RSC Advances

ROYAL SOCIETY OF CHEMISTRY

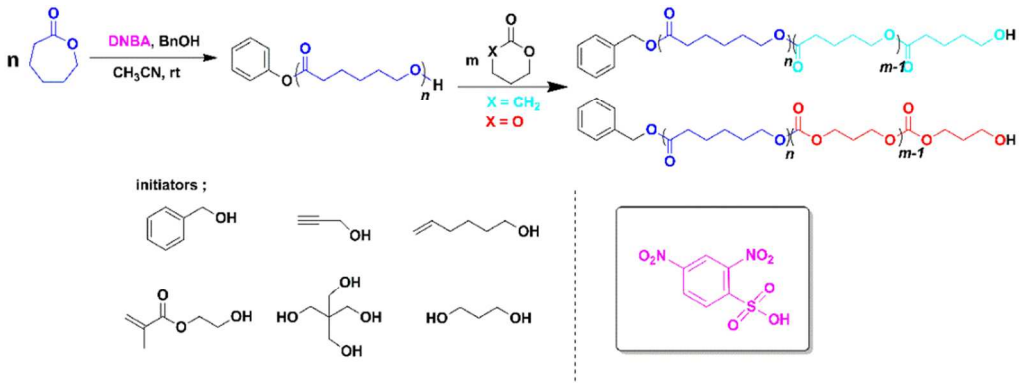
www.rsc.org/advances

GRAPHICAL ABSTRACT

2,4-Dinitrobenzenesulfonic Acid as an Efficient Brønsted Acid-Catalyzed Controlled/Living Ring-Opening Polymerization of *ε*-caprolactone

Huiying Wang, Wenzhuo Wu, Zhenjiang Li,* Xu Zhi, Cheng Chen, Chengxu Zhao, Xiaopei LI, Qiguo Zhang, Kai Guo*

2,4-Dinitrobenzenesulfonic acid as an efficient Brønsted acidic catalyst has been evaluated for the controlled/living ring-opening polymerization (ROP) of *ε*-caprolactone (*ε*-CL) with benzyl alcohol as initiator. Additionally, various initiators (propargyl alcohol, 5-hexen-1-ol, 2-hydroxyethyl methacrylate, 1,3-propanediol, pentaerythritol) were utilized to prepare end-functionalized and *α,ω*-dihydroxy telechelic Poly(*ε*-caprolactone). *δ*-Valerolactone and trimethylene carbonate were also successfully synthesised diblock copolymers of poly(*ε*-caprolactone)-*block*-poly(*δ*-valerolactone) and poly(*ε*-caprolactone)-*block*-poly(trimethylene carbonate).



RSC Advances

RSCPublishing

Paper

2,4-Dinitrobenzenesulfonic Acid as an Efficient Brønsted Acid-Catalyzed Controlled/Living Ring-Opening Polymerization of ε-Caprolactone

Cite this: DOI: 10.1039/xoxxoooooox

Received ooth January 2012,
Accepted ooth January 2012

DOI: 10.1039/xoxxoooooox

www.rsc.org/

Huiying Wang, Wenzhuo Wu, Zhenjiang Li,* Xu Zhi, Cheng Chen, Chengxu Zhao, Xiaopei Li, Qiguo Zhang, Kai Guo*

The ring-opening polymerization of ε-caprolactone (ε-CL) using benzyl alcohol (BnOH) as initiator and 2,4-dinitrobenzenesulfonic acid (DNBA) as catalyst in acetonitrile at room temperature with the $[\varepsilon\text{-CL}]_0/[\text{BnOH}]_0/[\text{DNBA}]_0$ ratio of 40/1/1 has been investigated. The polymerization proceeded to obtain poly(ε-caprolactone) (PCL) with controlled molecular weights. In addition, ^{1}H NMR, SEC, and MALDI-ToF MS measurements all demonstrate the initiator residue at the polymers chain end. Furthermore, propargyl alcohol, 5-hexen-1-ol, 2-hydroxyethyl methacrylate, 1,3-propanediol, pentaerythritol were used as functional initiators to successfully obtained end-functionalized and α,ω-dihydroxy telechelic polyesters. The block copolymerization of PCL and PVL or PTMC to afford well-defined poly(ε-caprolactone)-*block*-poly(δ-valerolactone) (PCL-*b*-PVL) and poly(ε-caprolactone)-*block*-poly(trimethylene carbonate) (PCL-*b*-PTMC).

