Ambient Temperature Polymerization of Styrene by Single Electron Transfer Initiation, Followed by Reversible Addition Fragmentation Chain Transfer Control

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A simple and alternative method of polymer synthesis with control, under ambient conditions, using a combination of ambient temperature single electron transfer initiation and propagation through the radical addition fragmentation chain transfer (SET-RAFT) method is reported. The results obtained from the polymerizations of styrene carried out using SET-living radical polymerization (LRP) at ambient temperature, the RAFT method at 70 °C, and the SET-RAFT method at ambient temperature are discussed. Under appropriate conditions, this method should enable the controlled polymerization of a variety of acrylates and methacrylates as well.

An alternate method of controlled polymerization at ambient temperature (25 ± 3 °C) involving initiation by single electron transfer (SET)[1] with controlled propagation via a combination of the SET and RAFT[2,3] mechanisms is reported. This method, coined SET-RAFT, is expected to have much wider applicability, especially for monomers that polymerize very rapidly by free/living radical polymerizations. Living free radical polymerization of styrene under RAFT conditions using ^{60}Co γ radiation[4] and UV radiation[5] were reported by Davis et al. In both of the cases, the polymerization showed linearity up to 30% monomer conversion. With UV radiation, the generation of initiating radicals was low with respect to the concentration of the RAFT agent, and hence it was reported that close to 100% of the chains have terminal units generated from the RAFT agent itself.[5]

Recently, an ultrafast synthesis of ultrahigh molecular weight polymers of acrylates, methacrylates, and vinyl chloride mediated by SET at 25 °C was reported.[1] In general, metal catalyzed "controlled" living radical polymerizations have evoked considerable interest in the literature.[6,7] Polymerization at lower temperatures would be advantageous for a variety of reasons. Thermal crosslinking, chain transfer, thermal self-initiation, and other side reactions occur less readily at lower temperatures.[8] Since styrene based di- and triblock copolymers have applications as thermoplastic elastomers and amphiphilic block copolymers, it is of commercial interest to find an alternate and simple route for the synthesis of polystyrene (PS). The polymerization of styrene at ambient temperature (25 °C) by the inner-sphere electron transfer (ATRP) or the outer-sphere electron transfer (SET) is still a significant unsolved problem. For the purpose of controlled radical polymerization or living radical polymerization, it may be preferable to use an organic soluble chain transfer agent (CTA) that would work in the RAFT mode, in comparison with Cu(II), as in the typical ATRP, since the solubility of Cu(II) is seriously limited in the organic medium even with the use of suitable ligands.

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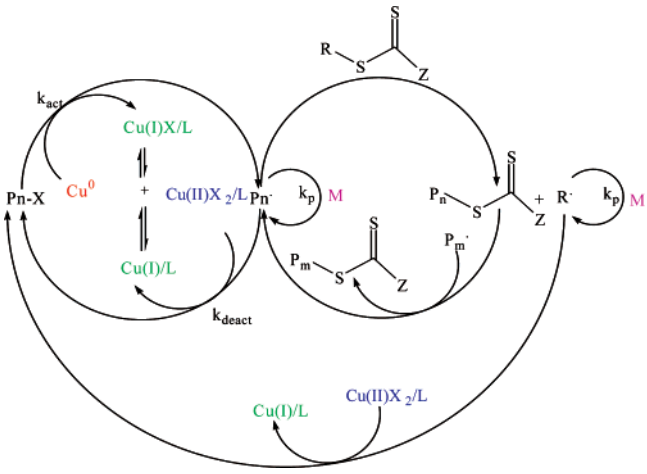
Scheme 1. Mechanism Proposed for SET-RAFT



Initially, styrene was polymerized at ambient temperature under various SET conditions (Supporting Information. Table 1). The polydispersity (PDI) of the PS obtained was high, and the chromatograms were very broad as shown in Figure 1. This is perhaps due to sluggish initiation, which is expected to be a heterogeneous reaction while the most significant portion of the propagation, involving the addition of several monomers to an active radical, is expected to be a homogeneous reaction and therefore could be relatively faster. The SET-LRP results with respect to the synthesis of ultrahigh molecular weight acrylates, methacrylates, and vinyl chloride involve monomers, which propagate rather fast in comparison with styrene. Styrene monomer was also polymerized by the conventional "RAFT only" polymerization at 70 °C using (2-ethoxy carbonyl) prop-2-yl-pyrrole-1-carbodithioate as the CTA to control propagation, and the results from these experiments are given in Supporting Information Figures 1 and 2. This polymerization could not be performed with a measurable rate at temperatures below 70 °C.

