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Activator Generated by Electron Transfer for Atom Transfer Radical Polymerization

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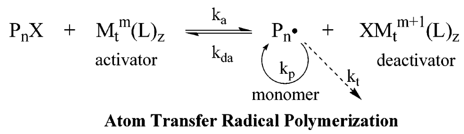
ABSTRACT: A novel procedure was developed for activation of an oxidatively stable catalyst complex added to an atom transfer radical polymerization (ATRP). Tin(II) 2-ethylhexanoate ($Sn(EH)_2$) was used as a reducing agent of various Cu(II) complexes in ATRP of various monomers initiated by alkyl halides. This approach further improves a simultaneous normal and reverse initiation (SR&NI) by eliminating free radical initiators for the activation of the higher oxidation state catalyst complex. As a result, "activator generated by electron transfer" (AGET) ATRP allows the preparation of pure block copolymers. Several combinations of monomer/catalyst complex precursor were studied, including styrene/$CuCl_2$/dNbpy, octadecyl methacrylate/$CuCl_2$/dNbipy, methyl methacrylate/$CuCl_2$/PMDETA, *n*-butyl acrylate/$CuBr_2$/PMDETA, and methyl acrylate/$CuCl_2$/Me_6TREN. Polymerization proceeded in a controlled way for all systems, producing well-defined polymers with controlled degree of polymerization and narrow molecular weight distribution, demonstrating the robust nature of AGET ATRP. Additionally, $Sn(EH)_2$ was used simultaneously as a reducing agent for ATRP of octadecyl methacrylate and a catalyst for ring-opening polymerization (ROP) of ϵ-caprolactone, allowing direct synthesis of the corresponding block copolymer.

Introduction

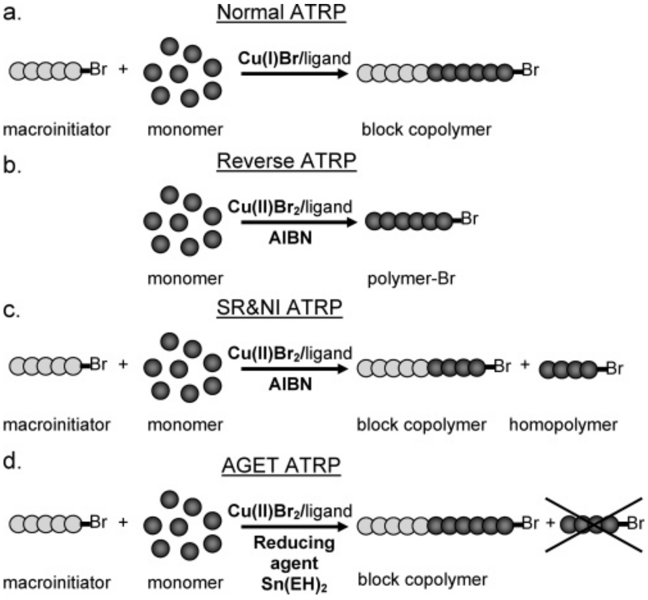
Atom transfer radical polymerization (ATRP) is one of the most successful "controlled/living" radical polymerization (CRP) developed during recent years.[1−6] ATRP relies on creation of a dynamic equilibrium between a large amount of a dormant species and a small amount of propagating radicals (Scheme 1).[7] The propagating species $P_n^\bullet$ are generated through a reversible redox process catalyzed by a transition metal complex $Mt^m(L)_z$ (activator) that undergoes the inner-sphere one-electron oxidation with abstraction of a radically transferable atom or group, most frequently a halogen atom, X, from the dormant species, P_nX. The growing radicals react reversibly with the oxidized metal complex, $XMt^{m+1}(L)_z$ (deactivator), to re-form the dormant species and the activator. This process occurs with rate constants of activation, k_a, and deactivation, k_{da}. If the concentration of propagating radicals is sufficiently low ($k_a \ll k_{da}$), the probability of bimolecular termination reactions is reduced. Additionally, if initiation is fast in comparison with propagation, molecular weight grows linearly with conversion, and the polymerization resembles a controlled/living system. Because of controlled/living nature of ATRP, this method is used to prepare not only homopolymers but also random,[8] gradient,[9] alternating,[10,11] block,[8,12,13] stereo-block,[14] graft,[15,16] branched or hyperbranched,[17−21] star,[13,22] and bottle brush[23−25] (co)polymer structures. This technique allows the controlled polymerization of a wide range of vinyl monomers including styrenics,[26] (meth)acrylates,[27−30] acrylonitrile,[31,32] vinyl acetate,[33−35] and others.[36,37]

However, ATRP has some limitations. Since ATRP is initiated by a redox reaction between an initiator with a radically transferable atom or group and a catalyst complex comprising a transition metal compound in a lower oxidation state (Scheme 2a), the transition metal complexes can be easily oxidized to a higher oxidation state. Therefore, to obtain consistent results, special handling procedures are required, and the preformed catalysts must be stored under an inert atmosphere. Oxygen or other oxidants should be removed from the system prior to addition of the catalyst in the lower oxidation state; therefore, the process of catalyst complex handling can be challenging.[38−40]

Scheme 1. Mechanism of ATRP



Scheme 2. Methods for Conducting ATRP



Reverse ATRP (Scheme 2b) was developed to overcome this limitation. It uses the more stable Cu(II) complexes in the initiating step. However, as more active catalyst complexes were developed,[41,42] a limitation inherent in reverse ATRP became clear. The transferable atom or group (X) is added to the reaction

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as a part of the copper salt, and therefore highly active catalysts should still be used in the amount comparable to concentration of radical initiator. Therefore, complex concentration cannot be independently reduced and block copolymers cannot be formed. Simultaneous normal and reverse initiation (SR&NI) ATRP (Scheme 2c) was developed to allow the precursors of highly active catalyst complexes to be added to the reaction in the higher oxidation state and at lower concentration.

SR&NI ATRP comprises a dual initiation system: standard free radical initiators and initiators comprising a transferable atom or group in conjunction with the stable precursor of an active catalyst complex.[43,44] This initiation system can be used to prepare any type of polymer that can be prepared by normal ATRP, and it can be conducted in bulk, solution, emulsion, miniemulsion, and heterogeneous polymerization from surfaces.[45] There are, however, some limitations to SR&NI ATRP. Since a standard free radical initiator is still added to the polymerization mixture to form radicals that reduce the Cu(II), chains initiated by these radicals are always present. These chains derived free radical initiator lead to a partial loss of control over functionality and topology (Scheme 2c).

