Immortal Ring-Opening Polymerization of ε-Caprolactone by a Neat Magnesium Catalyst System: An Approach to Block and Amphiphilic Star Polymers In Situ

Journal:	*Polymer Chemistry*
Manuscript ID:	PY-ART-03-2014-000384.R1
Article Type:	Paper
Date Submitted by the Author:	10-Apr-2014
Complete List of Authors:	Wang, Yang; Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Liu, Bo; Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Wang, Xue; Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Zhao, Wei; Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Liu, Dongtao; Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Liu, Xinli; Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Cui, Dongmei; Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 1State Key Laboratory of Polymer Physics and Chemistry

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/polymers

PAPER

Immortal Ring-Opening Polymerization of ε-Caprolactone by a Neat Magnesium Catalyst System: An Approach to Block and Amphiphilic Star Polymers *In Situ*†

Yang Wang [a,b], Bo Liu [a], Xue Wang[a,b], Wei Zhao[a,b], Dongtao Liu[a], Xinli Liu*[a] and Dongmei Cui*[a]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Catalyst systems arising from the cheap, ligand-free and commercially available Mg^nBu_2 and alcohols for the ring-opening polymerization (ROP) of ε-caprolactone (ε-CL) under mild conditions had been established. The catalytic system of Mg^nBu_2/Ph_2CHOH showed very high activity as compared with the system of Mg^nBu_2/Ph_3COH that applied a more bulky methanol derivative. Interestingly, at the presence of excess amount of alcohol Ph_2CHOH, namely, varying the OH-to-Mg ratio in a wide range from 10:1 to 800:1, the system Mg^nBu_2/Ph_2CHOH still remained high activity, thus producing up to 800 polycaprolactone (PCL) chains per Mg center, suggesting a living immortal polymerization mode. The molecular weights of the obtained PCLs are accurately controlled when the ratio of $[CL]_0/[Mg]_0$ changed from 500 to 8000, together with narrow molecular weight distributions. Also, diblock PCL-*b*-PLA copolymers with narrow PDIs have been facilely achieved. Moreover, the allyl and propargyl functionalized diphenylmethanols could be employed as the chain transfer reagents (CTA) in this immortal systems for constructing *in situ* the allyl and propargyl functionalized PCLs that were facilely modified further to be PCLs with multiple functionality and building blocks for amphiphilic and topological microstructured PCLs via coupling and click reactions.

Introduction

Polycaprolactone (PCL) is an important biomaterial due to its excellent mechanical property, biodegradability and miscibility with other polymers, and has found wide applications as scaffolds in tissue engineering,[1] long-term drug delivery matrixes,[2] microelectronics,[3] adhesives[4] and packaging materials.[5] There are two main pathways to produce PCL: the polycondensation of 6-hydroxyhexanoic acid,[6] and the ring-opening polymerisation (ROP) of ε-caprolactone (ε-CL).[7] It is now commonly accepted that the most efficient method for preparing well-controlled polyesters in terms of molecular weight, composition and microstructure is the ROP with organic, organometallic or enzyme catalysts. Of which the lithium,[8] sodium,[9] potassium,[10] magnesium,[11] calcium,[12] strontium,[13] aluminum,[14] stannum,[15] some transition metal[16] and rare-earth metal[17] complexes have attracted more attention because of their high activity and strong power to control microstructures of the resultant polymers. Whereas, "one catalyst one polymer chain" leads to high catalyst residue in the resulting polymers. Thus to design more efficient catalyst precursors has been a target of organometallic chemists.

In 1985, the "immortal" polymerization (IMP, alternatively, a living chain-transfer polymerization) concept was introduced by Inoue *et al*..[18] The IMP shows characteristics such as the rapid and reversible exchange reaction between the chain transfer agent (CTA) and the living active species that gives rise to generate more polymer chains from one metal center, and *in situ* capping the polymer chain ends with CTA moieties that might be functional groups such as hydroxyl, vinyl and amino groups.[19] This opens not only a new approach to prepare polymers in more efficient manner but also provide functionalized polymers that can facilely incorporate other substituents such as bioactive drugs or fluorescent tags to construct novel biopolymers.[20]

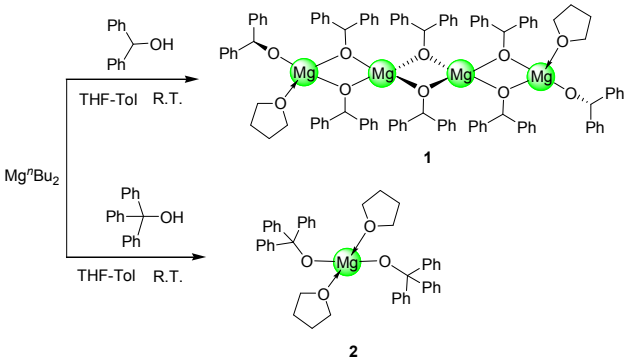
During our previous studies on the IMP of L-LA, we found that diphenylmethoxide magnesium was an excellent initiator for L-LA.[21] Herein, we extended this system to ROP of ε-CL, which showed extraordinarily high activity and an immortal mode with fantastic merits of low catalyst cost and minimal (non-toxic) metal residue in PCL production. In addition, the allyl and propargyl functionalized diphenylmethanols were also employed for the first time to construct the immortal catalytic systems for the ROP of ε-CL, allowing to access the functionalized PCLs with block, three-armed microstructures as well as amphiphilic nature in one-pot. The thus process of post-polymerization modification of chemoselective handles deriving from the CTA groups other than from the monomers, together with the immortal polymerization technique, is very fresh.

Results and Discussion

Synthesis and Structure Determination of Triphenylmethoxy Magnesium Complex $Mg(Ph_3CO)_2(THF)_2$ (2).

Following the similar procedure of synthesizing the tetranuclear complex $Mg_4(Ph_2CHO)_8(THF)_2$ (**1**), a highly active initiator for

the ROP of LA, the more steric hinderance triphenylmethanol (Ph_3COH) was used to react stoichiometrically with Mg^nBu_2 (Scheme 1). The resultant complex **2** ($Mg(Ph_3CO)_2(THF)_2$) was confirmed by X-ray diffraction to take a mononuclear structure (Fig. 1). The magnesium ion is four-coordinate bonding to two triphenylmethoxide ligands (Ph_3CO) and two tetrahydrofuran molecules, adopting a distorted tetrahedral geometry. All Mg–O bond lengths are comparable to those reported in literatures.[22]



Scheme 1. Stoichiometric reactions between Mg^nBu_2 and Ph_2CHOH or Ph_3COH.

ROPs of ε-CL

ROPs of ε-CL by complexes **1** and **2** were investigated. Complex **1** was highly active to transfer 500 equiv monomers to PCL in 5 min. In the presence of 5 to 10 equiv of Ph_2CHOH, complex **1** still maintained the same high activity to provide PCLs with more controllable molecular weights and narrow molecular weight distributions (Table 1, entries 1–3). On the contrary, the more steric hinderance of the two alkoxyl ligands in complex **2** may inhibit the ε-CL monomer from coordinating to the active metal center. As a result, complex **2** showed very low activity during the ROP ε-CL and almost inert in the presence of excess amount of Ph_3COH (Table 1, entries 4–6).

