New Segmented Copolymers by Combination of Atom Transfer Radical Polymerization and Ring Opening Polymerization

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Summary: Atom transfer radical polymerization (ATRP) and ring opening polymerization (ROP) were combined to synthesize various polymers with various structures and composition. Poly(ε-caprolactone)-*b*-poly(*n*-octadecyl methacrylate), PCL-PODMA, was prepared using both sequential and simultaneous polymerization methods. Kinetic studies on the simultaneous process were performed to adjust the rate of both polymerizations. The influence of tin(II) 2-ethylhexanoate on ATRP was investigated, which led to development of new initiation methods for ATRP, i.e., activators (re)generated by electron transfer (AGET and ARGET). Additionally, block copolymers with two crystalizable blocks, poly(ε-caprolactone)-*b*-poly(*n*-butyl acrylate)-*b*-poly(*n*-octadecyl methacrylate), PCL-PBA-PODMA, block copolymers for potential surfactant applications poly(ε-caprolactone)-*b*-poly(*n*-octadecyl methacrylate-*co*-dimethylaminoethyl methacrylate), PCL-P(ODMA-*co*-DMAEMA), and a macromolecular brush, poly(hydroxyethyl methacrylate)-graft-poly(ε-caprolactone), PHEMA-*graft*-PCL, were prepared using combination of ATRP and ROP.

Keywords: ATRP; block copolymers; graft copolymers; reducing agent; ring-opening polymerization

Introduction

More and more attention has been attracted to well-defined copolymers with different composition and architecture due to their unique properties and suitability for several important applications, including thermoplastic elastomers, surfactants for colloidal systems, impact resistant materials, compatibilizers for immiscible polymer blends or carriers for delivery of bioactive compounds. Generally, simple block copolymers as well as polymers with more complex topologies are prepared by the sequential polymerization of two different monomers, using the same chemistry e.g. controlled/living radical polymerization (CRP).[1,2]

Among CRP methods, the most studied and promising are: nitroxide mediated polymerization (NMP)[3], atom transfer radical polymerization (ATRP)[4–6] and degenerative transfer with alkyl iodides[7] or reversible addition-fragmentation transfer polymerization (RAFT)[8]. ATRP has attracted significant attention since it not only allows controlled polymerization of wide range of vinyl monomers under mild conditions but also allows preparation of copolymers with various topologies, compositions and functionalities.

While one polymerization technique is a successful approach for the preparation of different types of copolymers, it still remains difficult and constraining to synthesize copolymers using monomers which polymerize by fundamentally different mechanisms, e.g. ATRP and ring opening polymerization (ROP). ROP is successful for controlled synthesis of aliphatic polyesters[9–11] such as polylactide, polyglycolide, polymandelide,

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polyvalerolactone or poly(ε-caprolactone) and can be combined with CRP methods[12,13]. The main strategies for combination of CRP and ROP in the synthesis of diblock copolymers are shown on Scheme 1.

In the first approach (A), a monofunctional initiator is used but preparation of the block copolymer involves a multistep process. After polymerization of the first monomer, a transformation of the functional group has to be accomplished, so that polymerization of a second monomer via a different mechanism maybe possible. In the second approach (B), which is a two-step process, a difunctional initiator is used. One initiating group can initiate a polymerization without interfering with the second initiating group, leading to synthesis of an intermediate macroinititor. It can be sequentially chain extended with a second monomer via a different polymerization mechanism. In last approach (C), the block copolymer is prepared in a one step process without requiring any intermediate steps, such as functionalization reactions or recovery of macroinititor.