This prompted us to investigate the combination of SET and RAFT polymerization in the same system, at ambient temperature. It was expected that this methodology should provide the ambient temperature initiation of SET to be followed by the control propagation through the CTA via the RAFT mechanism. This combination is named as SET-RAFT polymerization, and the proposed mechanism is shown in Scheme 1. In the proposed mechanism, involving RX (initiator), the monomer, Cu(0), and the CTA, an initiating radical is generated from R−X (P_n−X in the propagating steps) using the SET initiation resulting in the formation of Cu(I)X. Cu(I)X/L instantaneously disproportionates into $Cu(II)X_2$ and Cu(0).[1] The radical formed (R• or P_n•) can propagate with the addition of monomer or it can be either deactivated using $Cu(II)X_2$/L or the thiocarbonyl group in the CTA, releasing the R group of the CTA as a radical along with a new CTA capped initiator (polymer). In this mechanism, the advantage is that any radical has the possibility of deactivation through reaction with $Cu(II)X_2$/L (persistent radical in the conventional ATRP[9]) or CTA (controlling agent in RAFT) to form a new CTA and a new radical for further polymerization. This can also result in polymers with a mixture of halogen and dithiocarbonyl endgroups. The polymerization of styrene, at ambient temperature, via various living radical polymerization (LRP) methods is described in Scheme 2.

Under the new SET-RAFT conditions, styrene was polymerized with fairly low polydispersity (<1.30) using diethyl

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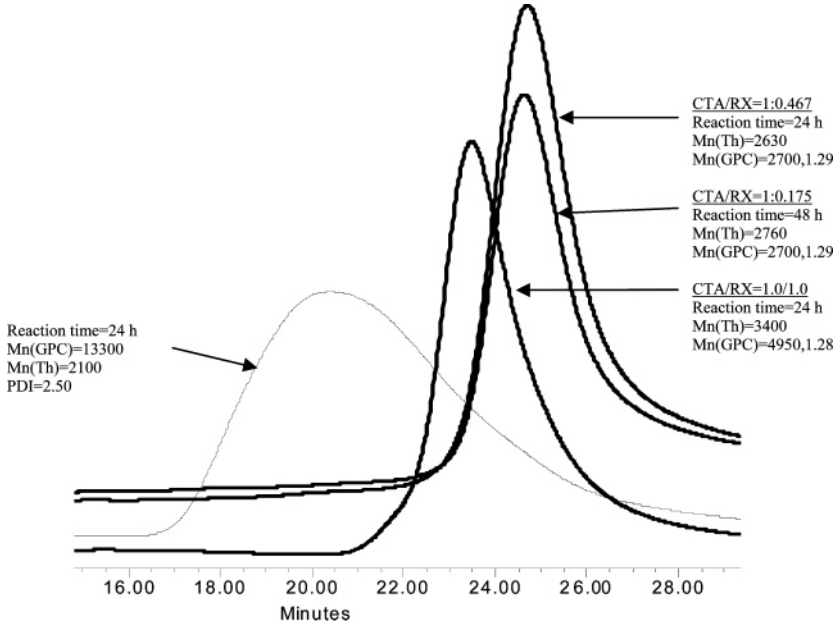


Figure 1. Comparison of GPC chromatograms of polystyrene samples prepared using the normal SET method and the SET-RAFT method with various RX to CTA ratios.

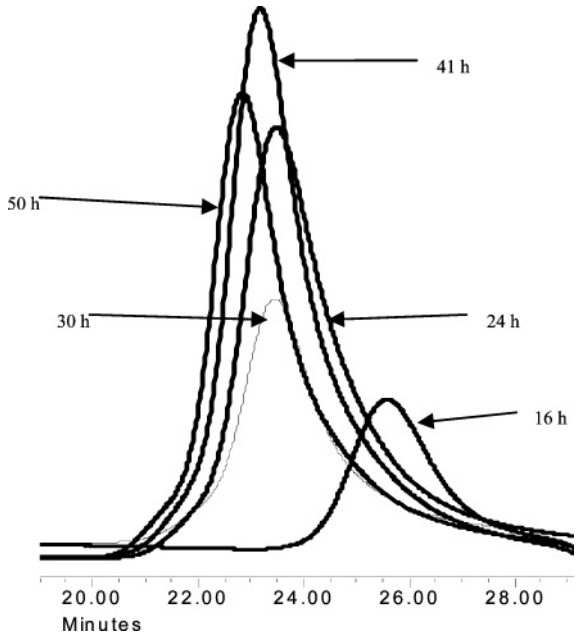


Figure 2. GPC traces of PS obtained with an increase in polymerization time under the SET-RAFT method.

