Controlled Radical Polymerization

DOI: 10.1002/ange.200600272

Activators Regenerated by Electron Transfer for Atom-Transfer Radical Polymerization of (Meth)acrylates and Related Block Copolymers**

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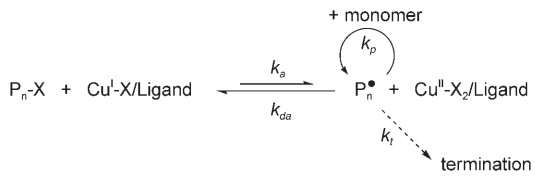
Atom-transfer radical polymerization (ATRP) is a controlled or living radical polymerization (CRP) technique[1,2] that enables the preparation of new nanostructured materials that are not accessible by conventional free-radical polymerization (FRP). Reported herein is the ATRP of polar monomers such as (meth)acrylates and related block copolymers by means of a new initiating/catalytic method based on activators regenerated by electron transfer (ARGET) with ppm (10^{-4} mol% vs. monomer) amounts of Cu catalyst.[3]

ATRP[4–7] provides a simple route to many well-defined (co)polymers with precisely controlled functionalities, topologies, and compositions.[8–10] It has been very successfully applied to the preparation of many nanocomposites, hybrids, and bioconjugates.[11–23] The advantages of ATRP, in comparison with other CRP processes, include the large range of available monomers and (macro)initiators, the simplicity of reaction setup, and the ability to conduct the process over a large range of temperatures, solvents, and dispersed media.[6,7,24]

ATRP (Scheme 1) is a repetitive atom-transfer process between a macromolecular alkyl halide P_n–X and a redox-active transition-metal complex Cu^I–X/ligand in which $P_n^\bullet$ radicals propagate (rate constant of propagation k_p) and are reversibly formed (rate constants k_a and k_{da}). The growing radicals also terminate by coupling or disproportionation (rate constant k_t).

An inherent feature, but also a limitation of ATRP, is the presence of a catalyst (a transition-metal complex with



Scheme 1. Mechanism for ATRP.

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[**] The authors thank the National Science Foundation (DMR-05-49353 and CHE-04-05627) and the members of the CRP Consortium at Carnegie Mellon University for financial support, and Ke Min for the synthesis of P*n*BA using glucose as reducing agent in ARGET ATRP.

various ligands). The catalyst is not bound to the end of the chain, as it is in coordination polymerization, and can therefore be used in a controlled or living process with substoichiometric amounts with respect to the initiator. Nevertheless, it is typically used at concentrations ranging from 0.1 to 1 mol% with respect to the monomer and therefore needs to be removed from the final polymer. There have been several attempts to remove and recycle the catalyst efficiently by extraction, precipitation, immobilization, or by using biphasic systems.[24–30] However, there is always some loss of polymerization control in biphasic systems or added cost associated with catalyst preparation.

Thus, another approach to reduce the amount of ATRP catalyst, while preserving a similar reaction rate, is to enhance the rate of activation significantly (augmenting the equilibrium constant by increasing the k_a/k_{da} ratio; Scheme 1). Indeed, CuBr complexed by tetradentate ligands such as tris[2-(dimethylamino)ethyl]amine (Me_6TREN) and tris(2-pyridylmethyl)amine (TPMA) is 10^3–10^5 times more active than the originally used CuBr/bipyridine complexes.[31–35] However, the catalyst concentration can not simply be reduced by 10^3 (from a concentration equimolar with the initiator (i.e., 1 mol% vs. monomer) to 10 ppm vs. monomer) owing to the radical termination and concurrent irreversible oxidation of the catalyst (Cu^I to Cu^{II}). All Cu^I species would be converted to Cu^{II} when less than 1% of the growing chains terminate. Furthermore, some impurities, such as oxygen or various radical inhibitors, deactivate these minute amounts of very active catalyst, and thus stringent purification methods and procedures similar to those used in ionic polymerizations are required.

These limitations can be overcome by the addition of an appropriate reducing agent, such as tin(II) 2-ethylhexanoate ($Sn(EH)_2$), which has been approved by the Food and Drug Administration (FDA), or sugars such as glucose. The $Sn(EH)_2$ reductant can reduce the Cu^{II} species that accumulate when radicals irreversibly terminate to restore the original Cu^I state needed for activation (Scheme 2). In this process, the activators are continuously regenerated by electron transfer (ARGET).