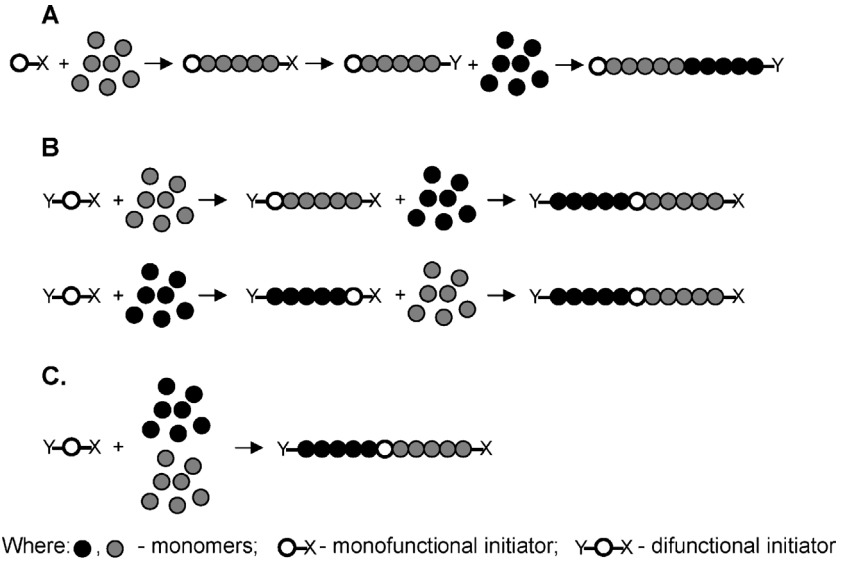
Although, the simultaneous polymerization strategy leads directly to block copolymers, the two polymerization mechanisms must be compatible and tolerant of one another, as well as of the monomers, the reaction temperature, etc. In most reported cases, CRP and ROP were studied independently for preparing well-defined copolymers. However, both techniques can be combined for synthesizing well-defined architectures using either a sequential approach[12–15] or a simultaneous polymerization by two mechanisms[16–21].

In this paper we report on the synthesis of different types of copolymers using a combination of ATRP and ROP while employing different synthetic strategies.

Experimental

Materials

Monomers: ε-Caprolactone (CL), (Aldrich, 99%) was dried over calcium hydride under nitrogen at 25 °C, distilled under reduced pressure and stored over molecular sieves.



Scheme 1.
General strategies for combination of CRP and ROP: (A) a three step method using a monofunctional initiator and transformation of functionality; (B) a two step method using a difunctional initiator; (C) a one step method using a difunctional initiator.

Styrene (St) (Aldrich, 99%) and *n*-butyl acrylate (BA) (Acros 99+%) were passed through a column filled with neutral alumina, dried over calcium hydride, and distilled under reduced pressure. Dimethylaminoethyl methacrylate (DMAEMA), (Aldrich, 99%) was passed through a column filled with neutral alumina, just before use. *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. Solvents: anisole (Aldrich, 99%), diphenylether (Acros, 99%), dimethylformamide (Acros, extra dry) were used as received. Toluene (Fisher Scientific, 99.9%) was distilled over sodium and stored over molecular sieves. Initiators and catalysts: copper(I) chloride (Acros, 95%) was washed with glacial acetic acid in order to remove any soluble oxidized species, filtered, washed with ethanol and dried. Tris(2-(dimethylamino)-ethyl)amine (Me_6TREN)[22], 4,4′-Di-(5-nonyl)-2, 2′-bipyridine (dNbpy)[23], 2-hydroxyethyl 2-bromoisobutyrate (HEBI)[24] were synthesized following previously reported procedures. Ethyl 2-bromoisobutyrate (EtBrIB) (Acros, 98%), Copper(II) chloride (Acros, 99%), tin(II) 2-ethylhexanoate ($Sn(EH)_2$) (Aldrich) were used as received.

Analytical Techniques

Molecular weight and polydispersity were determined by gel permeation chromatography (GPC) equipped with Waters 515 pump and Waters 410 differential refractometer. GPC was performed using PSS columns (Styrogel 10^5, 10^3, 10^2 Å) in THF as an eluent (flow rate: 1 mL/min). Linear poly(methyl methacrylate) and polystyrene standards were used for calibration. Conversion of ODMA was determined using GPC by detecting the decrease of the monomer peak area. GPC chromatograms were normalized to the peak intensity of diphenyl ether or toluene, used as an internal standard. Conversion of 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. ^{1}H-NMR measurement was performed using Bruker 300 MHz instrument with $CDCl_3$ as a solvent.

Ring Opening Polymerization (ROP) of ε-Caprolactone (CL), $DP_n = 50$

A typical experimental procedure for polymerization was as follows. A 25 mL round bottom flask, was degassed and filled with nitrogen then a measured amount of degassed monomer (CL, 4g, 3.50×10^{-2} mol) and toluene (4 mL, 1 vol. eq. vs. CL) were placed in the flask. Next, tin(II) ethylhexanoate (4 mg, 0.1 w% vs. CL) and 2-hydroxyethyl 2-bromoisobutyrate (148 mg, 7.01×10^{-4} mol) were added. The mixture was stirred for 22 hours at 90 °C, exposed to air, diluted with THF and precipitated into cold methanol. Polymer was dried under high vacuum.