Thus the detailed investigation of the ROP of ε-CL was performed by using **1**/Ph_2CHOH. Keeping the OH-to-Mg ratio as a constant (10:1) whilst increasing the monomer loading from 1000 to 8000 equiv relative to $[Mg]_0$, the polymerizations went on smoothly to reach high yields in short time. Meanwhile, the molecular weights of the resultant PCLs increased correspondingly from 1.08×10^4 g/mol to 6.17×10^4 g/mol in well consistence with the theoretic values (Table 2, entries 1–4), and the molecular weight distributions remained narrow (PDI = 1.16–1.19), suggesting a livingness polymerization mode. Fixing the CL-to-Mg ratio to 1000:1 whilst increasing the alcohol loading from 20 to 100 equiv, the polymerizations still remained rapid rates to achieve complete conversion in 30 min. This meant that excess amount of alcohol did not arouse termination of the polymerization as usual (alcohol is always used to stop polymerization), indicating that the ROP of ε-CL with complex **1** possessed the immortal nature. Alternatively, the exchange reaction between Ph_2CHOH and the metal alkoxide (or metal–O–PLA active species) were rapid and reversible. As a result, the molecular weights of the resultant PCLs decreased in inverse proportion with the alcohol loading while the molecular weight distributions were narrow (PDI = 1.07–1.13) throughout (Table 2, entries 5–10). Encouraged by the immortal fashion, we tried to find how CTA of this polymerization system can be endured.

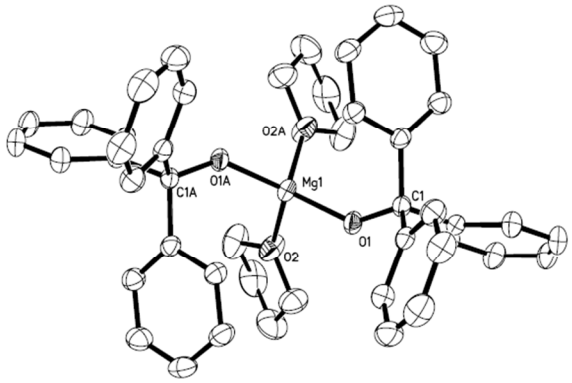


Figure 1. Molecular structure of complex **2** as 35% ellipsoids. All hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Mg(1)–O(1) 1.8645(12), Mg(1)–O(1A) 1.8645(12), Mg(1)–O(2A) 2.0224(15), Mg(1)–O(2) 2.0224(15); O(1)–Mg(1)–O(1A) 136.45(9), O(1)–Mg(1)–O(2A) 110.93(6), O(1A)–Mg(1)–O(2A) 97.64(5), O(1)–Mg(1)–O(2) 97.64(5), O(1A)–Mg(1)–O(2) 110.93(6), O(2A)–Mg(1)–O(2) 97.32(10), C(1)–O(1)–Mg(1) 138.52(11).

Table 1. ROP of ε-CL by Complexes **1** and **2** in Combination with Di(or Tri)phenylmethanol

Entry[a]	Cat.	ROH	$[CL]_0/[OH]_0/[Mg]_0$	Time(min)	Conv.[b](%)	$M_{n,calcd}\times10^{-4}$[c]	$M_{n,exp}\times10^{-4}$[d]	M_w/M_n[d]
1	**1**	–	500/-/1	5	100	2.87	2.99	1.70
2	**1**	Ph_2CHOH	500/5/1	5	100	0.83	1.05	1.44
3	**1**	Ph_2CHOH	500/10/1	5	100	0.49	0.80	1.19
4	**2**	–	500/-/1	360	13	0.40	*nd.*	*nd.*
5	**2**	Ph_3COH	500/5/1	360	5	0.08	*nd.*	*nd.*
6	**2**	Ph_3COH	500/10/1	360	5	0.05	*nd.*	*nd.*

[a] Polymerizations were carried out in THF at 25°C, $[CL]_0$ = 1.75 M. [b] Determined by ^1H NMR spectroscopy. [c] $M_{n,calcd}$ = $([CL]_0/[Mg]_0 \times 114.14 / ([OH]_0+2)) \times$ conv.(%) + M_{ROH}. [d] Determined by SEC against polystyrene standard, M_n values were obtained using a correcting factor for polylactides (0.56).[23]

Under the presence of up to 800 equiv of Ph_2CHOH, complex **1** was still able to transfer 8000 equiv of ε-CL albeit at a longer time and higher temperature (Table 2, entries 10–13). This meant that each Mg metal center experienced at least 800 times chain transfer reactions to generate 800 PCL polymeric chains, giving extremely high catalytic efficiency of 80000%. The resulting PCL macromolecular chains are capped with a hydroxyl group at one end (CH_2OH, 3.64 ppm, a), as the typical feature of IMP, and with the Ph_2CHO– group at the other end (6.89 ppm, –OC*H*Ph_2, *i*) (Fig. 2).

Because of the excellent degradability of PLA and the

distinguished permeability of PCL to drugs, researchers have been directed to explore the copolymerization of the two

Table 2. ROP of ε-CL with **1**/Ph_2CHOH

Entry[a]	$[CL]_0/[OH]_0/[Mg]_0$	Time (min)	Conv.[b] (%)	$M_{n,calcd}$ $\times10^{-4}$[c]	$M_{n,exp}$ $\times10^{-4}$[d]	M_w/M_n[d]
1	1000/10/1	2	100	0.97	1.08	1.18
2	2000/10/1	10	100	1.92	2.07	1.16
3	5000/10/1	30	96	4.58	5.81	1.10
4[e]	8000/10/1	60	93	7.10	6.17	1.19
5	1000/20/1	5	100	0.54	0.65	1.11
6	1000/30/1	5	100	0.38	0.59	1.12
7	1000/50/1	10	100	0.24	0.40	1.07
8	1000/70/1	20	100	0.18	0.38	1.13
9	1000/80/1	30	100	0.16	0.36	1.13
10	1000/100/1	30	100	0.13	0.19[b]	1.09
11	2000/200/1	60	100	0.13	0.44	1.09
12[e]	5000/500/1	60	100	0.13	0.21	1.09
13[e]	8000/800/1	120	100	0.13	0.18[b]	1.16

[a] Polymerizations were carried out in THF at 25°C, $[CL]_0$ = 1.75 M. [b]Determined by ^{1}H NMR spectroscopy. [c] $M_{n,calcd}$ = ($[CL]_0/[Mg]_0$ × 114.14 / ($[OH]_0$+2)) × conv.(%) + 184.23. [d]Determined by SEC against polystyrene standard. M_n values were obtained using a correcting factor for polylactides (0.56).[23] [e]At 70°C.

monomers, anticipating to access materials with adjusted composition and molecular weights to control the drug loading, degradability and permeability.[24] Intrigued by the immortal characteristics of the system **1**/Ph_2CHOH, the copolymerization of ε-CL and L-LA was promoted *in situ* by adding L-LA to the ROP of ε-CL system when ε-CL was completely converted. The copolymerization was performed at 70 °C for 10 h to reach over 90% conversion. All of the obtained copolymers showed nearly closed molecular weights to the theoretical values, and very narrow PDIs (Table 3). The ^{1}H NMR spectrum of a diblock copolymer gives peaks *e, f, g, h* attributed to the PCL unit and peaks *o, p* arising from the PLA sequence (Fig. 3).