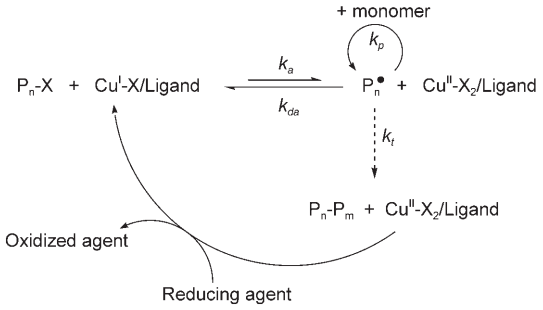
Furthermore, the process can be started with the oxidatively stable Cu^{II} species, which can be reduced in situ to the Cu^I state as in a previously reported AGET process (activators generated by electron transfer).[36,37] However, in AGET ATRP, the oxidatively stable Cu^{II} catalyst, present at a considerably higher concentration (>0.1 mol% vs. monomer), was reduced with nearly stoichiometric amounts of ascorbic acid or $Sn(EH)_2$. Other reducing agents were previously used to accelerate ATRP, but the concentration of copper catalyst was always very high, essentially equal to that of the initiator.[38–41]

In the ARGET system, a tiny amount of Cu catalyst is used together with a sufficiently large excess of reducing agent, which not only reduces Cu^{II} to Cu^I but is also responsible for scavenging oxygen and radical inhibitors. The concentration of the reducing agent and related rate of reduction can greatly influence the ARGET ATRP. Herein, we report the optimized conditions for the studied system; investigations of different reducing agents and rates of reduction will be presented elsewhere. ARGET provides a real breakthrough in ATRP since the repetitive reduction cycle enables the amount of catalyst to be decreased significantly (down to single digit ppm vs. monomer). For some applications, ARGET could even allow the residual copper to be left in the final, colorless products.

We have recently reported that ARGET ATRP of styrene with 10 ppm $CuCl_2/Me_6$TREN catalyst in the presence of an excess of $Sn(EH)_2$ was well controlled and gave polymers with low polydispersities ($M_w/M_n < 1.2$) and molecular weights that agreed excellently with theoretical values.[3] Control of the molecular weight was also good even with 1 ppm Cu, but the polydispersities were higher ($M_w/M_n \approx 1.6$), which indicated that there was not enough Cu to assure fast exchange between active and dormant species.

Herein, we present results of ARGET ATRP of *n*-butyl acrylate (*n*BA) and methyl methacrylate (MMA). These systems are more challenging, since the more polar acrylates coordinate more strongly to Cu[42,43] than does styrene, which could potentially affect the catalyst performance.

Table 1 presents the experimental conditions and properties of poly(*n*-butyl acrylate) (P*n*BA) prepared by ARGET ATRP. The polymerization of *n*BA was initiated by ethyl 2-bromoisobutyrate (EtBrIB), and a final molecular weight $M_n = 20000\ g\,mol^{-1}$ was targeted. A constant amount (10 mol% vs. initiator; 0.07 mol% vs. monomer) of $Sn(EH)_2$



Scheme 2. Mechanism for ARGET ATRP: The Cu^I activator is constantly regenerated by environmentally acceptable reducing agents (e.g. FDA-approved compounds, sugars etc.), which compensate for any loss of Cu^I as a result of radical termination.

Table 1: Experimental conditions and properties of P*n*BA prepared by ARGET ATRP.

Entry[a]	Cu[c] [ppm]	*t* [min]	Conv. [%]	$M_{n,theo}$[d] [g mol^{-1}]	$M_{n,GPC}$ [g mol^{-1}]	M_w/M_n
1	500	1210	97	19400	19600	1.18
2	50	370	91	18100	19400	1.26
3	10	360	90	17900	19100	1.40
4	2	1150	97	19500	24400	2.48
5[b]	50	1320	71	14300	15100	1.16
6[b]	10	1320	84	16800	19300	1.33
7[b]	2	1260	88	17600	23500	1.56

[a] Ratio of reactants: $[nBA]_0/[EtBrIB]_0/[Me_6TREN]_0/[Sn(EH)_2]_0 = 160/1/0.1/0.1$; $[nBA]_0 = 5.88$ M; $T = 60$ °C, in anisole (20% v/v vs. monomer); [b] TPMA (0.03 equiv) was used as a ligand instead of Me_6TREN; [c] molar ratio vs. monomer; [d] $M_{n,theo} = ([nBA]_0/[EtBrIB]_0) \times \text{conversion} \times M_{monomer}$.

and variable concentrations of the Cu-based catalyst with Me_6TREN and TPMA as ligands were employed. The amount of copper was varied from 500 down to 2 ppm vs. monomer (Table 1).