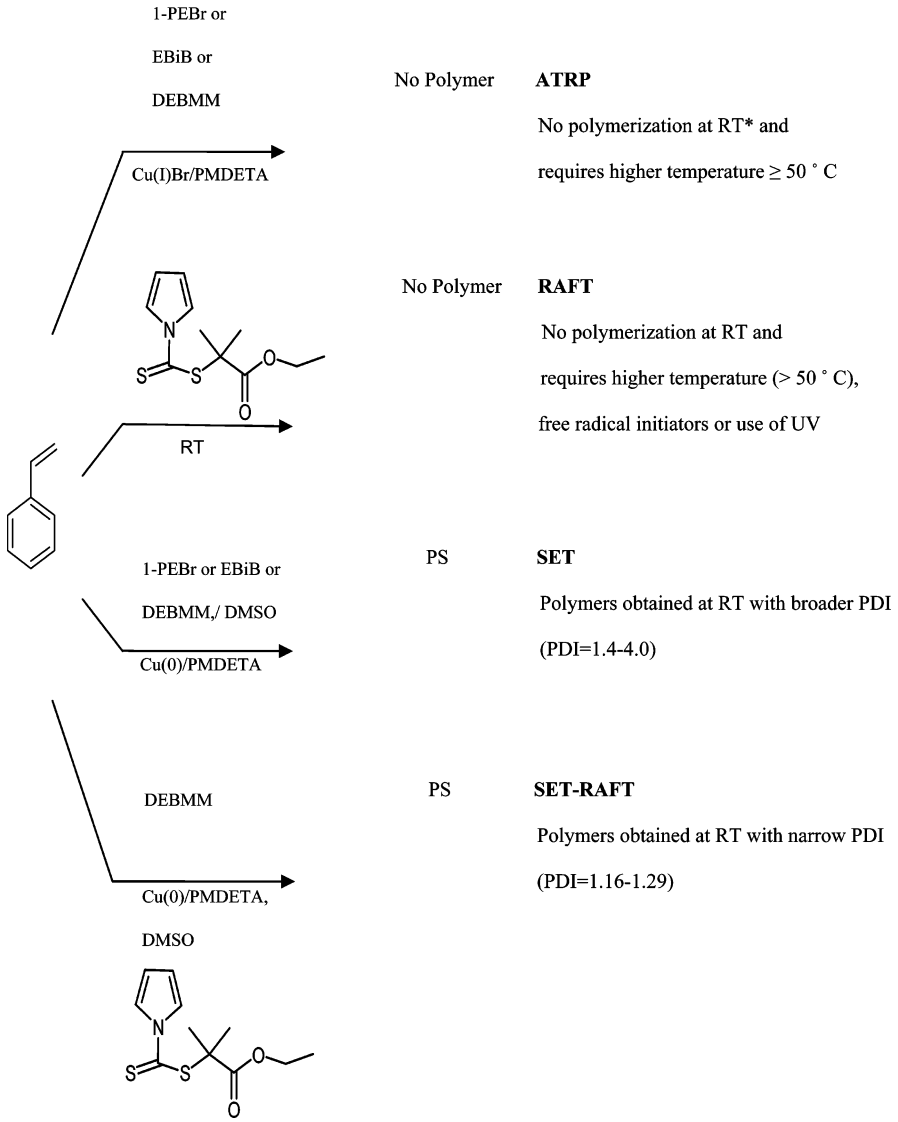
2-bromo-2-methyl malonate (DEBMM) as the initiator (Figures 1 and 2) and (2-ethoxy carbonyl) prop-2-yl-pyrrole-1-carbodithioate as the CTA. The result from one set of experiments is given in Table 1. It can be observed from the data in Table 1 that the molecular weight of the PS formed increases with polymerization time and the PDI values are narrow (as low as 1.16). Further the initiation efficiency decreases with increasing polymerization time and reaches a steady value after 30 h. The decrease in initiation efficiency at low molecular weights (<5000) suggests the presence of competing side reactions. It is also seen from Figure 2 that the chromatogram is shifted to the high-molecular weight region with an increase in the time of polymerization.