Extension of Poly(ε-Caprolactone) (PCL) with *n*-Octadecyl Methacrylate (ODMA), $DP_n = 40$

PCL ($M_{n,appar.} = 8.3 \times 10^3$; $M_w/M_n = 1.22$) (1.1 g; 0.13 mmol) and (ODMA, 1.80 g, 5.32 mmol) were added to a 25 mL Schlenk flask and the resulting solution was bubbled with nitrogen for 15 minutes. dNbpy (108 mg, 0.27 mmol), CuCl (13 mg, 0.13 mmol) and $CuCl_2$ (1 mg, 6.6×10^{-3} mmol) were dissolved in degassed diphenylether (2 mL) in a 10 ml round bottom flask and transferred via degassed syringe to the Schlenk flask. An initial sample was taken and the flask was placed in a thermostated oil bath at 70 °C and stirred. The polymerization was stopped after 3 hours, exposed to air, diluted with THF, filtered through a neutral Al_2O_3 and precipitated by addition to cold methanol. The solid polymer was dried under high vacuum.

Simultaneous Copolymerization of ε-Caprolactone (CL) and *n*-Octadecyl Methacrylate (ODMA)

CL (4.0 g; 35.0 mmol) and ODMA (4.0 g, 11.8 mmol) were placed in a 25 mL Schlenk

flask and bubbled with nitrogen for 15 minutes. dNbpy (163.5 mg, 0.4 mmol) and CuCl (39.6 mg, 0.4 mmol) were added to a 10 ml round bottom flask and dissolved in degassed toluene (2 mL) and the resulting solution transfered via degassed syringe to the Schlenk flask. Tin(II) ethylhexanoate (40 mg, 1 w% vs. CL) and 2-hydroxyethyl 2-bromoisobutyrate (81.8 mg, 0.4 mmol) were added next and the flask was placed in a thermostated oil bath at 90 °C and stirred. Samples were taken out from the flask at timed intervals, passed through an alumina, and analyzed by GC and GPC. The polymerization was stopped after 17 hours, exposed to air, diluted with THF and precipitated into cold methanol. Polymer was dried under high vacuum.

Results and Discussion

Preparation of a Diblock Copolymer poly(ε-Caprolactone)-*b*-poly(*n*-Octadecyl Methacrylate), PCL-PODMA, Using Different Synthetic Strategies

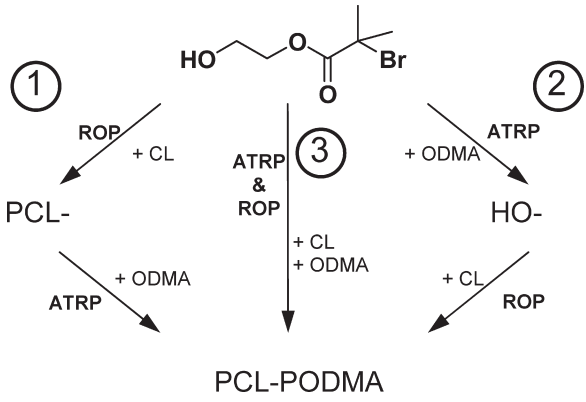
The strategies for synthesis of PCL-PODMA block copolymer using a difunctional initiator are shown in Scheme 2. In our studies we investigated pathways 1 and 3.

Preparation of Diblock Copolymer PCL-PODMA Using the Two Step Method

A sequential approach was first investigated for the synthesis of the diblock copolymer (Pathway 1). First, a well-defined PCL block was successfully prepared by ROP and next chain extended with an ODMA block via ATRP. Figure 1 presents the SEC chromatograms recorded after each step. The small shoulder on the GPC traces after the first step indicates the presence of a small amount of non-functionalized homopoly(ε-caprolactone) initiated by the traces of moisture. The chain extension with ODMA was successful. SEC chromatograms and the ^{1}H NMR spectra obtained after each step of the synthesis confirmed that the copolymer was efficiently prepared using Pathway 1.