Figure 1 presents the evolution of the molecular weights and polydispersities with conversion for polymerization of *n*BA with 50 ppm $CuCl_2$/Me_6TREN catalyst. Control of the molecular weight was excellent according to theoretical values based on quantitative initiation. However, with 2 ppm Cu catalyst, the molecular weights and polydispersities were higher (Table 1, entry 4), which indicates that there was not enough Cu to assure fast exchange between active and dormant species.

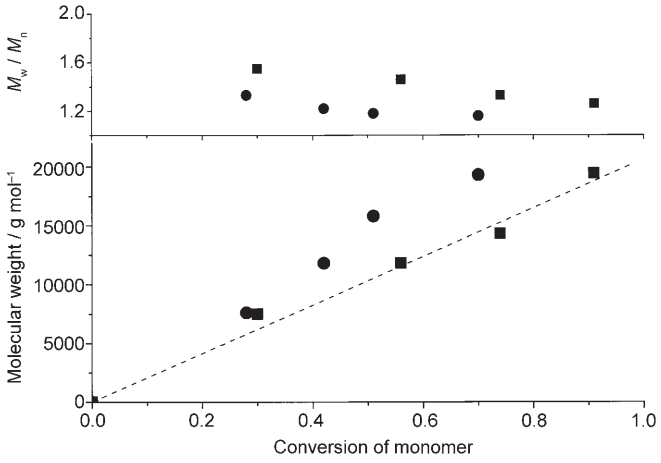


Figure 1. Molecular weights and polydispersities of poly(*n*-butyl acrylate) and poly(methyl methacrylate) as a function of degree of conversion of (■) *n*BA and (●) MMA. Experimental conditions for *n*BA are given in Table 1, entry 2 and for MMA in Table 2, entry 1.

Better results were obtained with the TPMA ligand, which binds more strongly to Cu than does Me_6TREN[44,45] (Table 1, entries 5–7). Although TPMA forms slightly less active complexes than Me_6TREN,[32,34,46] better control over polymerization was observed. This observation can be ascribed to a higher real concentration of Cu species in the system, since TPMA binds more strongly to Cu.

ARGET ATRP of *n*BA was also carried out in the presence of glucose (an organic reducing agent). Under conditions similar to those presented in Table 1, entry 5 (*n*BA/EtBrIB/$CuCl_2$/TPMA/glucose = 160/1/0.0078/0.03/0.1; 50 ppm Cu vs. monomer; $t = 2640$ min; $T = 80\,^{\circ}C$, in 20% v/v anisole), P*n*BA was formed in 48% yield with $M_n = 10\,500\ g\,mol^{-1}$ and $M_w/M_n = 1.47$ ($M_{n,theo} = 9600\ g\,mol^{-1}$).

Table 2 presents the experimental conditions and properties of poly(methyl methacrylate) (PMMA) prepared by ARGET ATRP. Ethyl α-bromophenylacetate (EtBPA) was used as initiator and TPMA as a ligand. As in the case of *n*BA, MMA was polymerized by ARGET ATRP with varied amounts of Cu catalyst. The molecular weight and polydispersity of the polymer with 50 ppm Cu catalyst as a function of degree of conversion are shown in Figure 1. Figure 2 shows a kinetic plot and the evolution of the molecular-weight distribution with polymerization (2 ppm Cu catalyst). The molecular weight was well controlled; a gradual increase in the molecular-weight distribution was observed, and the final polydispersity was relatively low ($M_w/M_n = 1.36$).

Table 2: Experimental conditions and properties of PMMA prepared by ARGET ATRP.

Entry[a]	Cu[b] [ppm]	t [min]	Conv. [%]	$M_{n,theo}$[c] [g mol^{-1}]	$M_{n,GPC}$ [g mol^{-1}]	M_w/M_n
1	50	360	70	14 000	19 300	1.16
2	10	370	61	12 200	15 900	1.34
3	2	335	66	13 300	15 300	1.36

[a] Ratio of reactants: $[MMA]_0/[EtBPA]_0/[TPMA]_0/[Sn(EH)_2]_0 = 200/1/0.03/0.1$; $[MMA]_0 = 6.23$ M; $T = 90\,^{\circ}C$, in anisole (50% v/v vs. monomer); [b] molar ratio vs. monomer; [c] $M_{n,theo} = ([MMA]_0/[EtBPA]_0) \times \text{conversion} \times M_{monomer}$.