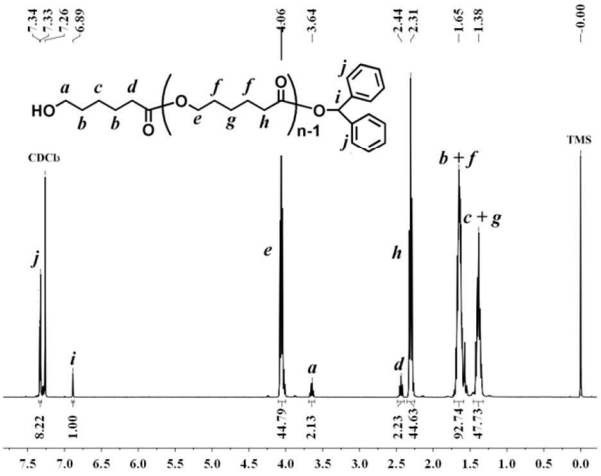


Figure 2. ^{1}H NMR spectrum of oligomer PCL (Table 2, entry 7; 400 MHz, $CDCl_3$, 25 °C).

Table 3. Preparation of PCL-*b*-PLA with **1**/Ph_2CHOH[a]

Entry	$[CL]_0/[LA]_0/[OH]_0/[Mg]_0$	PCL/PLLA found[b]	$M_{n,calcd}$ $\times10^{-4}$[c]	$M_{n,exp}$ $\times10^{-4}$[d]	M_w/M_n[d]
1	1000/1000/10/1	52/48	2.49	3.08	1.18
2	2000/2000/10/1	55/45	4.95	4.75	1.16

[a] In THF, after CL conversion reached 100% at 25 °C in 10 min, LLA was added to the system that was heated to 70 °C, $[CL]_0$ = 0.88 M, $[LA]_0$ = 0.88 M. [b] Composition found was determined by ^{1}H NMR. [c]Theoretical M_n was estimated considering monomers conversion. [d] Molecular weight and polydispersity index of the copolymer determined by SEC against polystyrene standard.

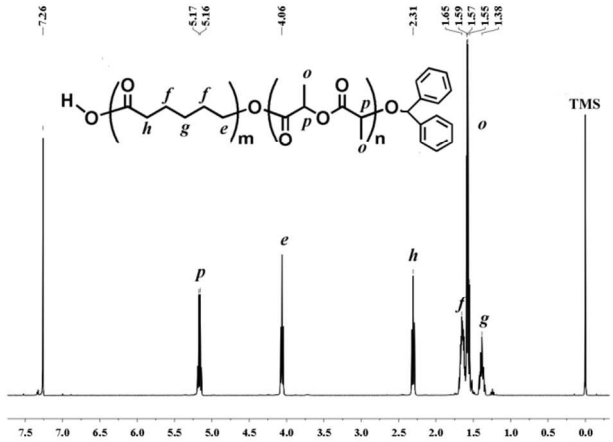
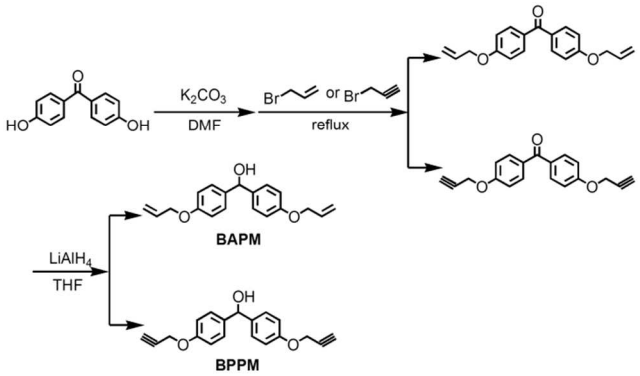


Figure 3. ^{1}H-NMR spectrum of PCL-*b*-PLA diblock copolymer (Table 3, entry 1; 400 MHz, $CDCl_3$, 25 °C).

Synthesis of α,ω-Functional PCL

The allyl and propargyl functionalized diphenylmethanols were synthesized straightforward as outlined in Scheme 2. The nucleophilic substitution reactions of allyl bromide and propargyl bromide with 4,4′-dihydroxybenzophenone in the presence of K_2CO_3 was followed by reduction of the carbonyl group with $LiAlH_4$ in refluxing THF to give readily bis(4-(allyloxy)phenyl)methanol (BAPM) and bis(4-prop-2-ynyloxy)phenyl)methanol (BPPM), respectively.[25]

The polymerization of ε-CL at 25 ºC catalyzed by dibutylmagnesium (Mg^nBu_2) using excess amount of BAPM or BPPM as the chain transfer agent went on quickly (25 °C , 5 min, conv. 100%) to afford the α-hydroxyl-ω-vinyl (Star-PCL-=) or α-hydroxyl-ω-ethynyl PCL (Star-PCL-≡), selectively (Table 4). ^{1}H NMR spectrum of oligomeric Star-PCL-= displays signals H_i, H_j, H_k, H_l, H_m, H_n ascribed to the allyl-functional diphenymethoxy end and signals H_a, H_b, H_c, H_d arising from the other end (Fig. 4a). Similarly, an oligomeric Star-PCL-≡ was also identified by ^{1}H NMR spectrum analysis (Fig. 4b).

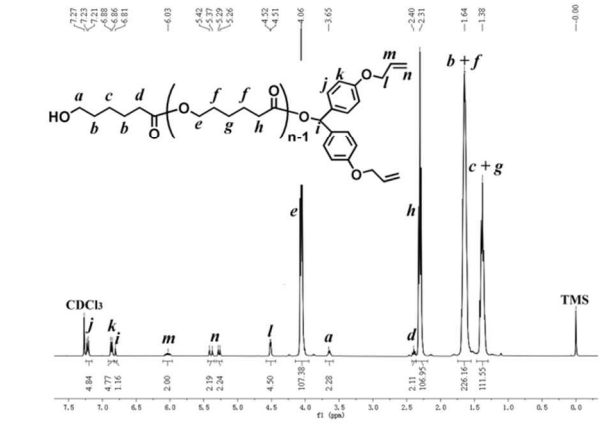


Scheme 2. Synthetic route to vinyl and ethynyl functional diphenylmethanols.