This paper describes a new method for formation of an active catalyst, a procedure for preparing an "activator generated by electron transfer" for ATRP (AGET ATRP), which overcomes those prior problems by using an electron transfer rather than organic radicals to reduce the higher oxidation state transition metal. Although many reducing agents can be applied for this in-situ reduction, in these studies, tin(II) 2-ethylhexanoate ($Sn(EH)_2$) was used to illustrate this concept (Scheme 2d). In this new system for activation the ATRP catalyst, the oxidized catalyst complex is reduced prior to normal initiation of the reaction from the added initiator molecule. This procedure has all benefits of normal ATRP (Scheme 2a) plus the benefits of adding a more stable catalyst complex to the reaction mixture. The use of oxidatively stable catalyst precursors can allow the more facile preparation, storage, and shipment of ATRP catalyst systems. The universal character of this approach was proved by applying the new activation/initiation process to a wide range of systems including styrene and octadecyl methacrylate polymerized with $CuCl_2$/dNbpy, methyl methacrylate and n-butyl acrylate polymerized by $CuCl_2$/PMDETA, and methyl acrylate using $CuCl_2/Me_6TREN$.

Since $Sn(EH)_2$ was used as a reducing agent for the catalyst precursor in an ATRP reaction, we sought to expand the utility of the concept and conduct a simultaneous copolymerization of octadecyl methacrylate and ϵ-caprolactone. $Sn(EH)_2$ was used simultaneously as the reductive agent for AGET ATRP and as a catalyst for ring-opening polymerization (ROP) of ϵ-caprolactone, allowing formation of block copolymer in a one step by a dual mechanism.

Experimental Section

Chemicals. Styrene (St) (Aldrich, 99%), methyl methacrylate (MMA) (Acros, 99%), n-butyl acrylate (nBA) (Acros 99+%), and methyl acrylate (MA), (Aldrich, 99%) were passed through a column filled with neutral alumina, dried over calcium hydride, and distilled under reduced pressure. n-Octadecyl methacrylate (ODMA) (Polysciences Inc.,99%) was purified by dissolution in hexane and extraction four times with 5% aqueous NaOH. After drying the organic phase over magnesium sulfate, the solution was passed through neutral alumina, and the solvent was removed under reduced pressure. ϵ-Caprolactone (CL), (Aldrich, 99%) was dried over calcium hydride under nitrogen at 25 °C and distilled under reduced pressure just before use ($T_b = 74-76$ °C at 0.5−0.6 mmHg). 4,4′-Di-(5-nonyl)-2,2′-bipyridine (dNbpy),[46] tris(2-(dimethylamino)ethyl)amine (Me_6TREN),[42] and 1,1,1-tris(4-(2-bromoisobutyryloxy)phenyl)ethane (TBriBPE)[47] were synthesized following previously reported procedures. *N,N,N′,N″,N″*-Pentamethyldiethylenetriamine (PMDETA) (Aldrich, 99%), ethyl 2-bromoisobutyrate (EtBrIB) (Acros, 98%), copper(II) chloride (Acros, 99%), copper(II) bromide (Acros, 99%), tin(II) 2-ethylhexanoate ($Sn(EH)_2$) (Aldrich), anisole (Aldrich, 99%), diphenyl ether (Acros, 99%), 2-bromoisobutyryl bromide (Aldrich, 97%), ethylene glycol (Aldrich, anhydrous), and triethylamine (Fisher 99%) were used as received. Toluene (Fisher Scientific, 99.9%) was distilled over sodium and stored over molecular sieves. Copper(I) chloride (Acros, 95%) and copper(I) bromide (Acros, 98%) were washed with glacial acetic acid to remove any soluble oxidized species, filtered, washed with ethanol, and dried.

General Procedure for Normal ATRP of *n*-Butyl Acrylate. TBriBPE initiator (25 mg, 3.3×10^{-2} mmol), CuBr (14 mg, 9.9×10^{-2} mmol), and $CuBr_2$ (2.2 mg, 0.1×10^{-2} mmol) were added to a 25 mL Schlenk flask, and the flask was thoroughly purged by vacuum and flushed with nitrogen. Nitrogen-purged nBA (5.0 mL, 35 mmol) was added via syringe. A solution of PMDETA (21 μL, 9.9×10^{-2} mmol) in degassed anisole was added, and the mixture was stirred for 15 min in order to preform the CuCl/PMDETA and $CuBr_2$/PMDETA complexes. The flask was then transferred to a thermostated oil bath at 70 °C, and the initial kinetic sample was taken. Samples were removed at different time intervals during polymerization, and conversion and molecular weights were determined by GC and GPC, respectively. The polymerization was stopped ($M_{n,GPC} = 131\,400$, $M_w/M_n = 1.10$, conversion = 88%) by opening the flask and exposing the catalyst to air.

General Procedure for SR&NI ATRP of *n*-Butyl Acrylate. TBriBPE initiator (25 mg, 3.3×10^{-2} mmol), AIBN (8.7 mg, 5.3×10^{-2} mmol), and $CuBr_2$ (22 mg, 9.9×10^{-2} mmol) were added to a 25 mL Schlenk flask, and the flask was thoroughly purged by vacuum and then flushed with nitrogen. Degassed nBA (5.0 mL, 35 mmol) was added via syringe. A purged solution of PMDETA (21 μL, 9.9×10^{-2} mmol) in anisole was added, and the mixture was stirred for 15 min in order to preform the $CuBr_2$/PMDETA complex. The flask was then transferred to a thermostated oil bath at 70 °C, where decomposition of the AIBN formed the active CuBr/PMDETA complex and the initial kinetic sample was taken. Samples were removed at different time intervals during polymerization, and conversion and molecular weights were determined by GC and GPC, respectively. The polymerization was stopped ($M_{n,GPC} = 43\,700$, $M_w/M_n = 1.45$, conversion = 81%) by opening the flask and exposing the catalyst to air.

General Procedure for Activator Generated by Electron Transfer (AGET) for ATRP of *n*-Butyl Acrylate. TBriBPE initiator (25 mg, 3.3×10^{-2} mmol) and $CuBr_2$ (22 mg, 9.9×10^{-2} mmol) were added to a 25 mL Schlenk flask, and the flask was thoroughly purged by vacuum and then flushed with nitrogen. Nitrogen-purged nBA (5.0 mL, 35 mmol) was added via syringe followed by a purged solution of PMDETA (21 μL, 9.9×10^{-2} mmol) in anisole. $Sn(EH)_2$ (15 μL, 4.5×10^{-2} mmol) was added, and the mixture was stirred for 15 min in order to preform the CuBr/PMDETA complex. The flask was then transferred to a thermostated oil bath at 70 °C, and the initial kinetic sample was taken. Samples were removed at different time intervals during polymerization, and conversion and molecular weights were determined by GC and GPC, respectively. The polymerization was stopped ($M_{n,GPC} = 86\,500$, $M_w/M_n = 1.09$, conversion = 63%) by opening the flask and exposing the catalyst to air.