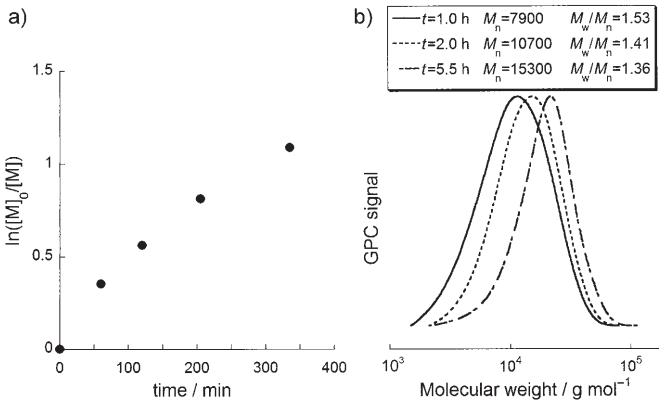


Figure 2. a) Kinetic plot and b) evolution of GPC traces during ARGET ATRP of MMA. Experimental conditions are given in Table 2, entry 3.

The new system was also successfully applied to the synthesis of block copolymers P*n*BA-*b*-PS and PS-*b*-P*n*BA (PS = polystyrene). Initially a P*n*BA block was prepared by using ARGET ATRP of *n*BA with 50 ppm Cu complex ($M_{n,GPC} = 19\,400\ g\,mol^{-1}$, $M_{n,theo} = 18\,100\ g\,mol^{-1}$, $M_w/M_n = 1.26$), and then it was used as a macroinitiator. Chain extension of the P*n*BA macroinitiator with styrene by ARGET ATRP with 15 ppm Cu catalyst was very efficient ($M_{n,GPC} = 34\,900\ g\,mol^{-1}$, $M_{n,theo} = 37\,000\ g\,mol^{-1}$, $M_w/M_n = 1.18$).

Figure 3 presents the size-exclusion chromatography (SEC) traces recorded after each step. The reactions were well controlled, as evidenced by the monomodal gel-permeation chromatography (GPC) traces. PS macroinitiator, also prepared by ARGET ATRP with 15 ppm Cu catalyst ($M_{n,GPC} = 17\,100\ g\,mol^{-1}$, $M_{n,theo} = 15\,300\ g\,mol^{-1}$, $M_w/M_n = 1.18$) was chain extended with *n*BA (50 ppm Cu catalyst) to provide a block copolymer with $M_{n,GPC} = 26\,300\ g\,mol^{-1}$ ($M_{n,theo} = 28\,900\ g\,mol^{-1}$) and $M_w/M_n = 1.33$.

In summary, we report the successful polymerization of the polar monomers *n*-butyl acrylate and methyl methacrylate by ARGET ATRP with ppm quantities of Cu catalyst. Better control was obtained with TPMA as a ligand which binds to copper more strongly than does Me_6TREN. The new ARGET system was also successfully applied to the efficient synthesis of styrene and *n*-butyl acrylate block copolymers. It is

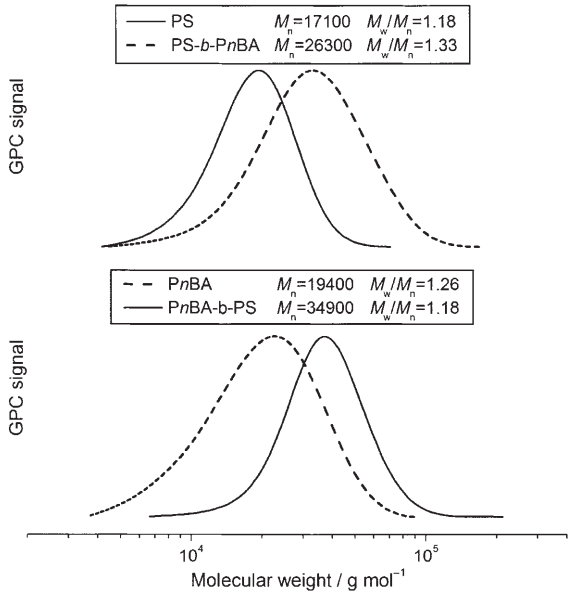


Figure 3. GPC traces after each step of the synthesis of block copolymers PS-*b*-P*n*BA (top) and P*n*BA-*b*-PS (bottom). Experimental conditions for the polymerization of *n*BA: *n*BA/EtBrIB/Cu^{II}/Me_6TREN/$Sn(EH)_2$ = 160/1/0.0078/0.1/0.1; $[nBA]_0$ = 5.88 M, Cu catalyst: 50 ppm vs. monomer, T = 60 °C, in anisole (20% v/v vs. monomer). Experimental conditions for polymerization of styrene: styrene/P*n*BA/$CuCl_2$/Me_6TREN/$Sn(EH)_2$ = 200/1/0.003/0.1/0.1; $[styrene]_0$ = 5.82 M, Cu catalyst: 15 ppm vs. monomer, T = 110 °C, in anisole (50% v/v vs. monomer).

anticipated that ARGET ATRP will facilitate the commercial application of ATRP and simplify the preparation of many new materials, including molecular hybrids, bioconjugates, and nanocomposites.