Table 4. ROP of ε-CL with Mg^nBu_2/BAPM and Mg^nBu_2/BPPM [a]

Entry	$[CL]_0/[OH]_0/[Mg]_0$	Time (min)	Conv. (%)	$M_{n,calcd}$ $\times10^{-4}$ [b]	$M_{n,exp}$ $\times10^{-4}$ [c]	M_w/M_n [c]
1	500/10BAPM/1	5	100	0.60	0.64	1.16
2	500/10BPPM/1	5	100	0.60	0.43	1.18

[a]In THF, 25 °C. [b]Theoretical M_n estimated considering monomers conversion. [c] Molecular weight was determined by ^1H NMR and polydispesrsity index of the final copolymer determined by SEC against polystyrene standard.



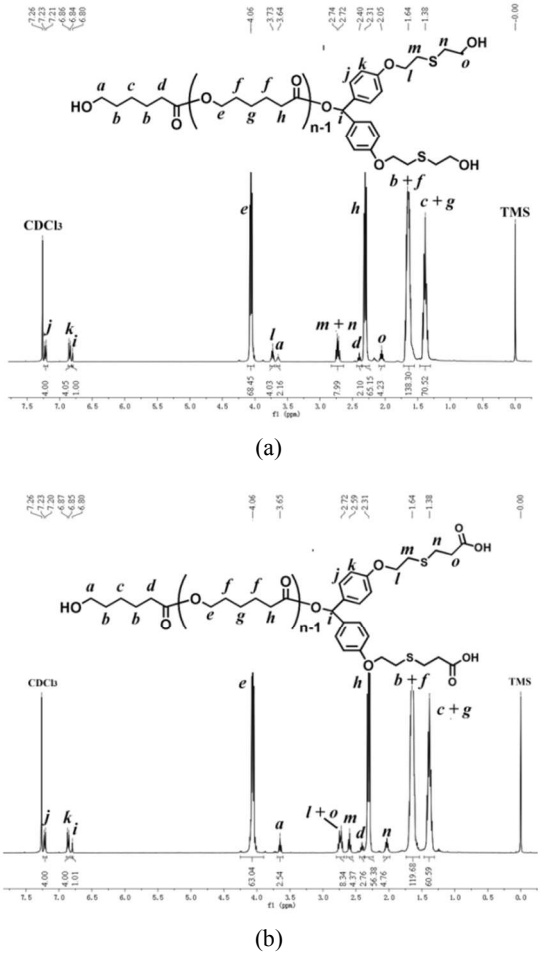
(a)

(b)

Figure 4. ^1H NMR of Star-PCL-= (a) and amphiphillic Star-PCL-≡ (b) (400 MHz, $CDCl_3$)

Synthesis of Multi-Functionalized Topologic PCL

The above isolated PCLs can be further post polymerization modified with thiols and azides, respectively, thus, become the excellent building blocks of the topologic PCLs. The thiol-ene coupling reaction[26] was photo-initiated by 5% DMPA in THF solution by *in situ* adding excess amount of 2-mercaptoethanol (relative to BAPM) to the polymerization system for preparing Star-PCL-=. The reaction was highly efficient confirmed by disappearance of the resonances *l*, *m* and *n* at 6.03, 5.42~5.26 and 4.51 ppm from the vinyl protons (Fig. 5a). SEC analysis showed the resultant telechelic multiple hydroxyl functionalized Star-PCL-OH remained the similar molecular weight to its vinyl precursor and narrow polydispersity ($M_n = 0.46 \times 10^4$ g/mol, PDI = 1.04). Following the same strategy, the reaction of Star-PCL-≡ with mercaptopropionic acid catalyzed by DMPA in THF was

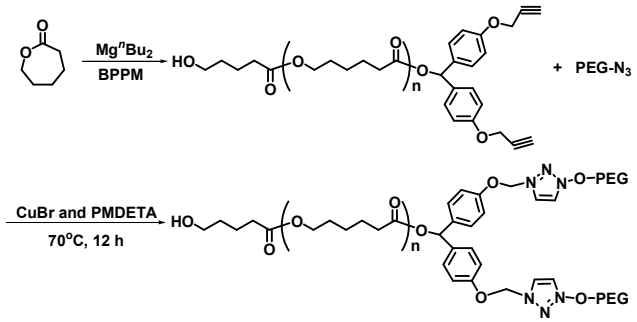


(a)

(b)

Figure 5. ^1H NMR spectra (400 MHz, 25 °C, $CDCl_3$) of Star-PCL-OH (a) and Star -PCL-COOH (b).

carried out. ^1H NMR analysis revealed that complete disappearance of the alkyne groups and emergence of methylene from mercaptopropionic acid was in about 3 h to generate a hydroxyl and carboxyl acid multi functionalized Star-PCL-COOH (Fig. 5b).



Scheme 3. Synthetic route to amphiphillic Star-PCL-PEG.

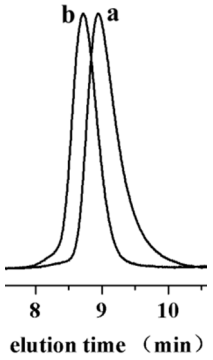


Figure 6. SEC (Size Exclusion Chromatography at 40 °C using THF as the eluent with a flowing rate of 0.35 mL/min) traces of (a)Star-PCL-≡, M_n = 1.99 × 10^4 g/mol, PDI = 1.05; (b) Star-PCL-PEG, M_n = 2.75 × 10^4 g/mol, PDI = 1.04.

THF solution of 10% copper (I) bromide, PMDETA and PEG-N_3 (M_n = 0.35 × 10^4 g/mol, PDI = 1.03) were added into the THF polymerization system of Star-PCL-≡ (M_n = 1.99 × 10^4 g/mol, PDI = 1.05) *in situ*. The above click reaction carried out at 70 ºC and finished after 12 h to give exclusively the 1,4-disubstituted adduct (Scheme 3). ^{1}H NMR spectrum showed that the resonances of the ethynyl proton at 4.68 ppm from –CH_2C≡C*H* disappeared completely, and the signal at 7.82 ppm is assigned to the newly formed triazole ring (Fig. S3), indicating the formation of three hetero-armed amphiphilic Star-PCL-PEG (M_n = 2.75 × 10^4 g/mol, PDI = 1.04) jointed by triazole rings. The SEC traces showed the unimodal and narrow distributions of the polymers before and after the reaction, indicative of neat and complete click reaction (Fig. 6).