Introduction

Aliphatic polyesters are attractive biodegradable and biocompatible polymers used in pharmaceutical and medical areas.[1-4] In the past years, polyesters were primarily prepared by ring-opening polymerization (ROP) using metal-based catalysts,[5-11] however, the residual metals limited their wider applications. In order to avoid this disadvantage, much effort was made in metal-free catalysis. Metal-free catalysts what are called organocatalysts are developing rapidly.[1, 12] In particular, using organocatalysts to synthesize well-controlled macromolecular architectures has been studied extensively. Since the first report in 2001, Hedrick and Waymouth have utilized 4-dimethylaminopyridine[13] for living ROP of Lactide. Later on, various organic base catalysts were developed, such as N-heterocyclic carbene,[14-17] thiourea/amine,[18, 19] guanidine,[20] phosphazene,[21, 22] 1,5,7-triazabicyclo [4.4.0] dec-5-ene,[23, 24] and 1,8-diazabicyclo[5.4.0]-undec-7-ene[25, 26] that all promoted the ROP of cyclic esters.

State Key Laboratory of Materials-Oriented Chemical Engineering, College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, 30 Puzhu Rd South,, Nanjing, 211816, China.

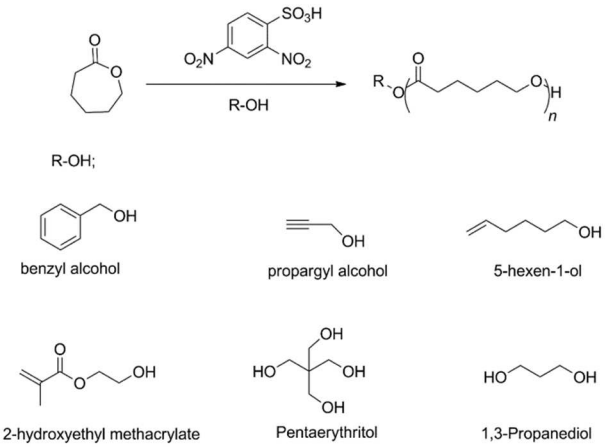
E-mail: zjli@njtech.edu.cn; guok@njtech.edu.cn;

† Electronic supplementary information (ESI) available: 1. ^{1}H NMR for End-Functionalized and a,ω-Dihydroxy Telechelic Poly(ε-caprolactone) and block copolymerization. 2. The calculation details ε-CL conversion. See DOI: 10.1039/b000000x/

Comparatively, Brønsted acid catalysts have not been widely reported. Pioneered in 2000 by Endo and co-workers using $HCl{\cdot}Et_2O$-catalyzed in ROP of lactone,[27, 28] acid catalysts, such as methanesulfonic acid,[29, 30] trifluoromethane sulfonic acid,[29, 31] diphenylphosphate,[32-34] and triflimide,[35, 36] catalyse the ROP of cyclic esters and have attracted more and more attentions. To further extend the scope of acid catalysis system, our group reported several efficient acid catalysts for the controlled/living ROP of cyclic esters.[37-40]

Previously, 2,4-dinitrobenzenesulfonic acid (DNBA) as Brønsted acid proved efficient catalytic performance in Hosomi–Sakurai,[41, 42] Ritter,[43] Friedel–Crafts,[44] and enantioselective protonation[45] reactions. Additionally, DNBA is commercially available, inexpensive, low in toxicity, and easy to store and handle. Comparing to the reported by Córdova in 2004,[46] the advantages of the organic catalyst are inexpensive and low toxicity, however, in Córdova's paper about ROP with organic catalysts, the ROP of CL needed a high temperature 120 °C, and we just conducted in the room temperature. In accordance with those excellent properties of 2,4-dinitrobenzenesulfonic acid, we decide to evaluate the ability of DNBA as catalyst in ROP of ε-CL. Remarkably, 2,4-dinitrobenzenesulfonic acid is a powerful organocatalyst for controlled/living ROP of ε-CL, which promoted a rapid polymerization. A strong electron-withdrawing group can strengthen the acidity of Brønsted acids,[47] since the structural components of DNBA was a benzene ring connected with two