Experimental Section

Styrene (Aldrich, 99%), *n*-butyl acrylate (*n*BA) (Acros, 99 + %), and methyl methacrylate (MMA) (Acros, 99%) were passed through a column filled with neutral alumina, dried over calcium hydride, and distilled under reduced pressure. Tris[2-(dimethylamino)ethyl]amine (Me_6TREN),[31] tris(2-pyridylmethyl)amine (TPMA)[47] were synthesized following previously reported procedures. Ethyl 2-bromoisobutyrate (EtBrIB) (Acros, 98%), ethyl α-bromophenylacetate (EtBrPA) (Aldrich, 97%), copper(II) chloride (Acros, 99%), tin(II) 2-ethylhexanoate ($Sn(EH)_2$) (Aldrich), and anisole (Aldrich, 99%) were used as received.

General procedure for ARGET ATRP of *n*BA, (targeted number-average degree of polymerization (DP_n) = 160; 50 ppm Cu catalyst): Degassed *n*BA (5.0 mL, 35 mmol) and anisole (0.5 mL) were transferred via degassed syringes to a dry, nitrogen-purged Schlenk flask, and the Cu complex ($CuCl_2$ 0.24 mg, 0.18×10^{-2} mmol; Me_6TREN 0.51 μL, 0.18×10^{-2} mmol) in degassed anisole (0.5 mL) was added. The resulting mixture was stirred for 10 minutes, and then a purged solution of $Sn(EH)_2$ (7.29 μL, 2.2×10^{-2} mmol) and Me_6TREN (5.8 μL, 2.2×10^{-2} mmol) in anisole (0.5 mL) was added. EtBrIB (32.4 μL, 22.1×10^{-2} mmol) was added to initiate the polymerization. An initial sample was taken, and the sealed flask was placed in an oil bath at 60 °C. Samples were taken at timed intervals and analyzed by gas chromatography (GC) and gel-permeation chromatography (GPC) to follow the progress of the reaction. The polymerization was stopped after 6.2 h ($M_{n,GPC}$ = 19400, M_w/M_n = 1.26, conversion = 91%) by opening the flask and exposing the catalyst to air.

Synthesis of diblock copolymer P*n*BA-*b*-PS by ARGET ATRP: A P*n*BA macroinitiator (M_w = 19400, M_w/M_n = 1.26, 2.35 g, 0.12 mmol) was dissolved in styrene monomer (2.75 mL, 24.0 mmol) in a 25-mL Schlenk flask and bubbled with nitrogen for 15 minutes. Next, a solution of Cu complex ($CuCl_2$ 4.84×10^{-2} mg, 0.36×10^{-3} mmol; Me_6TREN 0.10 μL, 0.36×10^{-3} mmol) in degassed anisole (0.7 mL) was added. The resulting mixture was stirred for 10 minutes, and then a purged solution of $Sn(EH)_2$ (3.9 μL, 1.2×10^{-2} mmol) and Me_6TREN (3.2 μL, 1.2×10^{-2} mmol) in anisole (0.7 mL) was added. An initial sample was taken and the sealed flask was placed in an oil bath at 110 °C. Samples were taken at timed intervals and analyzed by GC and GPC. The polymerization was stopped after 30.8 h ($M_{n,GPC}$ = 34900, M_w/M_n = 1.18, conversion = 88%) by opening the flask and exposing the catalyst to air.

Analysis: Molecular weight and polydispersity were determined by GPC (Waters 515 pump and Waters 2414 differential refractometer, PSS columns (Styrogel 10^5, 10^3, 10^2 Å), THF eluent, T = 35 °C, flow rate = 1 mL min^{-1}). Linear polystyrene and poly(methyl methacrylate) standards were used for calibration. The conversion of the monomers was determined by using a Shimadzu GC 14-A gas chromatograph (FID detector, J&W Scientific 30 m DB WAX Megabore column, anisole internal standard). The injector and detector temperatures were kept constant at 250 °C. The analysis was carried out isothermally at 60 °C for 2 min, and then the temperature was increased to 140 °C at a rate of 40 °C min^{-1} and held at 140 °C for 2 min. The degree of conversion was calculated by measuring the decrease of the peak area of the monomer relative to the peak areas of the standards.

Received: January 21, 2006
Published online: June 13, 2006

Keywords: atom-transfer radical polymerization · block copolymers · polymerization · redox chemistry

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