bipyridine (bpy), CuBr/tris[2-(dimethylamino)ethyl]amine (Me_6TREN), or CuBr/*tris*-[(2-pyridyl)methyl)amine] (TPMA), can directly activate RAFT chain transfer agents, including dithioesters, so that they act as alkyl pseudohalides.[12,25−32] When the CTA is activated by an ATRP catalyst, the need for a constant supply of external radicals is eliminated and purer block copolymers can be prepared. The mechanism of ATRP with alkyl pseudohalides (i.e., concurrent ATRP/RAFT or a copper-catalyzed RAFT) is shown in Scheme 1b.

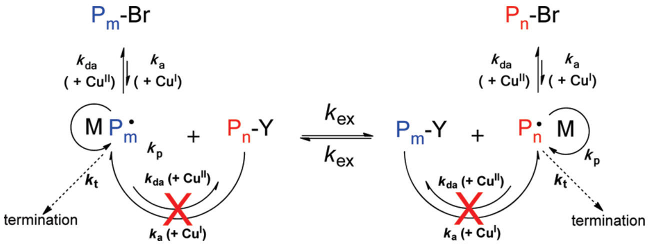
The concept of concurrent ATRP/RAFT with alkyl pseudohalides was then extended to ARGET systems with diminished amount of catalyst and Cu^0 as the reducing agent. Both concurrent ATRP/RAFT and ARGET with alkyl pseudohalides successfully polymerized styrene (St) and methacrylates in a controlled manner.[33] However, these procedures encountered difficulty in the polymerization of acrylates due to the inability of the available catalysts to activate the less active polyacrylate pseudohalide chain ends.

This work reports the use of alkyl halides as co-initiators in the new dual concurrent ATRP/RAFT of acrylates (Scheme 2). In these systems, alkyl halides (first low molar mass initiators and then macromolecular dormant species) were used to continuously generate propagating radicals while alkyl pseudohalides retained control over molecular weight and molecular weight distribution even at low concentration of metal complexes.

Scheme 1. Mechanism for RAFT (a) and Concurrent ATRP/RAFT with Alkyl Pseudohalides (b)



Scheme 2. Mechanism for Dual Concurrent ATRP/RAFT of Acrylates Co-initiated by Alkyl Halides



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RESULTS AND DISCUSSION

Previous concurrent ARGET ATRP/RAFT polymerizations of methyl methacrylate (MMA) and St were carried out with 5 ppm of initially added copper halide and a similar concentration of catalyst was selected for this study. However, in the previous systems no alkyl halide (R—Br) as traditional ATRP co-initiator was needed. The new dual concurrent ATRP/RAFT system developed for acrylates is comprised of seven components: monomer methyl acrylate (MA); the ATRP co-initiator, ethyl 2-bromoisobutyrate (EBiB); alkyl pseudohalide, i.e., CTA, cumyl dithiobenzoate (CDB); transition metal salt, copper(II) bromide ($CuBr_2$); TPMA ligand; solvent, anisole; and reducing agent, copper wire.

Concurrent ATRP/RAFT without alkyl halide ATRP co-initiator was unable to polymerize MA (Table 1, entry 1). After 48 h, no polymer was detected via GPC and ^{1}H NMR showed no conversion of monomer. Table 1 (entry 2) shows the results of the initial study starting with a targeted degree of polymerization DP = 500. The ratio of [MA]/[EBiB]/[CDB] was set to 1,000/1/1, giving a (50%) alkyl halide (R—Br) co-initiated system. As seen in Figure 1, the addition of the alkyl halide ATRP initiator to the concurrent ATRP/RAFT system allowed for the controlled polymerization of MA, utilizing low catalyst concentrations. Figure 1 also shows that this system can be applied to higher degrees of polymerization (Table 1, entry 3). When DP = 5000 was targeted, the addition of alkyl halide again allowed for a controlled polymerization of MA. Both polymerizations showed linear first-order kinetics. The values of number-average molecular weights (M_n) follow the theoretical molecular weights values ($M_{n,th}$) and polymers have a molecular weight distribution (M_w/M_n) near 1.1 at 40% conversion of monomer (Figure 1b).

Table 1. Conditions and Results of Dual Concurrent ATRP/RAFT of MA[a]

entry	% R—Br	EBiB	CDB	t (h)	conv[b]	$M_{n,GPC}$	M_w/M_n[c]	M_w/M_n[d]
1	0	0	1	48	0	N/A	N/A	N/A
2	50	1	1	7	0.41	20 000	1.14	1.15
3[e]	50	1	1	4	0.42	169 400	1.14	1.14
4	70	1.4	0.6	8	0.41	23 000	1.11	1.3
5	85	1.7	0.3	8	0.42	22 500	1.11	1.33
6	100	2	0	3	0.39	17 200	1.19	1.6

[a] All polymerizations were conducted in 50% (v/v) anisole at 50 °C with Cu^0 wire (L = 20 cm and d = 1 mm), while targeting a DP = 500 with [TPMA]/[$CuBr_2$] = 3. [b] Determined by ^{1}H NMR. [c] At 40% monomer conversion. [d] At 10% monomer conversion. [e] This reaction was targeting DP = 5000.