Conclusion

In summary, complex **2**, the derivative from the reaction of the bulky triphenylmethanol (Ph_3COH) with dibutylmagnesium (Mg^{n}Bu$_2$), or its combination with excess Ph_3COH, could hardly initiated the ROP of ε-CL, as the crowded metal center inhibited the coordination of the monomer. On the contrary, the system composed of complex **1**, a tetranuclear diphenylmethoxy magnesium arising from reaction of Ph_2CHOH with Mg^{n}Bu$_2$, together with an excess amount of less bulky Ph_2CHOH, showed very high activity and immortal polymerization mode by producing up to 800 PCL macromolecular chains from each magnesium center. In addition, the multi functional alcohols, bis(4-(allyloxy)phenyl)methanol and bis(4-prop-2-ynyloxy)phenyl)methanol, could also combined with Mg^{n}Bu$_2$ to construct the immortal catalyst systems to initiate the ROP of ε-CL, affording multiple functional PCLs with hydroxyl, vinyl and ethynyl end groups. These functional PCLs were excellent building blocks for the multi functionalized PCLs and novel PCL-based block copolymers as well as the amphiphilic three hetero-armed PCLs. This work established a new strategy to access functional biomaterials to bind with drugs or fluorescent tags in one pot.

Experiment section

Materials

All operations were carried out under an atmosphere of argon using standard Schlenk techniques or in a nitrogen gas filled MBraun glovebox. Solvents were reagent grade, dried by standard methods[28] and distilled under nitrogen prior to use. Toluene, tetrahydrofuran (THF) were dried over Na. Deuterated NMR solvents were purchased from Cambridge Isotopes, dried over Na (for C_6D_6) and CaH_2 (for $CDCl_3$), and stored in the glovebox. Mg^{n}Bu$_2$ was purchased from Sigma-Aldrich. ε-CL (from Aladdin) was dried by molecular sieve (4 Å) then distilled under vacuum. Biphenylmethanol and triphenylmethanol were purchased from Darui, their tetrahydrofuran solutions were dried over by anhydrous magnesium sulfate then the solvent were removed under vacuum. PEG-N_3 (M_n = 0.35 × 10^4 g/mol, PDI = 1.03) was purchased from Aladdin. Glassware and vials used in the polymerization were dried in an oven at 115 °C overnight and undergone the vacuum-argon cycle three times.

Techniques

Organometallic samples for NMR measurements were prepared in NMR tubes and sealed with paraffin film in the glovebox. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV300 or a Bruker AV400 (FT, 300 MHz for ^{1}H, 75 MHz for ^{13}C, or 400 MHz for ^{1}H, 100 MHz for ^{13}C) spectrometer. The number-average molar mass (M_n) and polydispersity index (PDI) of the polymer were measured by Size Exclusion Chromatography (SEC) on a TOSOH HLC-8220 SEC instrument (Column: Super HZM-H×3) at 40 °C using THF as eluent with a flowing rate of 0.35 mL/min; the values were relative to polystyrene standards.

Synthesis

Synthesis of Magnesium Alkoxide Mg(Ph$_3$CO)$_2$(THF)$_2$ (2). Under a nitrogen atmosphere, triphenylmethanol (521 mg, 2.00 mmol) in 5 mL mixture of toluene-tetrahydrofuran (V_{Tol}: V_{THF} = 1:1) was added to a toluene-tetrahydrofuran (5 mL, V_{Tol}: V_{THF} = 1:1) solution of Mg^{n}Bu$_2$ (1.00 mL, 1.0 M in *n*-heptane, 1.00 mmol) in a 25 mL vial. The reaction mixture was stirred at room temperature for 2 h and concentrated to approximately 2 mL; the residue was cooled to –35°C over 2 days to afford colourless crystalline solids (340 mg, 87.0% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C), δ = 7.33 (d, 8 H, *p*-Ph–*H*), 7.13 (t, 8 H, *m*-Ph–*H*), 7.08 (d, 4 H, *p*-Ph–*H*), 7.04 (t, 6 H, *o*-Ph–*H*), 6.94 (t, 4 H, *o*-Ph–

H), 3.60 (8 H, THF), 1.67 ppm (8 H, THF) ; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C), 155.23 (6C, Ar), 129.32 (4 C, Ar), 128.89 (8 C, Ar), 128.16 (4 C, Ar), 127.68 (8 C, Ar), 125.67 (6 C, Ar), 69.78, 25.87 ppm (THF).

X-Ray Diffraction Analysis. A suitable single crystal of complex **2** was sealed in a thin-walled glass capillary, and the data collection was performed at –88.5 °C on a Bruker SMART diffractometer with graphite-monochromated Mo-Kα radiation (l =0.71073Å). The SMART program package was used to determine the unit-cell parameters. The absorption correction was applied using SADABS.[29] The structure was solved by direct methods and refined on F^2 by full-matrix least squares techniques with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were placed at calculated positions and were included in the structure calculation without further refinement of the parameters. All calculations were carried out using the SHELXS-97 program.[30] The molecular structure was resolved using ORTEP program.[31] The cif. and checkcif files of complex **2** were given as support information.

Typical Polymerization Procedure. A typical polymerization procedure (Table 2, entry 1) was described as follows. Under a nitrogen atmosphere a Schlenk flask was charged with a solution of complex **1** [$Mg_4(Ph_2CHO)_8(THF)_2$] (3.74 mg, 2.19 μmol) and Ph_2CHOH (0.016 g, 87.6 μmol) in 5 mL THF. Next, ε-CL (1.00 g, 8.76 mmol, 1000 equiv.) was added, and the reaction mixture was stirred vigorously at 25 °C for 2 min. After a small sample of the crude material was removed with a pipette for characterization by ^{1}H NMR (the separated NMR-samples were precipitated and washed by ethanol before measurement, similarly hereinafter), the reaction was quenched with acidified ethanol (0.5 mL of a 1.0 M HCl solution in EtOH). The polymer was precipitated with excess ethanol (80 mL) and dried under a vacuum to a constant weight.

Synthesis of Diblock Copolymer PCL-*b*-PLA. To a rapidly stirred solution of [$Mg_4(Ph_2CHO)_8(THF)_2$] (3.74 mg, 2.19 μmol) and Ph_2CHOH (0.016 g, 87.6 μmol) in THF (10 ml) was added ε-CL (1.00 g, 8.76 mmol, 1000 equiv.). The reaction mixture was stirred at room temperature for 10 min. Then L-LA (1.26 g, 8.76 mmol, 1000 equiv.) was added to the above solution. The mixture was stirred vigorously at 70 °C for 10 h. After a small sample of the crude material was removed with a pipette for characterization by ^{1}H NMR, the reaction was quenched with acidified ethanol (0.5 mL of a 1.0 M HCl solution in EtOH). The polymer was precipitated with excess ethanol (80 mL) and dried under a vacuum to a constant weight.