General Procedure for AGET ATRP of Styrene. Styrene (5.0 mL, 44 mmol), $CuCl_2$ (29.3 mg, 21.8×10^{-2} mmol), and dNbipy (178 mg, 43.6×10^{-2} mmol) were placed in a 25 mL Schlenk flask and bubbled with nitrogen for 15 min. $Sn(EH)_2$ (32 μL, 9.8×10^{-2} mmol) and a purged solution of EtBrIB (29.7 μL, 20.3×10^{-2} mmol) in toluene were added, and the sealed flask was placed in thermostated oil bath at

110 °C. The polymerization was stopped ($M_{n,GPC}$ = 14 000, M_w/M_n = 1.37, conversion = 83%) by opening the flask and exposing the catalyst to air.

The same procedure was applied for the polymerization of octadecyl methacrylate, except that a temperature of T = 60 °C was employed.

General Procedure for AGET ATRP of Methyl Methacrylate. MMA (4.0 mL, 37 mmol) and $CuCl_2$ (25.2 mg, 18.7 × 10^{-2} mmol) were added to a 25 mL Schlenk flask, and the mixture was bubbled with nitrogen for 15 min. A purged solution of PMDETA (39.1 μL, 18.7 × 10^{-2} mmol) in anisole was added, and the mixture was stirred. $Sn(EH)_2$ (27 μL, 8.4 × 10^{-2} mmol) and a purged solution of EtBrIB (27.4 μL, 18.7 × 10^{-2} mmol) in anisole were added, and the sealed flask was heated in thermostated oil bath at 90 °C. The polymerization was stopped ($M_{n,GPC}$ = 23 000, M_w/M_n = 1.45, conversion = 79%) by opening the flask and exposing the catalyst to air.

The same procedure was applied for polymerization of methyl acrylate, except that Me_6TREN was used as ligand and toluene as solvent and the temperature was held at 25 °C.

Procedure for Free Radical Polymerization of Methyl Acrylate. AIBN (5.4 mg, 3.3 × 10^{-2} mmol) was placed in a 25 mL Schlenk flask. The flask was thoroughly purged by flushing with nitrogen, and then degassed MA (0.6 mL, 6.4 mmol) was added via degassed syringes. Next, $Sn(EH)_2$ (4.0 μL, 1.2 × 10^{-2} mmol) in a purged solution of toluene (4.0 mL) was added, and the sealed flask was placed in thermostated oil bath at 60 °C. The polymerization was stopped ($M_{n,GPC}$ = 64 900, M_w/M_n = 1.61, conversion = 84%) after 25 h.

Synthesis of Diblock Copolymer PODMA-*b*-PMMA by AGET ATRP. In a 25 mL Schlenk flask, PODMA macroinitiator (M_w = 13 800, PDI = 1.10) (3.0 g, 0.2 mmol) and $CuCl_2$ (31 mg, 7.3 × 10^{-5} mol) were dissolved in monomer (MMA, 9.4 g, 0.1 mol) and bubbled with nitrogen for 15 min. A purged solution of PMDETA (48 μL, 0.23 mmol) in toluene (5 mL) was added, and the mixture was stirred. $Sn(EH)_2$ (34 μL, 0.1 mmol) in toluene (4 mL) was added next, and an initial sample was taken. Flask was placed in a thermostated oil bath at 90 °C and stirred. The polymerization was stopped ($M_{n,GPC}$ = 38 100, M_w/M_n = 1.09, conversion = 58%) by opening the flask and exposing the catalyst to air.

Synthesis of 2-Hydroxyethyl 2-Bromoisobutyrate (HEBI).[48] 2-Bromoisobutyryl bromide (2.7 mL, 22 mmol) was added dropwise over 2 h to a cold solution of ethylene glycol (28.2 mL, 496 mmol) and triethylamine (2.9 mL, 22 mmol) at 0 °C. The reaction was held at 0 °C for another 2 h and then heated to 40 °C for 5 h. The reaction mixture was cooled, added to 500 mL of water, and extracted with chloroform three times. The combined chloroform layers were washed successively with diluted HCl, saturated $NaHCO_3$, and water. The organic layer was dried over anhydrous magnesium sulfate and evaporated to dryness to provide the product. The product was vacuum-distilled (yield 70%) and characterized by ^{1}H NMR spectroscopy ($CDCl_3$): $(\mathbf{CH_3})_2{-}CBr{-}$ δ = 1.80 (s, 6H), $-CH_2-\mathbf{CH_2}-OH$ δ = 3.70 (t, 2H), $-\mathbf{CH_2}-CH_2-OH$ δ = 4.15 (t, 2H).

Simultaneous Copolymerization of ϵ-Caprolactone (CL) and Octadecyl Methacrylate (ODMA). CL (4.0 g, 35 mmol) and ODMA (4.0 g, 12 mmol) were added to a 25 mL Schlenk flask, and the mixture bubbled with nitrogen for 15 min. dNbpy (164 mg, 0.40 mmol) and $CuCl_2$ (52 mg, 0.4 mmol) were dissolved in toluene (2 mL) in a 10 mL round-bottom flask and transferred via syringe to the Schlenk flask. $Sn(EH)_2$ (78 μL, 0.3 mmol) and 2-hydroxyethyl 2-bromoisobutyrate (82 mg, 0.4 mmol) were added, and the flask was placed in a thermostated oil bath at 90 °C and stirred. The polymerization was stopped($M_{n,GPC}$ = 31 500, M_w/M_n = 1.22, conversion_{CL} = 63%, conversion_{ODMA} = 96%) after 17 h by exposure to air, diluted with THF, precipitated into cold methanol, and dried under high vacuum.

Analysis. Molecular weight and polydispersity were determined by gel permeation chromatography (GPC). The GPC was conducted with a Waters 515 pump and Waters 410 differential refractometer using PSS columns (Styrogel 10^5, 10^3, 10^2 Å) in THF as an eluent at 35 °C and at a flow rate of 1 mL/min. Linear poly(methyl methacrylate) and polystyrene standards were used for calibration. Conversion of ODMA was also determined using GPC by following the decrease of the monomer peak area relative to the peak area of the solvent (Figure 1). Conversion of all other monomers was determined using a Shimadzu GC 14-A gas chromatograph equipped with a FID detector using a J&W Scientific 30 m DB WAX Megabore column and anisole or toluene as an internal standard. Injector and detector temperatures were kept constant at 250 °C. Analysis was carried out isothermally at 40 °C for 2 min followed by an increase of temperature to 160 °C at a heating rate of 40 °C/min and holding at 160 °C for 3 min. Conversion was calculated by detecting the decrease of the monomer peak area relative to the peak areas of the standards. ^{1}H NMR spectroscopy was performed using a Bruker 300 MHz instrument with $CDCl_3$ as a solvent.