The effect of changing the relative proportion of ATRP initiator was then examined by keeping the same targeted DP (the same total initiator concentration), while varying the amount of EBiB relative to CDB. Table 1 (entries 2, 4—6) shows the reaction conditions for DP = 500 at 1:1 (50% R—Br), 1.4:0.6 (70% R—Br), 1.7:0.3 (85% R—Br), and 2:0 (100% R—Br). While targeting DP = 500 for increasing [R—Br] (50—100%) two trends can be observed. The first is related to the M_w/M_n values for each polymerization. The data in Table 1 show that all polymerizations resulted in low values of M_w/M_n after 40% monomer conversion. However, it is interesting to analyze the M_w/M_n values at lower monomer conversion. For 100% ARGET ATRP (no CDB, Table 1, entry 6) at ca. 10% conversion the M_w/M_n value was significantly higher than for systems which included alkyl pseudohalides. As the overall amount of alkyl halide was decreased and alkyl pseudohalide (CTA) was increased, the M_w/M_n early in the conversion of monomer decreases. This indicates that RAFT agent as alkyl pseudohalide allows for more uniform chain growth throughout the polymerization at very low catalyst concentration, especially at low conversion. This is in agreement with eq 1 which correlates M_w/M_n with conversion and concentrations of initiators (R—Br and R—Y) and deactivators (R—Y and Cu^{II} species that should be essentially constant, as defined by the ligand concentration) where p defines monomer conversion.

$$\frac{M_w}{M_n} = 1 + \left(\frac{k_p([R-Br]+[R-Y])}{k_d[Cu^{II}]+k_{ex}[R-Y]}\right)\left(\frac{2}{p}-1\right) \qquad (1)$$

The second trend seen by varying the relative amount of alkyl halide relates to polymerization rate. Without alkyl halide present, no polymerization occurred because the alkyl pseudohalides alone are not active enough to initiate polymerization. However, with alkyl halide present to generate radicals, polymerization occurred. Therefore, as the relative concentration of alkyl halide to alkyl pseudohalide increased, the time required to

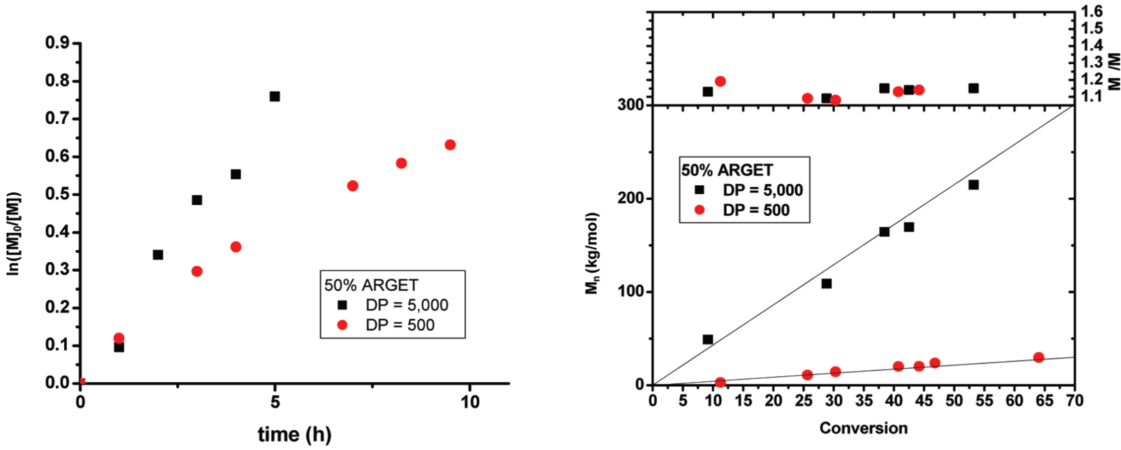

Figure 1. (a) First-order kinetic plots of 50% R—Br co-initiated dual concurrent ATRP/RAFT at targeted DP = 5000 (black) and DP = 500 (red) and (b) number average molar mass evolution and MWD versus conversion as a function of degree of polymerization. All polymerizations were conducted in 50% (v/v) anisole at 50 °C with [EBiB]$_0$/[CDB]$_0$ = 1, [TPMA]/[$CuBr_2$] = 3, and Cu^0 wire (L = 20 cm and d = 1 mm) (Table 1, entries 2 and 3).

reach 40% monomer conversion decreased, indicating an increased polymerization rate.

CONCLUSIONS

It was shown that addition of an alkyl halide as a co-initiator to concurrent ATRP/RAFT (i.e., ATRP with alkyl pseudohalides or a copper-catalyzed RAFT) allows for the polymerization of MA at low concentrations of copper catalyst over a range of degrees of polymerization. The presence and relative concentrations of alkyl pseudohalide and alkyl halide affected the molecular weight distribution at early monomer conversion and rate of polymerization; an increase in the concentration of alkyl pseudohalide resulted in lower M_w/M_n values but decreased rates of polymerization. In summary, it is possible to achieve a well-controlled polymerization of methyl acrylate at various DP in new dual concurrent ATRP/RAFT, at ARGET levels of copper catalyst concentration. Increasing the relative amount of alkyl pseudohalide afford polymers with narrow molecular weight distribution, even at early stages of monomer conversion.

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