Synthesis of the Derivatives of Diphenylmethanol (Bis(4-(allyloxy)phenyl)-methanone (BAPM) and Bis(4-prop-2-ynyloxy)phenyl)methanol (BPPM)). To a solution of 4,4′-dihydroxybenzophenone (5.0 g, 23.3 mmol) in DMF (50 mL) were added K_2CO_3 (8.05 g, 58.3 mmol) and allyl bromide (5.1 mL, 58.4 mmol) or propargyl bromide (4.34 mL, 58.4 mmol). The reaction mixture was stirred at room temperature for 24 h, quenched with H_2O (10 mL), and consecutively washed with EtOAc (100 mL × 3). The organic layers were combined, washed with brine (50 mL × 3), dried over anhydrous $MgSO_4$, filtered, and concentrated. The desired product **BAPM** (6.77 g, 99%) or **BPPM** (5.90 g, 98%) was obtained as a white crystal (or red oil) after reduction reaction with excess amount of lithium aluminium hydride in THF solution and following purification by column chromatography. ^{1}H NMR of **BAPM** (400 MHz, $CDCl_3$): δ = 7.25 (d, 4H, Ar-*H*), 6.87 (d, 4H, Ar-*H*), 6.04 (m, 2H, vinyl-*H*), 5.74 (s, 1H, -C*H*-OH), 5.42, (dd, 2H, vinyl-*H*), 5.27 (dd, 2H, vinyl-*H*), 4.51 (d, 4 H, -CH_2-), 2.15 (s, 1 H, -O*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.3, 161.8, 132.6, 132.1, 130.8, 118.1, 114.1, 68.8. ^{1}H NMR of **BPPM** (400 MHz, $CDCl_3$): δ = 7.28 (d, 4H, Ar-*H*), 6.95 (d, 4H, Ar-*H*), 5.78 (s, 1H, -C*H*-OH), 4.67 (s, 4H, ethynyl-*H*), 2.51 (s, 2H, ethynyl-*H*), 2.15 (s, 1H, -C*H*-OH). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.2, 132.6, 129.3, 114.8, 79.6, 78.8, 76.4, 57.0.

Synthesis of Star-**PCL-OH (or** Star-**PCL-COOH).** For the reaction of 2-mercaptoethanol (or mercaptopropanoic acid) with Star-PCL-= (or Star-PCL-≡), DMPA was used as the catalyst and the mole ratio of thiol-ene was kept as 5: 1 to avoid cross link reaction. In a 20 ml quartz vial, 2-mercaptoethanol (0.10 g, 1.28 mM) or mercaptopropionic acid (0.14 g, 1.28 mM) was dissolved in THF, the solution was directly added into the polymerization solution of PCL, then 1 mL THF solution of DMPA (0.05 g, 0.41 mM) was added. The combination was stirred at ambient temperature under 365 nm UV light. After 3 h, the reaction was quenched with acidified ethanol (0.5 mL of a 1.0 M HCl solution in EtOH). The polymer was precipitated with excess ethanol (80 mL) and dried under a vacuum to a constant weight, then determined by SEC.

Synthesis of Star-**PCL-PEG.** Initially a 0.085 mM catalyst stock solution was prepared by dissolving CuBr (0.085 mM, 1 equiv), and PMDETA (0.085 mM, 1 equiv) in 5 mL toluene. In a Schlenk tube, PEG-N_3 (0.168 mM, 2 equiv) was dissolved in the polymerization solution of Star-PCL-≡ (0.084 mM alkynyl groups, 1 equiv; M_n = 1.99 × 10^4 g/mol, PDI = 1.05) in THF. Then the catalysts were added into the solution under 70 ºC, the reaction solution was stirred for 12 h. The polymer was precipitated with excess diethyl ester (80 mL) and dried under a vacuum to a constant weight, then determined by SEC.

Acknowledgment

We thank financial supports from the National Natural Science Foundation of China for projects Nos. 21361140371, 21274143 and 51021003.

References

1 (a) C. X. F. Lam, S. H. Teoh and D. W. Hutmacher, *Polym. Int.*, 2007, **56**, 718–728. (b) J. Peña, T. Corrales, I. Izquierdo-Barba, A. L. Doadrio and M. Vallet-Regí, *Polym. Degrad. Stab.*, 2006, **91**, 1424–1432. (c) M. J. Jenkins, K. L. Harrison, M. M. C. G. Silva, M. J. Whitaker, K. M. Shakesheff and S. M. Howdle, *Eur. Polym. J.*, 2006, **42**, 3145–3151. (d) D. W. Hutmacher, T. Schantz, I. Zein, K. W. Ng, S. Hin, T. Kim and C. Tan, J. Biomed. *Mater. Res.*, 2001, **55**, 203–216.

2 (a) V. R. Sinha, K. Bansal, R. Kaushik, R. Kumria and A. Trehan, *Int. J. Pharm.*, 2004, **278**, 1-23. (b) R. Chandra and R. Rustgi, *Prog. Polym. Sci.*, 1998, **23**, 1273-1335. (c) D. R. Chen, J. Z. Bei and S. G. Wang, *Polym. Degrad. Stab.*, 2000, **67**, 455-459.

3 J. L. Hedrick, T. Magbitang, E. F. Connor, T. Glauser, W. Volksen, C. J. Hawker, V. Y. Lee and R. D. Miller, *Chem.–Eur. J.*, 2002, **8**, 3308–3319.

4 P. Joshi and G. Madras, *Polym. Degrad. Stab.*, 2008, **93**, 1901–1908.

5 Y. Ikada and H. Tsuji, *Macromol. Rapid Commun.*, 2000, **21**, 117–132.

6 (a) B. Buchholz, DE Pat., 4005415, 1991. (b) K. Enomoto, M. Ajioka and A. Yamaguchi, WO Pat., 9312160, 1993.(c) E. M. Filachione and C. H. Fisher, US Pat., 2396994, 1946. (d) E. M. Filachione and C. H. Fisher, US Pat., 2447693, 1948. (e) Y. Yoshida, M. Miyamoto, S. Obuchi, K. Ikeda and M. Ohta, EP Pat., 0710684, 1996.

7 K. M. Stridsberg, M. Ryner and A.-C. Albertsson, *Adv. Polym. Sci.*, 2002, **157**, 41–65.

8 C.-C. Lin and B.-T. Ko, *J. Am. Chem. Soc.* 2001, **123,** 7973–7977.

9 M.Yuan, C. Xiong and X. Deng, *J. Polym. Sci., Part A: Polym. Chem.*, 1998, **67**, 1273–1276.

10 (a) Y. Lemmouchi, M. C. Perry, A. J. Amass, K. Chakraborty and S. Etienne, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 5348–5362. (b) X. Deng, Z. Zhu, C. Xiong, and L. Zhang, *J. Polym. Sci., Part A: Polym. Chem.* 1997, **35**, 703–708. (c) Z. Jedliński and W. Wałach, *Makromol. Chem.* 1991, **192**, 2051–2057.

11 (a) L. F. Sanchez-Barba, A. Garces, M. Fajardo, C. Alonso-Moreno, J. Fernandez–Baeza, A. Otero, A. Antinolo, J. Tejeda, A. Lara-Sanchez and M. I. Lopez–Solera, *Organometallics*, 2007, **26**, 6403–6411. (b) T.-L. Yu, C.-C. Wu, C.-C. Chen, B.-H. Huang, J. Wu and C.-C. Lin, *Polymer*, 2005, **46**, 5909–5917. (c) B.-T. Ko and C.-C. Lin, *J. Am. Chem. Soc.*, 2001, **123**, 7973–7977. (d) M.-L. Shueh, Y. -S. Wang, B.-H. Huang, C.-Y. Kuo and C.-C. Lin, *Macromolecules*, 2004, **37**, 5155–5162. (e) Y. Wang, W. Zhao, D. Liu, S. Li, X. Liu, D. Cui, and X. Chen, *Organometallics*, 2012, **31**, 4182–4190.