Preparation of a Diblock Copolymer, PCL-PODMA, Using a Simultaneous Method

Next, synthesis via a simultaneous polymerization approach was investigated (Pathway 3). In this case, the polymer chain should grow independently via two different mechanisms (radical and pseudoanionic). The results from ^{1}H NMR and GPC traces of the copolymer show monomodal distribution of molecular weight (Figure 2a) prove that this reaction was also successful. However, further analysis by 2D-chromatography revealed co-existence of two different species (Figure 2b). The two areas 1 and 2 on 2D-chromatogram represents respectively the main product, the block copolymer PCL-PODMA and homopolymer, PCL, probably initiated by



Scheme 2.
Different synthetic pathways for preparation of PCL-PODMA.

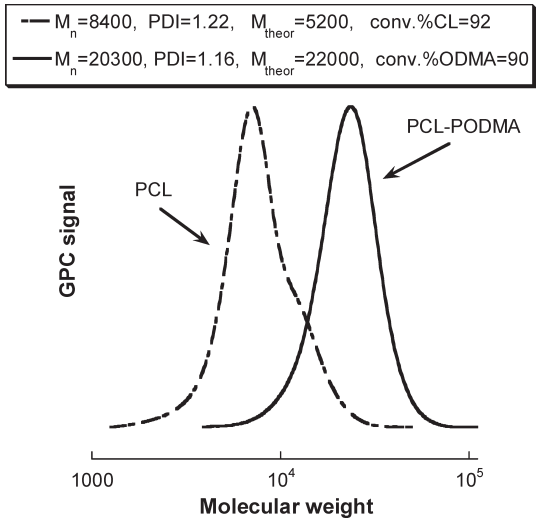


Figure 1.
GPC traces after each step of the synthesis of PCL-PODMA via a two step process (Pathway 1). Experimental conditions for the first step: CL/HEBI/$Sn(EH)_2$ = 50/1/0.05; $[CL]_0$ = 4.42 M, T = 75 °C, in toluene (1 volume equivalents vs. CL); for the second step: ODMA/PCL/CuCl/$CuCl_2$/dNbipy/ = 40/1/1/0.05/2; $[ODMA]_0$ = 1.37 M, T = 70 °C, in diphenylether (1 volume equivalents vs. monomer).

the traces of moisture. These results show that ^{1}H NMR and GPC analysis cannot provide full information on the structure of synthesized material via the simultaneous method and that 2D-chromatography is needed to confirm the purity of the final block copolymer. The detailed study of purity of the copolymers synthesized via step or simultaneous method, by 2D-chromatography and gradient elution chromatography, will be presented in another report.

Figure 3a presents the kinetic plot for the simultaneous polymerization of

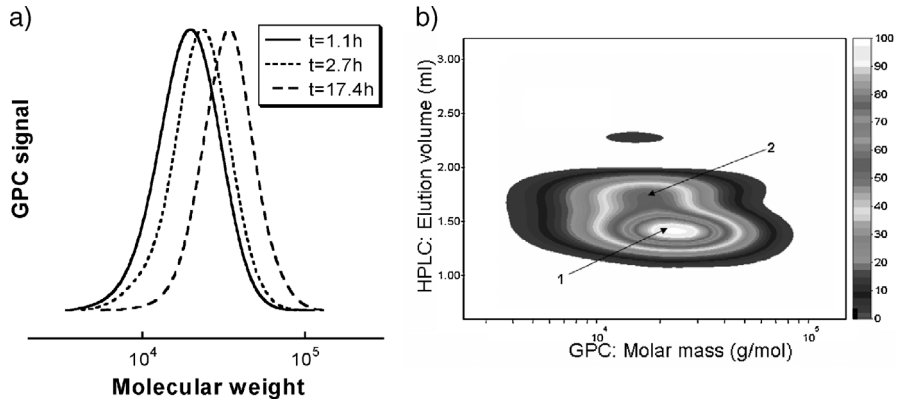


Figure 2.
Evolution of molecular weight distribution (a) and 2D-chromatogram (b) of block copolymer PCL-b-PODMA synthesized via simultaneous method (pathway 3). Experimental conditions: ODMA/CL/HEBI/CuCl/$CuCl_2$/dNbipy/$Sn(EH)_2$ = 30/85/1/0.5/0/0.5/0.8; $[CL]_0$ = 2.92 M, T = 75 °C, in toluene (1 volume equivalents vs. CL). The first dimension is HPLC under the critical condition for PODMA, and the second dimension is GPC with PMMA standard as calibration.