In addition, the rate of monomer consumption is first order (Supporting Information Figure 3A), indicating the presence of a constant number of growing chains. The increase in M_n(GPC) with percentage of conversion is shown in Supporting Information Figure 3B. The presence of the end groups were confirmed from ^{1}H NMR (Supporting Information Figure 4). When the CTA/RX ratio was increased, the polymerization was slowed down and the M_n(Th) was very close to M_n(GPC), thus indicating the suppression of side reactions. Further, from the ^{1}H NMR, as the CTA concentration is increased, the concentration of polymers with dithio end groups also increased (Supporting Information Figure 5). The assignments of the peaks were based on the following: the bromide ω end group of polystyrene synthesized via ATRP using 1-PEBr appears at around 4.1 ppm as reported in a recent publication of Bibiao et al.;[10] the thioester end group appears around 4.5 to 5.1 ppm and it depends on the Z group of the CTA as reported earlier by Chong et al.[11] This was also consistent with the ^{1}H NMR spectra of the PS synthesized by us using "SET-LRP" (Supporting Information Figure 6A,B) and "RAFT" (Supporting Information Figure 7).

The living nature of the polymer was further confirmed by chain extension reaction with *tert*-butyl acrylate (*t*BA). In one experiment, the PS macroinitiator was chain extended via conventional ATRP at ambient temperature using Cu(I)Br/Me_6-TREN. In another experiment, the macroinitiator was chain extended via conventional RAFT at 90 °C (that is the macroinitiator was heated in the presence of *t*BA). The GPC traces of two such block copolymers are shown in Figure 3. In both of the cases, diblock copolymers with a small component of the uninitiated macroinitiator are seen. It is clear from this result that most of the end groups are active for block copolymerization, especially via ATRP at ambient temperature where macroinitiators with the halogen end group can be activated in the presence of the macro CTAs thus resulting in complete utilization of all the end groups.

Acetonitrile was used as a solvent for the SET-RAFT polymerization of styrene and the chromatogram was shown in Supporting Information Figure 8A. The SET-RAFT method was also carried out without the use of a ligand and thus reducing the solubility of Cu(I) and eliminating the possibility of deactivation via the Cu(II) complex (Supporting Information Figure 8B). In both of the cases it has been reported that Cu(I)

Scheme 2. Comparison of Polymerization of Styrene via SET, ATRP, RAFT, and the Newly Developed SET-RAFT Method



*RT, room temperature (25 ± 3 °C); 1-bromoethyl benzene (1-PEBr); ethyl 2-bromo isobutyrate (EBiB); diethyl-2-bromo-2-methyl malonate (DEBMM); diethyl-2-bromo malonate (DEBM); pentamethyl diethylene triamine (PMDETA); dimethyl sulfoxide (DMSO).

Table 1. Summary of the Polymerization Time, Conversion, Molecular Weights, and Polydispersities of Various Polymers (PS) Synthesized via the New SET-RAFT Method, under Ambient Conditions

time (h)	% conversion	M_n (Th)[a]	M_n (GPC)[b]	PDI
16	19.30	1970	2000	1.16
24	33.10	3400	4950	1.28
30	38.18	3900	5360	1.26
41	43.57	4500	5770	1.28
50	48.73	5000	6800	1.29

[a] For SET-RAFT conditions, the theoretical molecular weight [M_n(Th)] can be given as M_n(Th) = [styrene]/{[RX] + [CTA]}(% yield)(molecular weight of styrene). [b] THF eluent; PS standards.

will not disproportionate to give Cu(0) and Cu(II).[1] Hence the SET process is limited to initiation only. Under these conditions, SET-RAFT can be considered as metal catalyzed ambient temperature RAFT polymerization. Both of the methods gave PS with PDI around 1.40 suggesting that once the SET initiation is enabled, the propagation via RAFT control takes place with the assistance of CTA at ambient temperature. The new SET-RAFT condition also works well with *p*-toluene sulfonyl chloride (TsCl) as an initiator and the PS obtained exhibited a PDI of 1.20. The chromatogram of PS synthesized from SET-LRP and SET-RAFT are shown in Supporting Information Figure 9.