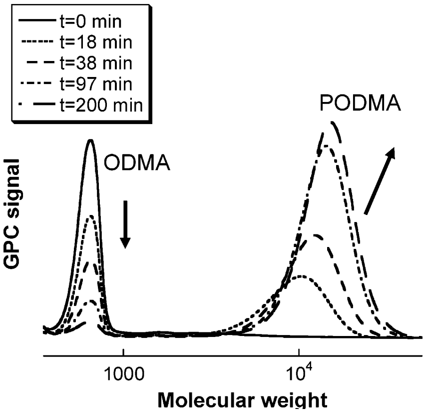
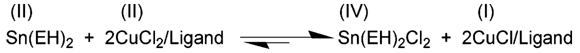


Figure 1. GPC traces of monomer ODMA and PODMA. Conversion of ODMA was calculated by detecting decrease of the monomer peak area.

Scheme 3. Reduction of Cu(II) to Cu(I) by Tin(II) 2-Ethylhexanoate



$$\overset{(II)}{Sn(EH)_2} + \overset{(II)}{2CuCl_2/Ligand} \rightleftharpoons \overset{(IV)}{Sn(EH)_2Cl_2} + \overset{(I)}{2CuCl/Ligand}$$

Results and Discussion

A new method was developed for activation of the catalyst complex to overcome the problem of unavoidable formation of small amount of homopolymers previously reported with reverse and SN&RI ATRP. This new procedure has been termed "activator generated by electron transfer" ATRP (AGET ATRP) since the ATRP activator is formed from a stable catalyst precursor, reduced by an agent which does not form radicals capable of initiation. This novel procedure has all the benefits of a normal ATRP process plus the benefit of being able to add the catalyst complex in its more stable higher oxidation state to the reaction mixture. One requirement for the catalyst activation is that the oxidatively stable transition metal complex should be quickly and efficiently reduced to the desired degree by a nonradical forming reducing agent. If this condition is fulfilled, the reduction can be conducted in-situ. Tin(II) 2-ethylhexanoate ($Sn(EH)_2$) is one of the several possible reducing agents that fulfills these requirements. $Sn(EH)_2$ can reduce Cu(II) to Cu(I), as shown by Scheme 3. To demonstrate the universality of AGET ATRP using $Sn(EH)_2$ as a reducing agent, different monomer/catalyst precursor systems were studied: *n*-butyl acrylate and methyl methacrylate with $CuBr_2$/PMDETA, styrene and octadecyl methacrylate using $CuCl_2$/dNbpy, and methyl acrylate with $CuCl_2/Me_6TREN$.

Comparison of Different Procedures for the Polymerization of *n*-Butyl Acrylate Using a Trifunctional Initiator. To demonstrate the prime ad-

Table 1. Experimental Conditions and Properties of P*n*BA Prepared by Different ATRP Methods[a]

	ATRP method	TBriBPE/Cu(I)/Cu(II)/PMDETA/AIBN/Sn(EH)$_2$	time (min)	conv (%)	$M_{n,theo}$[b]	$M_{n,GPC}$	M_w/M_n
1	normal	1/3/0.3/3/–/–	1147	88	118 800	131 400	1.10
2	SR&NI	1/–/3/3/1.6/–	1170	81	109 350	43 700	1.45
3	AGET	1/–/3/3/–/1.4	1150	63	85 050	86 500	1.09

[a] $[nBA]_0/[TBriBPE]_0 = 1050$; $[nBA]_0 = 7.01$ M; $T = 70$ °C, anisole used as a GC standard. [b] $M_{n,theo} = ([M]_0/[EtBrIB]_0) \times$ conversion.

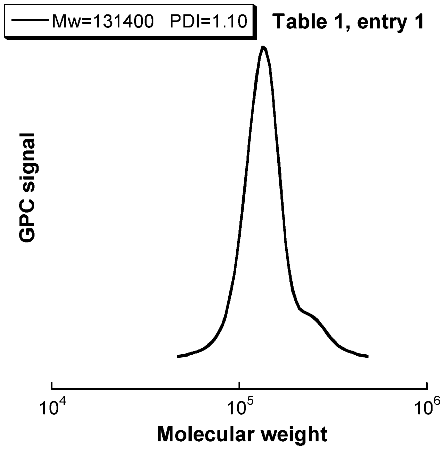
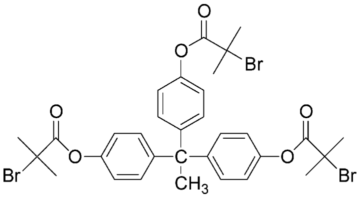


Figure 2. GPC result for a normal ATRP of *n*BA initiated by a trifunctional initiator. Experimental conditions: *n*BA/TBriBPE/Cu(I)/Cu(II)/PMDETA = 1050/1/3/0.3/3; $[nBA]_0 = 7.01$ M; $T = 70$ °C, anisole used as a GC standard.

Chart 1. Structure of Trifunctional Initiator 1,1,1-Tris(4-(2-bromoisobutyryloxy)phenyl)ethane (TBriBPE) Used in Polymerization of *n*BA



vantage of AGET ATRP, three different procedures were used for the polymerizations of *n*BA: a normal ATRP, a SN&RI ATRP, and the new AGET ATRP. The conditions and results for these reactions are shown in Table 1. A trifunctional initiator, TBriBPE (Chart 1), was used in each case to clearly show the presence of any nonfunctionalized homopolymers in a GPC analysis of the products. During normal ATRP (Table 1, entry 1), the reaction was well controlled and a low polydispersity index, PDI, was achieved ($M_w/M_n = 1.1$). The high molecular weight shoulder in the GPC traces (Figure 2) is caused by a coupling reaction commonly observed at high monomer conversion (>90%).[44] Figure 3a shows the GPC traces for the polymers formed when *n*BA was polymerized using SR&NI ATRP with AIBN (Table 1, entry 2). A clear bimodal distribution is observed. The low molecular weight peak is due to the presence of linear homopolymer originally from AIBN, and the high molecular weight peak is attributed to triarm star polymer. In the next reaction (Table 1, entry 3) the same conditions were used, but AIBN was replaced by Sn(EH)$_2$, creating the conditions for a AGET ATRP. The results, in Table 1 (entry 3) and Figure 3b, show that a pure star polymer was obtained without any linear polymer byproduct. The reaction was also well controlled, and a low PDI (1.09) was achieved. It can be concluded that the Cu(II) complex added to the reaction mixture was efficiently reduced to Cu(I) by reaction with tin(II) 2-ethylhexanoate in a nonradical process.