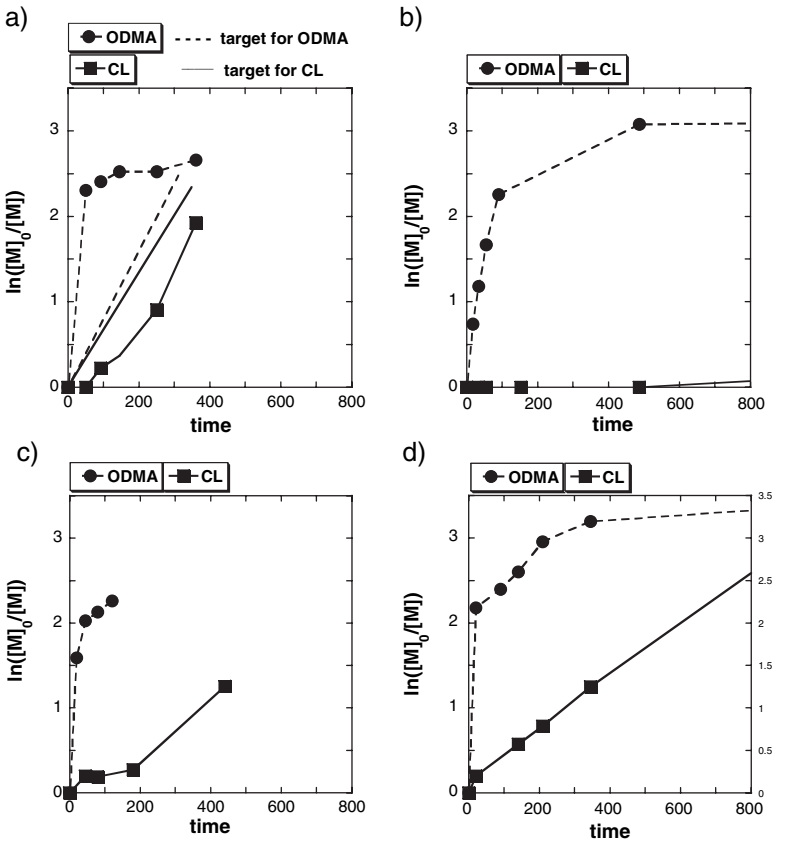


Figure 3.
Kinetic plots for simultaneous copolymerization of ODMA and CL under different conditions. The ratio of ODMA/CL/HEBI/CuCl/$CuCl_2$/dNbipy/$Sn(EH)_2$ was: (a) 30/85/1/0.5/0/0.5/0.8; T = 75 °C; (b) 30/85/1/0.25/0/0.25/2.5; T = 60 °C; (c) 30/85/1/0.25/0.05/0.25/1.5; T = 90 °C; (d) 30/85/1/0.25/0.18/0.25/1.5; T = 90 °C; and $[CL]_0 = 2.92$ M in toluene (1 volume equivalents vs. CL).

ODMA and CL. It can be seen that the both monomers polymerize with different rates, ODMA polymerizes much faster than CL. It could be stated that while the synthesis is a one step process the polymer blocks are not growing simultaneously. The conditions were changed to achieve targeted simultaneous growth. Figure 3 presents the kinetic plots after changing the conditions of the reactions. In the first attempt, (Figure 3b) the temperature was decreased from 75 to 60 °C to slow down the polymerization of ODMA. As a result, the rate of polymerization of ODMA was slightly decreased but polymerization of CL did not occur. This is probably due to the high activation energy of ROP catalyzed by the $Sn(EH)_2$. Therefore, in the next reaction a higher temperature (90 °C) was used. In subsequent attempts, (Figure 3c an 3d) in addition to the change of temperature, a higher amount of Cu(II) was used to slow down polymerization of ODMA. Surprisingly, even when the amount of Cu(II) species was increased to 70% vs. Cu(I), polymerization of ODMA did not stop or slow down but accelerated. This observation led to the inference, that $Sn(EH)_2$ can reduce Cu(II) to Cu(I). As a result, the Cu(I)/Cu(II) ratio increases, which influences the overall rate of polymerization of ODMA. Finally, while simultaneous growth of two different monomers by two different mechanisms was not achieved, the reductive ability of

$Sn(EH)_2$ led to the development of new initiation methods for ATRP. In the next section, a more detailed study of the influence of $Sn(EH)_2$ on ATRP is presented.