12 (a) Z. Zhong, P. J. Dijkstra, C. Birg, M. Westerhausen and J. Feijen, *Macromolecules*, 2001, **34**, 3863–3868. (b) L. Piao, M. Deng, X. Chen, L. Jiang and X. Jing, *Polymer*, 2003, **44**, 2331–2336. (d) G. Rong, M. Deng, C. Deng, Z. Tang, L. Piao, X. Chen and X. Jing, *Biomacromolecules*, 2003, **4**, 1800–1804.

13 Z. Tang, X. Chen, Q. Liang, X. Bian, L. Yang, L. Piao and X. Jing, *J. Polym. Sci., Part A: Polym. Chem.*, 2003, **41**, 1934–1941.

14 (a) R. H. Platel, L. M. Hodgson and C. K. Williams, *Polym. Rev.*, 2008, **48**, 11–63. (b) Y. Wang and M. Kunioka, *Macromol. Symp.*, 2005, **224**, 193–206. (c) P. Dubois, P. Degee, R. Jerome and P. Teyssie, *Macromolecules*, 1992, **25**, 2614–2618. (d) Z. Florjańczyk, A. Plichta and M. Sobczak, *Polymer*, 2006, **47**, 1081–1090. (e) A. Duda, Z. Florjanczyk, A. Hofman, S. Slomkowski and S. Penczek, *Macromolecules*, 1990, **23**, 1640–1646. (f) A. Duda, *Macromolecules*, 1996, **29**, 1399–1406. (g) N. Ropson, P. Dubois, R. Jerome and P. Teyssie, *Macromolecules*, 1993, **26**, 6378–6385. (h) N. Ropson, P. Dubois, R. Jerome and P. Teyssie, *Macromolecules*, 1994, **27**, 5950–5956. (i) A. Duda and S. Penczek, *Macromolecules*, 1995, **28**, 5981–5992. (j) H. R. Kricheldorf, M. Berl and N. Scharnagl, *Macromolecules*, 1988, **21**, 286–293. (k) M. Akatsuka, T. Aida and S. Inoue, *Macromolecules*, 1995, **28**, 1320–1322. (l) I. Taden, H.-C. Kang, W. Massa and J. Okuda, *J. Organomet. Chem.*, 1997, **540**, 189–192. (m) A. Arbaoui, C. Redshaw and D. L. Hughes, *Chem. Commun.*, 2008, 4717–4719. (m) N. Iwasa, J. Liu and K. Nomura, *Catal. Commun.*, 2008, **9**, 1148–1152. (n) N. Nomura, T. Aoyama, R. Ishii and T. Kondo, *Macromolecules*, 2005, **38**, 5363–5366. (o) W. Yao, Y. Mu, A. Gao, Q. Su, Y. Liu and Y. Zhang, *Polymer*, 2008, **49**, 2486–2491.

15 (a) M. Möller, R. Kånge and J. L. Hedrick, *J. Polym. Sci., Part A: Polym. Chem.*, 2000, **38**, 2067–2074. (b) M. Degirmenci, G. Hizal and Y. Yagci, *Macromolecules*, 2002, **35**, 8265–8270. (c) M. Degirmenci, O. Izgin and Y. Yagci, *J. Polym. Sci., Part A: Polym. Chem.*, 2004, **42**, 3365–3372. (d) B. Kiskan and Y. Yagci, *Polymer*, 2005, **46**, 11690–11697. (e) A. Kowalski, A. Duda and S. Penczek, *Macromolecules*, 2000, **33**, 689–695. (f) J. Libiszowski, A. Kowalski, A. Duda and S. Penczek, *Macromol. Chem. Phys.*, 2002, **203**, 1694–1701. (g) A. D. Celiz and O. A. Scherman, *Macromolecules*, 2008, **41**, 4115–4119.

16 (a) I. Barakat, P. Dubois, R. Jerome and P. Teyssie, *Macromolecules*, 1991, **24**, 6542–6545. (b) Y. Sarazin, M. Schormann and M. Bochmann, *Organometallics*, 2004, **23**, 3296–3302. (c) L. Liao, L. Liu, C. Zhang and S. Gong, *Macromol. Rapid Commun.*, 2006, **27**, 2060–2064.(d) P. Dobrzynski, *Polymer*, 2007, **48**, 2263–2279. (e) B. J. O'Keefe, L. E. Breyfogle, M. A. Hillmyer and W. B. Tolman, *J. Am. Chem. Soc.*, 2002, **124**, 4384–4393. (f) M. G. Davidson, M. D. Jones, M. D. Lunn and M. F. Mahon, *Inorg. Chem.*, 2006, **45**, 2282–2287. (g) A. J. Chmura, M. G. Davidson, M. D. Jones, M. D. Lunn and M. F. Mahon, *Dalton Trans.*, 2006, 887–889. (h) A. J. Chmura, M. G. Davidson, M. D. Jones, M. D. Lunn, M. F. Mahon, A. F. Johnson, P. Khunkamchoo, S. L. Roberts and S. S. F. Wong, *Macromolecules*, 2006, **39**, 7250–7257. (i) D. Takeuchi, T. Nakamura and T. Aida, *Macromolecules*, 2000, **33**, 725–729. (j) Y. Mahha, A. Atlamsani, J.-C. Blais, M. Tessier, J. –M. Brégeault and L. Salles, *J. Mol. Catal. A: Chem.*, 2005, **234**, 63–73.

17 (a) N. Nomura, A. Taira, T. Tomioka and M. Okada, *Macromolecules*, 2000, **33**, 1497–1499. (b) N. Nomura, A. Taira, A. Nakase, T. Tomioka and M. Okada, *Tetrahedron*, 2007, **63**, 8478–8484. (c) X. M. Deng, Z. Zhu, C. Xiong and L. Zhang, *J. Appl. Polym. Sci.*, 1997, **64**, 1295–1299. (d) W. M. Stevels, M. J. K. Ankone, P. J. Dijkstra and J. Feijen, *Macromolecules*, 1996, **29**, 8296–8303. (e) O. Poncelet, W. J. Sartain, L. G. Hubert-Pfalzgraf, K. Folting and K. G. Caulton, *Inorg. Chem.*, 1989, **28**, 263–267. (f) S. Agarwal, M. Karl, K. Dehnicke, G. Seybert, W. Massa and A. Greiner, *J. Appl. Polym. Sci.*, 1999, **73**, 1669–1674. (g) W. Lin, W. L. Sun and Z. Q. Shen, *Chin. Chem. Lett.*, 2007, **18**, 1133–1136. (h) M. Nishiura, Z. Hou, T.-A. Koizumi, T. Imamoto and Y. Wakatsuki, *Macromolecules*, 1999, **32**, 8245–8251. (i) M. Yamashita, Y. Takemoto, E. Ihara and H. Yasuda, *Macromolecules*, 1996, **29**, 1798–1806. (j) E. Martin, P. Dubois and R. Jerome, *Macromolecules*, 2000, **33**, 1530–1535. (k) E. Martin, P. Dubois and R. Jérome, *Macromolecules*, 2003, **36**, 5934–5941. (l) W. M. Stevels, M. J. K. Ankone, P. J. Dijkstra and J. Feijen, *Macromolecules*, 1996, **29**, 3332–3333. (m) Y. Wang, L. F. Zhang, P. Wang and L. J. Shen, *Chinese. J. Polym. Sci.*, 2010, **28**, 509–515.