Effect of Sn(EH)$_2$/Cu(II) Ratio on AGET ATRP of ODMA. In the first series of runs ODMA was polymerized by both normal and AGET ATRP employing different levels of a reducing agent. In the case of the AGET ATRP dNbpy/CuCl$_2$ was added to the reaction as the precursor of active complex, and EtBrIB was added as the initiator. The conditions and results of these polymerizations are shown in Table 2. During normal ATRP (Table 2, entry 1), the reaction was well controlled, as evidenced by the GPC traces being monomodal, and a polymer with a low polydispersity was formed (PDI = 1.2). Next, ODMA was polymerized using

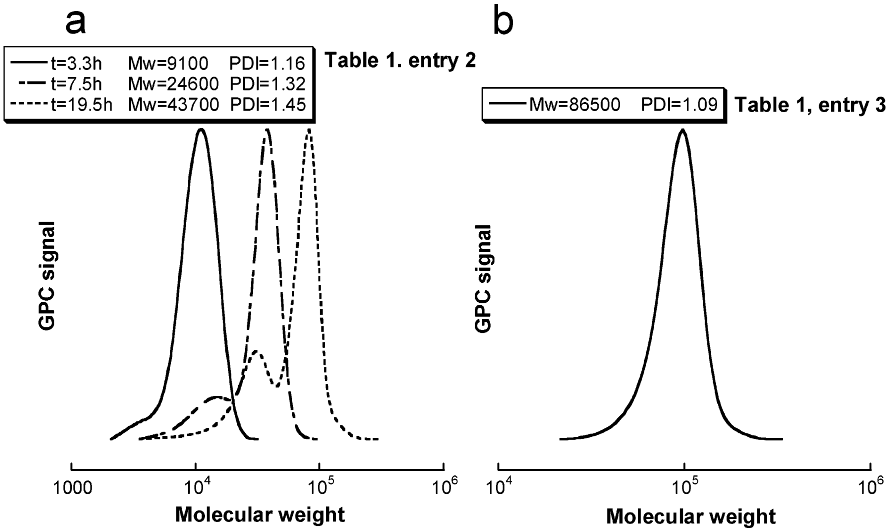


Figure 3. Evolution of molecular weight followed by GPC during SR&NI ATRP (a) vs AGET ATRP (b) for *n*BA polymerization initiated by trifunctional initiator. Experimental conditions: (a) nBA/TBriBPE/Cu(I)/Cu(II)/PMDETA/AIBN/Sn(EH)$_2$ = 1050/1/–/3/3/1.6/– and (b) nBA/TBriBPE/Cu(I)/Cu(II)/PMDETA/AIBN/Sn(EH)$_2$ = 1050/1/–/3/3/–/1.4; $[nBA]_0 = 7.01$ M; $T = 70$ °C, anisole used as a GC standard.

Table 2. Experimental Conditions and Properties of PODMA Prepared by Different ATRP Methods[a]

	ATRP method	EtBrIB/Cu(I)/Cu(II)/dNbipy/Sn(EH)$_2$	time (min)	conv (%)	$M_{n,theo}$[b]	$M_{n,GPC}$	M_w/M_n
1	normal	1/1/0.05/2/–	1080	95	19 000	19 600	1.23
2	AGET	1/–/1/2/2	1020	92	18 400	18 300	1.45
3	AGET	1/–/1/2/0.9	1125	98	19 600	22 800	1.34
4	AGET	1/–/1/2/0.45	1100	66	13 200	13 800	1.10
5	Sn(EH)$_2$ alone	1/–/–/–/0.45	960	11	2 200	3 100 000	1.5

[a] $[ODMA]_0/[EtBrIB]_0 = 60$; $[ODMA]_0 = 0.85$ M; $T = 60$ °C, in toluene (2 vol equiv vs monomer). [b] $M_{n,theo} = ([M]_0/[EtBrIB]_0) \times$ conversion.

Table 3. Experimental Conditions and Properties of PMMA Prepared by Different ATRP Methods[a]

	ATRP method	EtBrIB/Cu(I)/Cu(II)/PMDETA/Sn(EH)$_2$	time (min)	conv (%)	$M_{n,theo}$[b]	$M_{n,GPC}$	M_w/M_n
1	normal	1/1/–/1/–	180	88	17 600	27 000	1.29
2	AGET	1/–/1/1/2	70	77	15 400	23 000	1.99
3	AGET	1/–/1/1/0.45	145	79	15 800	23 000	1.45
4	AGET	1/–/0.4/0.4/0.18	360	78	15 600	14 200	1.10
5	AGET	1/–/0.2/0.2/0.09	360	52	10 400	9 600	1.12

[a] $[MMA]_0/[EtBrIB]_0 = 200$; $[MMA]_0 = 6.22$ M; $T = 90$ °C, in anisole (0.5 vol equiv vs monomer). [b] $M_{n,theo} = ([M]_0/[EtBrIB]_0) \times$ conversion.

AGET ATRP. The amounts of reducing agent, Sn(EH)$_2$, were varied to define conditions for better control of the polymerization. The amounts of Sn(EH)$_2$ used were 2.00, 0.90, and 0.45 equiv vs Cu(II). The best result was obtained when 0.45 equiv of Sn(EH)$_2$ was used (Table 2, entry 4). In this case, assuming that the equilibrium represented by Scheme 3 is strongly shifted to the products, not all of the Cu(II) will be reduced to Cu(I), and as a result of the remaining fraction of Cu(II) (~10%), better control over the reaction is possible. In all reactions polymers with monomodal molecular weight distributions were observed. The evolution of molecular weights for AGET ATRP of ODMA is shown by the GPC traces in Figure 4.

Since Sn(EH)$_2$ can reduce Cu(II) to Cu(I) species, it can be also considered as ATRP activator. Thus, ATRP, of ODMA was attempted in the presence of EtBrIB and Sn(EH)$_2$, alone, without any Cu species (Table 2, entry 5). Very low conversion (11%) and extremely low initiator efficiency were observed (0.07%). The very high molecular weight of PODMA suggests that although Sn(EH)$_2$ is a powerful reducing agent for Cu species, it is a poor ATRP activator. This indicates that the reduction plausibly occurs via outer-sphere electron transfer rather than via inner-sphere electron transfer (i.e., halogen atom transfer).