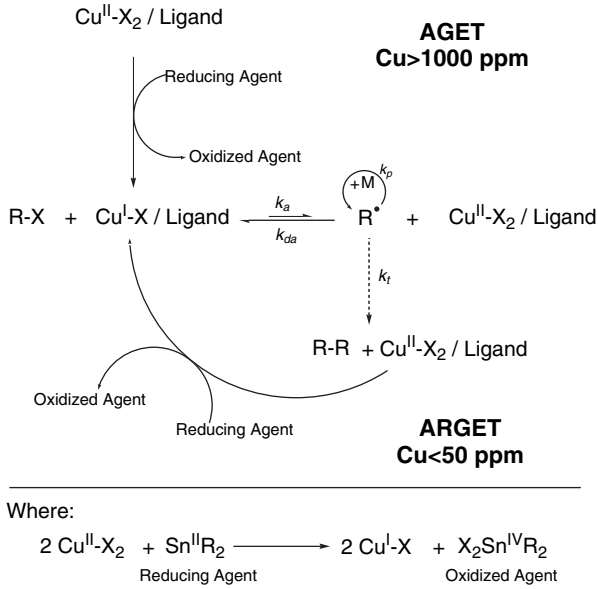
The Influence of tin(II) 2-Ethylhexanoate on ATRP

As shown in the previous section, $Sn(EH)_2$ can reduce Cu(II) to Cu(I). This process occurs via electron transfer and it does not produce new initiating radicals. This important observation led to improvement of the initiation procedures called reverse and/or simultaneous normal and reverse initiation (SR&NI) ATRP by replacing organic initiators (e.g. AIBN), which can initiate new chains, with $Sn(EH)_2$. This new procedure was called activator generated by electron transfer for ATRP (AGET ATRP) (Scheme 3).[21,25]

Additionally, it was possible to perform a continuous controlled ATRP with significantly reduced amounts of copper based catalyst complex (down to ~10 ppm) due to a constant regeneration of the Cu(I) activator species by $Sn(EH)_2$ to compensate for any loss of Cu(I) by termination. The second procedure was called activators regenerated by electron transfer for ATRP (ARGET ATRP) (Scheme 3).[26] Both new methods are described below.

Activator Generated by Electron Transfer for ATRP (AGET ATRP)

A detailed study on AGET ATRP was already reported.[21] In general, a new method was developed for the activation of the catalyst complex to overcome the problem of unavoidable formation of a small amount of homopolymers previously reported with SN&RI ATRP.[25,27] In this new procedure the ATRP activator is formed from a stable catalyst precursor, by a reducing agent, $Sn(EH)_2$, 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 to the reaction mixture in its more stable higher oxidation state.



Scheme 3.
Proposed mechanisms for activators (re)generated by electron transfer for atom transfer radical polymerization (AGET/ARGET ATRP).

Activators Regenerated by Electron Transfer for ATRP (ARGET ATRP)

One disadvantage of ATRP that limits its widespread industrial utilization, is that the transition metal complexes have to be removed from the reaction mixture, and preferably recycled. A new method, ARGET ATRP, allows a homogeneous ATRP to be conducted with very low concentration of catalyst in the reaction. A preliminary study on ARGET ATRP was already reported.[26] In general, this new catalytic system is based on continuous regeneration of the activator by electron transfer, (Scheme 3) which compensates for the loss of Cu(I) by termination reactions. This allows for a significant reduction in the amount of copper species (down to ~10 ppm from typically >1000 ppm), or any other catalyst complex employed in ATRP. Moreover, use of the reducing agent allows starting an ATRP with the oxidatively stable Cu(II) species. The reducing/reactivating cycle may also eliminate residual air or other radical traps in the system. The tolerance to a limited amount of air, or other radical traps in the system, along with reduced levels of copper in the final polymer(s) could eliminate or significantly simplify pre- and post-polymerization purification of the reagents and the products of the reactions.

An example of ARGET ATRP of styrene is presented below and compared to normal and AGET ATRP (Table 1). The reaction conditions and results of these polymerizations are shown in Table 1. All the reactions were well controlled resulting in a narrow monomodal molecular weight distribution.