In principle, this method should be applicable to a variety of monomers including acrylates and methacrylates. In addition, the new SET-RAFT polymerization is expected to offer the following advantages: (i) the typical RAFT polymerization requires thermal/photochemical initiation and one of the end groups will be a fragment from the initiator. Under the SET-RAFT conditions, the ambient temperature initiation and the use of functional initiators will thus overcome the above limitation of RAFT; (ii) polymers obtained under SET-RAFT conditions will have a minimum number of dead chains along with halogen end polymers and dithiocarbonyl end polymers. The halogen end group can be easily converted to a dithiocarbonyl end group;[12] (iii) control can be achieved with relative ease in the case of monomers, which polymerize very fast under the SET conditions such as acrylates, methacrylates, and vinyl chloride. Further compared to a typical SET or ATRP or RAFT polymerization, termination is expected to be less competitive in view of the presence of the CTA as well as Cu(II) generated in situ; (iv) the polymerization in aqueous medium[13−15] with a water soluble initiator, monomer, and CTA should in principle

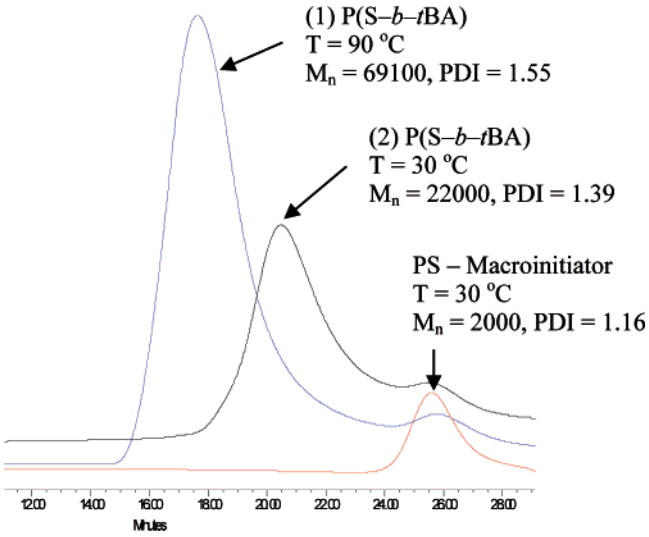


Figure 3. GPC traces of PS macroinitiator (SET-RAFT at ambient temperature) and block copolymers (1, RAFT only and 2, ATRP using Cu(I)Br and Me_6TREN). **(**ATRP**)** *t*BA/PS−MI/Cu(I)Br/Me_6TREN = 273/1/0.5/0.5. (Bulk, 30 °C, 24 h) **(**RAFT**)** PSMI/*t*BA = 1/400 (bulk, 90 °C, 24 h).

provide an ideal means for synthesizing water soluble polymers with low polydispersity under milder conditions. There is one disadvantage associated with the polymerization of styrene: the propagation of styrene for example is intrinsically slow and hence ∼50% monomer conversion is attained after 50 h (for the target DP of 200). However it can be overcome by mildly increasing the temperature for propagation as well as by synthesizing short blocks of PS with a narrow molecular weight distribution.

In summary, this SET-RAFT method can be considered as an alternative approach to synthesize polymers under ambient conditions in a "controlled" manner. The polymerization of styrene via the SET-RAFT method was shown to proceed with living characteristics (linear evolution of molecular weight with conversion, narrow molecular weight distribution, and good adherence to expected molecular weight). Especially, this SET-RAFT condition is expected to be very effective for monomers with a slower rate of initiation compared to the rate of propagation and those with a very high rate of propagation that require control. In view of this, the SET-RAFT system reported would open up avenues to research that would lead to the use of various chain transfer agents (CTA) with different Z and R groups along with different alkyl halides to increase the effectiveness of this system in terms of control and a faster rate for various monomers in the family of (meth)acrylates and styrene.

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Supporting Information Available: Experimental data from the polymerization of styrene uder various SET-LRP conditions, synthesis procedure of CTA, relationships between $\ln([M]_0/[M]_t)$ and polymerization time and between M_n (GPC) and % conversion, variation of PDI with % conversion, experimental data from SET-RAFT, ^{1}H NMR spectra, and GPC traces. This material is available free of charge via the Internet at http://pubs.acs.org.

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