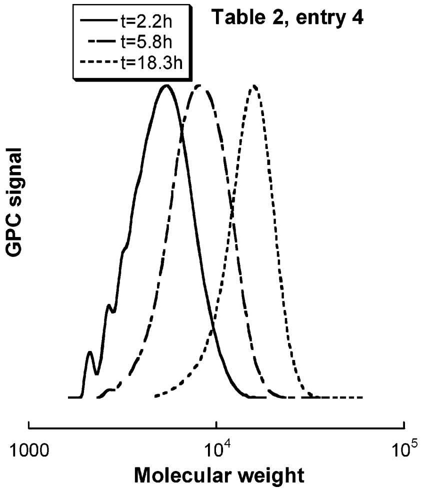


Figure 4. Evolution of MW GPC traces during AGET ATRP of ODMA. Experimental conditions: ODMA/EtBrIB/Cu(I)/Cu(II)/dNbipy/Sn(EH)$_2$ = 60/1/–/1/2/0.45; $[ODMA]_0 = 0.85$ M; $T = 60$ °C, in toluene (2 vol equiv vs monomer).

Effect of Initiator/Cu(II) Ratio on AGET ATRP of MMA. MMA was polymerized by normal and AGET ATRP employing different initiator to Cu(II) ratios. In this case PMDETA/CuCl$_2$ was used as the precursor of the active complex and EtBrIB as the initiator. The conditions and results for the reactions are shown in Table 3. During normal ATRP (Table 3, entry 1), the reaction was relatively well controlled as evidenced by the monomodal molecular weight distribution and low PDI (1.34). The amounts of Sn(EH)$_2$ used in the AGET ATRP were 2.00 and 0.45 equiv vs Cu(II). Similar to the polymerization of ODMA, better results were obtained when 0.45 equiv of Sn(EH)$_2$ was used; however, the final polymer synthesized using AGET ATRP had a higher PDI than the polymer synthesized using normal ATRP. Nonetheless, the polymerizations were controlled as evidenced by the evolution of the monomodal GPC traces for AGET ATRP of MMA. In next reactions (Table 3, entries 4 and 5) the amounts of Cu(II) were decreased from 1 to 0.4 and 0.2 equiv vs initiator, since Cu(I)/PMDETA is a relatively active catalyst for (meth)acrylates.[49,50] In both cases better results were obtained; monomodal molecular weight distribution as shown in Figure 5 and low PDI (1.10 and 1.12) were observed. This also demonstrates that concentration of

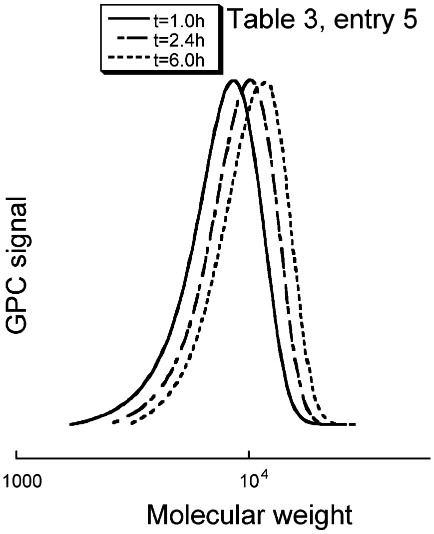


Figure 5. Evolution of MW GPC traces during AGET ATRP of MMA. Experimental conditions: MMA/EtBrIB/Cu(I)/Cu(II)/PMDETA/Sn(EH)$_2$ = 200/1/–/0.2/0.2/0.09; $[MMA]_0 = 6.22$ M; $T = 90$ °C, in anisole (0.5 vol equiv vs monomer).

Table 4. Experimental Conditions and Properties of PS Prepared by Different ATRP Methods[a]

	ATRP method	EtBrIB/Cu(I)/Cu(II)/dNbipy/Sn(EH)$_2$	time (min)	conv (%)	$M_{n, theo}$[b]	$M_{n, GPC}$	M_w/M_n
1	normal	1/1/–/2/–	1580	95	19 000	15 600	1.27
2	AGET	1/–/1/2/0.45	420	83	17 200	14 000	1.37
3	AGET	1/–/0.4/0.8/0.18	420	64	12 800	8 500	1.22

[a] $[St]_0/[EtBrIB]_0 = 200$; $[St]_0 = 8.72$ M; $T = 110$ °C, toluene used as a GC standard. [b] $M_{n,theo} = ([M]_0/[EtBrIB]_0) \times$ conversion.

Table 5. Experimental Conditions and Properties of PMA Prepared by Different ATRP Methods[a]

	ATRP method	EtBrIB/Cu(I)/Cu(II)/Me$_6$TREN/Sn(EH)$_2$	time (min)	conv (%)	$M_{n,theo}$[b]	$M_{n,GPC}$	M_w/M_n
1	normal	1/1/0/1/–	1110	96	19 200	18 000	1.30
2	AGET	1/–/1/1/0.45	2760	61	12 100	13 100	1.16

[a] $[MA]_0/[EtBrIB]_0 = 230$; $[MA]_0 = 5.37$ M; $T = 25$ °C, in toluene (1 vol equiv vs monomer). [b] $M_{n,theo} = ([M]_0/[EtBrIB]_0) \times$ conversion.

Sn/Cu(II) can be varied independently of the initiator concentration to optimize the control of the reaction.

AGET ATRP of Styrene (St) and Methyl Acrylate (MA). The universal character of AGET ATRP was investigated by polymerization of other types of monomers with different catalyst systems: styrene with CuCl$_2$/dNbpy and methyl acrylate using CuCl$_2$/Me$_6$TREN. In each case, the product formed in a normal ATRP was compared to the product formed using AGET ATRP.

For the polymerization of styrene, dNbpy/CuCl$_2$ was added to the reaction as the oxidatively stable precursor of an active catalyst complex. The conditions and results for normal and AGET ATRP are shown in Table 4. All reactions were well controlled with experimental molecular weights being close to theoretical values. However, a slightly higher PDI (1.37) was observed for AGET ATRP when used amount of Cu(II) vs initiator was 1:1 (Table 4, entry 2) although the final GPC traces remained monomodal. Decreasing the ratio of Cu(II)/initiator to 0.3 in AGET ATRP (Table 4, entry 3) resulted in better controlled reaction and a final polymer with lower PDI (1.22) (Figure 6).