Preparation of an ABC Triblock Copolymer with Two Crystalizable Blocks, Poly(ε-Caprolactone)-*b*-Poly(*n*-Butyl Acrylate)-*b*-poly(*n*-Octadecyl Methacrylate), PCL-PBA-PODMA

The combination of ATRP and ROP was successfully applied to the synthesis of a triblock copolymer PCL-PBA-PODMA. First, a PCL-Br macroinitiator was prepared by high vacuum technique.[28–30] Next it was sequentially chain extended with BA and ODMA. These chain extensions were successful. SEC chromatograms obtained after each step of the synthesis (Figure 4a) confirmed that the copolymer was efficiently prepared using this sequential step method. This material has two crystallizable blocks PCL and PODMA with soft block PBA in the middle. An AFM image (Figure 4b) shows phase separation of the final material. Detailed synthesis and morphology studies on this triblock copolymer will be reported in a forthcoming paper.

Preparation of Segmented Copolymer Poly(ε-Caprolactone)-*b*-poly(*n*-Octadecyl Methacrylate-*co*-Dimethylaminoethyl Methacrylate), PCL-P(ODMA-*co*-DMAEMA), for Surfactant Applications

Syntheses of copolymers of CL, DMAEMA and ODMA via various pathways (sequential or simultaneous) was already reported.[31] In general, for the preparation of these copolymers an initiator with dual functionality for ATRP/AROP, 2-hydroxyethyl 2-bromoisobutyrate (HEBI), was

Table 1.
Experimental conditions and properties of PSt prepared by different ATRP methods.

	ATRP method	I/Cu(I)/Cu(II)/L/Sn(EH)$_2$	Cu [ppm]	Time (min)	Conv. (%)	Mn, theor[c]	Mn, GPC	PDI
1	Normal[a]	1/1/-/2/-	5000	1580	95	19000	15600	1.27
2	AGET[a]	1/-/1/2/0.45	5000	420	83	17200	14000	1.37
3	ARGET[b]	1/-/0.003/0.1/0.1	15	1830	90	18700	20600	1.15

[a] I = initiator EtBrIB, L = ligand dNbipy; $[St]_0/[EtBrIB]_0 = 200$; $[St]_0 = 8.72$ M; T = 110 °C, toluene used as a GC standard.
[b] I = initiator EtBrIB, L = ligand Me_6TREN; $[St]_0/[EtBrIB]_0 = 200$; $[St]_0 = 5.82$ M; T = 110 °C, in anisole (0.5 volume equivalent vs. monomer).

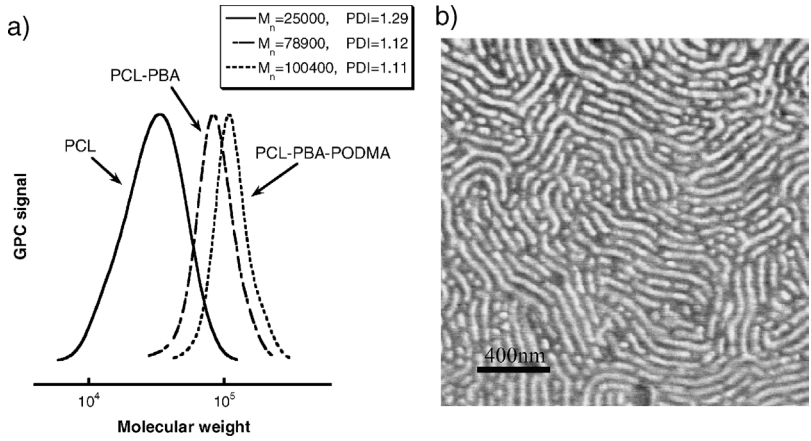


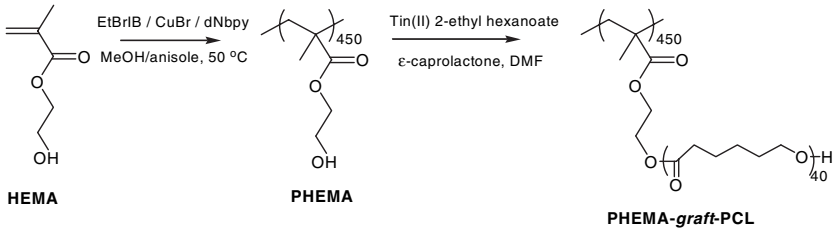
Figure 4.
GPC traces after each step of synthesis (a) and AFM image (b) of PCL-PBA-PODMA triblock copolymer.