18 S. Asano, T. Aida and S. Inoue, *J. Am. Chem. Soc.*, 1985, **107**, 1148–1149.

19 C. K. Williams, *Chem. Soc. Rev.*, 2007, **36**, 1573–1580.

20 (a) T. Aida, Y. Maekawa, S. Asano and S. Inoue, *Macromolecules*, 1988, **21**, 1195–1202. (b) H. Sugimoto, T. Aida and S. Inoue, *Macromolecules*, 1990, **23**, 2869–2875. (c) T. Aida and S. Inoue, *Acc. Chem. Res.*, 1996, **29**, 39–48. (d) S. Inoue, *J. Polym. Sci., Part*

A: Polym. Chem. 2000, **38**, 2861–2871. (e) M. Akatsuka, T. Aida and S. Inoue, *Macromolecules* 1994, **27**, 2820–2825.

21 Y. Wang, W. Zhao, X. Liu, D. Cui and E. Y.-X Chen, *Macromolecules*, 2012, **45**, 6957–6965.

22 C. A. Zechmann, T. J. Boyle, M. A. Rodriguez and R. A. Kemp, *Inorg. Chim. Acta.*, 2001, **319**, 137–146.

23 (a) T. Biela, A. Duda and S. Penczek, *Macromol. Symp.* 2002, **183**, 1–10. (b) M. Save, M. Schappacher and A. Soum, *Macromol. Chem. Phys.*, 2002, **203**, 889–899. (c) S. J. McLain and N. E. Drysdale, *Polym. Prepr.*, 1992, **33**, 463–464.

24 (a) M. T. Casas, J. Puiggalí, J.-M. Raquez, P. Dubois, M. E. Córdova and A. J. Müller, *Polymer*, 2011, **35**, 5166–5177. (b) L. Piao, J. Sun, Z. Zhong, Q. Liang, X. Chen, J.-H. Kim and X. Jing, *J. Appl. Polym .Sci.*, 2006, **102**, 2654–2660. (c) N. Niamasa and Y. Baimark, *J. Appl. Polym .Sci.*, 2007, **106**, 3315–3320. (d) R. V. Castillo, *Macromolecules*, 2010, **43**, 4149–4160.

25 (a) W. Susanto, W. J. Ang, Y. Lam, C.-Y. Chu, T.-C. Chou and L.-C. Lo, *Green Chem*, 2012, **14**, 77–80. (b) G. Temel, N. Karaca and N. Arsu, *Polym. Chem.*, 2010, **48**, 5306–5312.

26 (a) J.-T. Wu, C.-H. Huang, W.-C. Liang, Y.-L. Wu, J. Yu and H.-Y. Chen, *Macromol. Rapid Commun.* 2012, **33**, 922−927. (b) D. J. Hall, H. M. Van Den Berghe and A. P. Dove, *Polym. Int.*, 2011, **60**, 1149–1157. (c) Q. Zhang, G.-Z Li, R. Becer and D. M. Haddleton, *Chem. Commun.*, 2012, **48**, 8063–8065. (d) S. Onbulak, S. Tempelaar, R. J. Pounder, O. Gok, R. Sanyal and A. P. Dove, *Macromolecules* 2012, **45**, 1715−1722. (e) M. J. Stanford, R. L. Pflughaupt and A. P. Dove, *Macromolecules*, 2010, **43**, 6538–6541.

27 (a) H. Freichels, V. Pourcelle, C. S. Le Duff, J. Marchand-Brynaert and C. Jérôme, *Macromol. Rapid Commun.*, 2011, **32**, 000–000. (b) J. M. Ren, J. T. Wiltshire, A. Blencowe and G. G. Qiao, *Macromolecules*, 2011, **44**, 3189–3202. N. W. Polaske, D. V. McGrath and J. R. McElhanon, *Macromolecules*, 2011, **44**, 3203–3210. (c) A. Hanisch, H. Schmalz and A. H. E. Müller, *Macromolecules*, 2012, **45**, 8300–8309.

28 D. D. Perrin, W. L. F. Armarego and D. R. Perrin, *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon: Oxford, England, 1980.

29 G. M. Sheldrick, SADABS. 1996. University of Gottingen, Germany.

30 G. M. Sheldrick, *Acta Cryst.* 2008, **A64**, 112–122.

31 L. J. Farrugia, ORTEP–III for Windows–Version 2.0, *J. Appl. Crystallogr.* 1997, **30**, 565. University of Glasgow (2008 copyright).

[a] *State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin street, Changchun 130022, China. Fax: +86 431 85262774; Tel: +86 431 85262773; E-mail: dmcui@ciac.jl.cn; xlliu@ciac.jl.cn;*

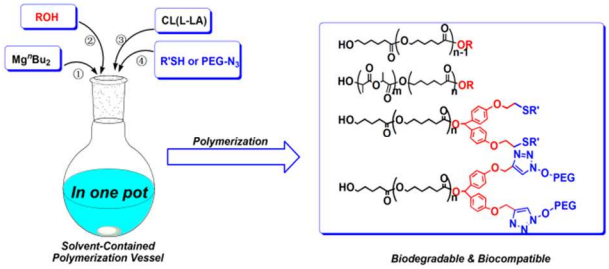
[b] *Graduate School of the Chinese Academy of Sciences, Beijing 100039, China*

† Electronic Supplementary Information (ESI) available: The data of Complex **2** and NMR spectrums of oligomer for end group study and the NMR spectrum of topologic Star-PCL-PEG. See DOI: 10.1039/b000000x/

Table of Content use only

Immortal Ring-Opening Polymerization of ε-Caprolactone by a Neat Magnesium Catalyst System: An Approach to Block and Amphiphilic Star Polymers *In Situ*

Yang Wang[a,b], Bo Liu[a], Xue Wang[a,b], Wei Zhao[a,b], Dongtao Liu[a], Xinli Liu*[a] and Dongmei Cui*[a]



Building of various functional and topological microstructured PCLs via immortal catalyst system Mg^{n}Bu$_2$/ROH and "click reation".