MA was also polymerized by both normal and AGET ATRP; in this case Me$_6$TREN/CuCl$_2$ was used to generate the active complex, and EtBrIB was added as the initiator. The conditions used for the reactions and the results are shown in Table 5. Figure 7 shows the kinetic plot for the reactions, and it can be seen that the normal ATRP was faster then the AGET ATRP. This is plausibly due to incomplete reduction of Cu(II) to Cu(I). The remaining Cu(II) slows down the reaction due to an increased rate of deactivation, and the final rate of the AGET polymerization is lower than normal ATRP, where pure Cu(I) was employed initially. To ensure the slower rate of polymerization was not due to interaction of Sn(EH)$_2$ with the monomer or growing polymer chain end, two conventional radical polymerization were performed, with and without Sn(EH)$_2$. The rates of both polymerizations were the same, indicating that AGET ATRP was slower than normal ATRP plausibly due to the difference in the concentration of Cu(II) for each system with the result that the AGET ATRP was better controlled and the final polymer had a lower PDI, due to efficient deactivation of growing species by Cu(II). The GPC traces showed monomodal distributions of molecu-

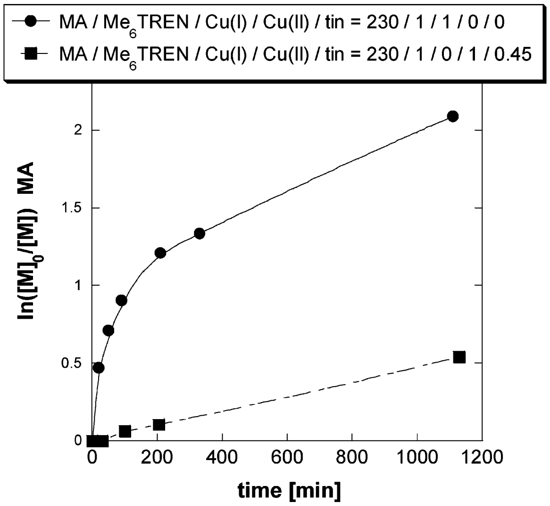


Figure 7. Kinetic plot for ATRP of MA. Experimental conditions: $[MA]_0 = 5.37$ M; $T = 25$ °C, in toluene (1 vol equiv vs monomer).

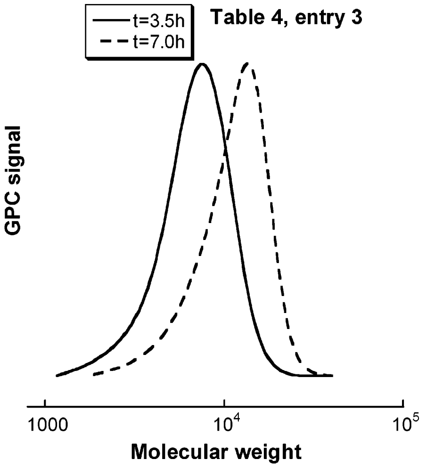


Figure 6. Evolution of MW GPC traces during AGET ATRP of St. Experimental conditions: St/EtBrIB/Cu(I)/Cu(II)/dNbipy/Sn(EH)$_2$ = 200/1/–/0.4/0.8/0.18; $[St]_0 = 8.72$ M; $T = 110$ °C, toluene used as a GC standard;

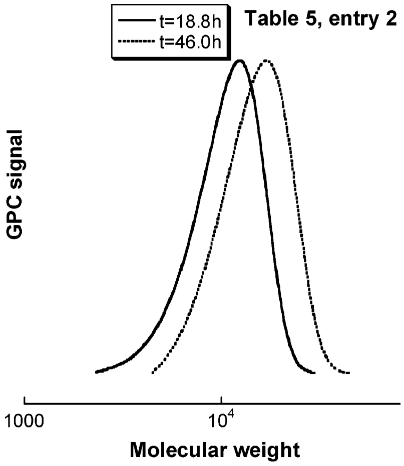


Figure 8. Evolution of MW GPC traces during AGET ATRP of MA. Experimental conditions: MA/EtBrIB/Cu(I)/Cu(II)/Me$_6$TREN/Sn(EH)$_2$ = 230/1/–/1/1/0.45; $[MA]_0 = 5.37$ M; $T = 25$ °C, in toluene (1 vol equiv vs monomer).

Table 6. Experimental Conditions and Properties of Block Copolymer PODMA-*b*-PMMA Prepared by Step Method Using AGET ATRP

		ATRP method	initiator/Cu(I)/Cu(II)/ligand/Sn(EH)$_2$	time (min)	conv (%)	$M_{n,\,theo}$[c]	$M_{n,\,GPC}$	M_w/M_n
1	PODMA[a]	AGET	1/−/1/2/0.45	1100	66	13 200	13 800	1.10
2	PODMA-*b*-PMMA[b]	AGET	1/−/1/1/0.45	120	58	37 200	38 100	1.09

[a] $[ODMA]_0/[EtBrIB]_0 = 60$; $[ODMA]_0 = 0.85$ M; $T = 60$ °C, in toluene (2 vol equiv vs monomer). [b] $[MMA]_0/[PODMA]_0 = 400$; $[MMA]_0 = 6.22$ M; $T = 90$ °C, in anisole (0.5 vol equiv vs monomer). [c] $M_{n,theo} = ([M]_0/[EtBrIB]_0) \times$ conversion.

Table 7. Experimental Conditions and Properties of Block Copolymer Prepared by Simultaneous Copolymerization of Octadecyl Methacrylate and ϵ-Caprolactone[a]

		solvent	T (°C)	time (min)	conv CL [%]	conv ODMA [%]	$M_{n,GPC}$	M_w/M_n	F_{CL}[b]	F_{ODMA}[b]
1	PCL-*b*-PODMA[a]	toluene	75	1020	0.63	0.96	31 500	1.22	0.30	0.70

[a] $[ODMA]_0:[CL]_0:[HEBI]_0:[Sn(EH)_2]_0:[CuCl_2]_0:[dNbipy_2]_0 = 30:85:1:\ 0.6:1:1$; $[ODMA]_0 = 1.25$ M. [b] Measured by ^{1}H NMR spectroscopy.

lar weights (Figure 8). These results are in agreement with the preceding studies of ATRP of MA in the presence of Me$_6$TREN.[42,51] The Me$_6$TREN ligand generates the most reducing copper complexes, and Sn(EH)$_2$ plausibly cannot reduce it completely to the Cu(I) state.[52,53]