used. Copolymers were prepared with good structural control and low polydispersities ($M_w/M_n < 1.2$) but one limitation was identified: DMAEMA block had to be synthesized after ε-caprolactone block. ROP could not proceed in the presence of DMAEMA segments, because the amine groups in PDMAEMA complexed and deactivated $Sn(EH)_2$, used as a catalyst for ROP. The synthesized copolymers were successfully used as surfactants for the preparation of PLA microspheres.[31,32]

Preparation of a Poly(Hydroxyethyl Methacrylate)-*graft*-Poly(ε-Caprolactone), PHEMA-*graft*-PCL Macromolecular Brush

A macromolecular brush, PHEMA-*graft*-PCL, was successfully synthesized using a combination of ATRP and ROP. The synthetic route for preparation of the brush with PCL grafts is outlined in Scheme 4.

ATRP was used first to prepare the linear PHEMA backbone with controlled molecular weight and low polydispersity. Next PHEMA was used as a multifunctional macroinitiator for polymerization of CL by ROP. SEC chromatograms obtained after each step of the synthesis (Figure 5a) and AFM image (Figure 5b) confirmed that a macromolecular brush was efficiently prepared using the sequential step method. The small signal on GPC traces after the second step indicates the presence of a small amount of low molecular weight homopoly(ε-caprolactone), presumably initiated by traces of moisture or methanol, which was used as solvent in first step of synthesis. The detailed synthesis and



Scheme 4.
Synthesis of a molecular brush PHEMA-*graft*-PCL by combination of ATRP and ROP.

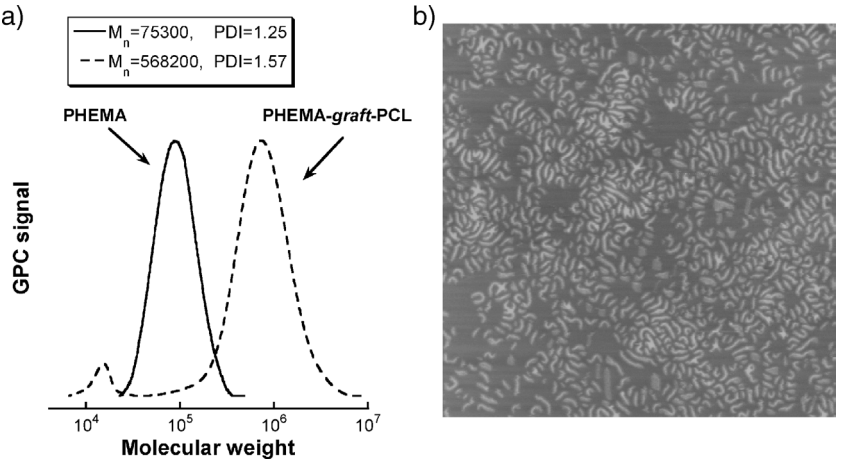


Figure 5.
GPC traces after each step of synthesis (a) and AFM image (2 × 2 μm) (b) of PHEMA-graft-PCL brush.

properties of this graft copolymer will be reported elsewhere.

Conclusions

ATRP and ROP were combined for the synthesis of various segmented copolymers with different structures and compositions. PCL-PODMA diblock copolymers were successfully prepared by both two step and a one step method. In the one step method, simultaneous growth of two different monomers was not achieved but a simple one pot process was demonstrated. The reductive ability of $Sn(EH)_2$ led to the development of new initiation methods for ATRP: AGET and ARGET ATRP. The AGET ATRP method allows addition of the ATRP catalyst complex to the reaction mixture in its more stable higher oxidation state. The second process improvement, ARGET ATRP, additionally allows a reduced amount of catalyst to be used in an ATRP processes, down to a few ppm. The combination of ATRP and ROP was also successful in synthesis of block copolymers with two crystallizable blocks PCL-PBA-PODMA and block copolymers for potential application as surfactants, PCL-P(ODMA-*co*-DMAEMA), and macromolecular brush, PHEMA-*graft*-PCL.

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