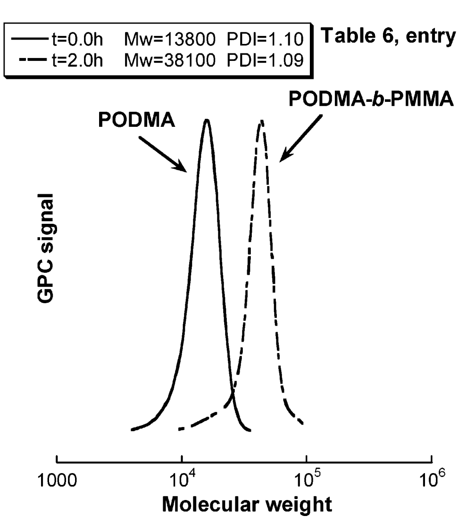


Figure 9. GPC traces after each step of synthesis of block copolymer PODMA-*b*-PMMA. Experimental conditions: PODMA: ODMA/EtBrIB/Cu(I)/Cu(II)/dNbipy/Sn(EH)$_2$ = 60/1/−/1/2/0.45; $[ODMA]_0 = 0.85$ M; $T = 60$ °C, in toluene (2 vol equiv vs monomer); PODMA-*b*-PMMA: MMA/PODMA/Cu(I)/Cu(II)/Me$_6$TREN/Sn(EH)$_2$ = 400/1/−/1/1/0.45; $[MMA]_0 = 6.22$ M; $T = 90$ °C, in anisole (0.5 vol equiv vs monomer).

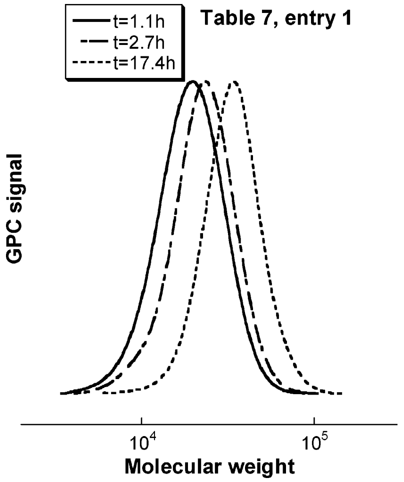


Figure 10. Evolution of MW GPC traces during simultaneous polymerization of ODMA and CL. Experimental conditions: ODMA/CL/HEBI/Sn(EH)$_2$/CuCl$_2$/dNbipy = 30:85:1: 0.6:1:1; $[ODMA]_0 = 1.25$ M; in toluene (1 vol equiv vs CL), $T = 75$ °C.

Preparation of a Block Copolymer by a Two-Step Method Using AGET ATRP. AGET ATRP was used in the two-step synthesis of block copolymer PODMA-*b*-PMMA. First, PODMA block was prepared using AGET ATRP and then used as a macroinitiator. Extension with MMA using AGET ATRP was very efficient. Table 6 shows the experimental conditions and properties of synthesized polymers. Figure 9 presents the SEC chromatograms recorded after each step. The reactions were well controlled, as evidenced by the GPC traces being monomodal, and final block copolymer with a narrow polydispersity was formed (PDI = 1.09).

Preparation of a Block Copolymer by Simultaneous Polymerization of Octadecyl Methacrylate and ϵ-Caprolactone. Sn(EH)$_2$ was concurrently used as a reducing agent for ATRP and as a catalyst for ring-opening polymerization (ROP), allowing copolymerization of octadecyl methacrylate and ϵ-caprolactone. In this case, each monomer should independently propagate via two different mechanisms (radical and pseudoanionic), forming a block copolymer. The results shown in Table 7 prove that the block copolymerization was successful. GPC traces showed monomodal distributions (Figure 10), and ^{1}H NMR spectra obtained after syn-

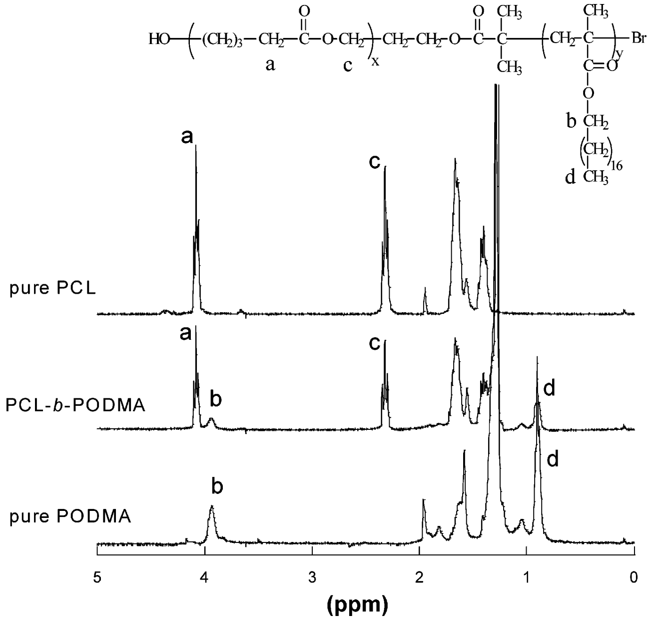


Figure 11. Comparison of ^{1}H NMR spectra of pure PCL, pure PODMA and PCL-*b*-PODMA block copolymer synthesized by simultaneous copolymerization. Experimental conditions: ODMA/CL/HEBI/Sn(EH)$_2$/CuCl$_2$/dNbipy = 30:85:1: 0.6:1:1; $[ODMA]_0 = 1.25$ M; in toluene (1 vol equiv vs CL), $T = 75$ °C.

thesis (Figure 11) indicate that a diblock copolymer was formed.

Conclusion. A new method for conducting ATRP was developed. The procedure used to generate activator relies on electron transfer rather than reduction by organic radicals; therefore, this method is called AGET ATRP. This novel procedure has all the benefits of a normal ATRP process combined with the additional benefit of adding the catalyst complex to the reaction mixture in its more stable higher oxidation state. Tin(II) 2-ethylhexanoate (Sn(EH)$_2$) was used as the reducing agent in this series of examples, demonstrating the benefits of the procedure.[54] The universal character of AGET ATRP was illustrated by applying the new process to the polymerization of several monomers with various catalyst precursors. The reduced in situ active catalyst complexes achieved controlled polymerization with a range of monomers that resulted in synthesis of well-defined polymers with controlled degree of polymerization and molecular weight distribution. In contrary to reverse ATRP, concentration of active catalyst in AGET ATRP can be change independently of the initiator to improve control of reactions. A successful synthesis of block copolymer using AGET ATRP was achieved. In addition, simultaneous block copolymerization of octadecyl methacrylate and ϵ-caprolactone was conducted with Sn(EH)$_2$ acting in a dual role of a reducing agent for AGET ATRP and a catalyst for ring-opening polymerization (ROP) in the same reaction vessel. The use of oxidatively stable catalyst precursors can potentially allow the more facile preparation, storage, and shipment of ATRP catalyst systems.

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