nitro-groups and a sulfonic group. Probably it is the strong electron-withdrawing group (NO_2) that makes the organic acid catalyst with a high reactivity. To date, as far as we know, DNBA was not yet applied in ring-opening polymerization. In this article, we described (1) the characterization and optimization of the DNBA for controlled ROP of ε-caprolactone, (2) the controlled/living nature of the DNBA-catalyzed ROP of ε-CL by ^{1}H NMR, SEC, and MALDI-ToF MS analyses, (3) various initiators being used to initiate the polymerizations and produce end-functionalized and *a,ω*-dihydroxy telechelic polymers (as shown in scheme 1), (4) the synthesis of diblock copolymers consisting of PCL with PVL or PTMC.



Scheme 1 Ring-opening polymerization (ROP) of ε-caprolactone (ε-CL) using 2,4-dinitrobenzenesulfonic acid (DNBA) as the organocatalyst and various alcohols (R-OH) as initiators.

Experimental

Materials

ε-Caprolactone (ε-CL; 99% Sinopharm Chemical Reagent) and δ-valerolactone (δ-VL; 99%, Sinopharm Chemical Reagent) were all distilled over CaH_2 under an inert environments. Trimethylene carbonate (TMC) was synthesized on the basis of the literature method.[48] Acetonitrile (CH_3CN; >99% water content, <0.001%) was dried over 3 Å molecular sieve pellets for 48 h before use. Benzyl alcohol (BnOH; 99%, Acros) was refluxed over CaH_2 prior to its distillation. 2,4-Dinitrobenzenesulfonic acid (DNBA; Tokyo Kasei Kogyo Co., Ltd. (TCI)) were dried prior to use. 5-Hexen-1-ol (Energy Chemical, 98%) and 2-hydroxyethyl methacrylate (J&K Scientific Co. 99.5%) were all distilled under reduced pressure before use. 1,3-Propanediol (Arocs, 99%,) was azeotropically distilled with toluene. Pentaerythritol (Arocs, 99%) was dried over P_2O_5 under high vacuum. Propargyl alcohol (Alfa Aesar, 99%) was distilled over CaH_2. Triethylamine (98%, Sinopharm Chemical Reagent Co.) was used as received.

Characterizations

The number-average molecular weight ($M_{n,NMR}$) and monomer conversion were determined from the ^{1}H NMR spectra in $CDCl_3$ on a Bruker ARX-250 spectrometer at 300 MHz at ambient temperature. Size exclusion chromatography (SEC) was performed in THF using SSI 1500 pump equipped with Waters (5 μm, 300×7.8 mm) column at a flow rate of 0.7 mL min^{-1} at 25 °C, Wyatt Optilab rEX differential refractive index (DRI) detector with a 658 nm light source. Polystyrene were used as standards to determine the number-average molecular weight (M_n) and molecular weight distributions (M_w/M_n) of the polymers. All SEC dates were applied in Wyatt Astra V 6.1.1 software. Matrix assisted laser desorption/ionization time-of-flight mass spectra (MALDI-ToF MS) was performed using a mass spectrometer (ultraflextreme; Bruker Co.) with Smartbeam/Smartbeam II modified Nd: YAG laser. The MALDI-ToF mass spectra represent averages over 500 laser shots at a 25 KV acceleration voltage. The polymer sample was dissolved in $CHCl_3$ at a concentration of 5 mg mL^{-1}, the matrix 2,5-DHB (2,5-dihydroxybenzoic acid) was dissolved in aqueous (1%, 10 μL) solution of trifluoroacetic acid and acetonitrile (volume ratio = 70/30).

General Procedure for Polymerization of ε-Caprolactone

All the reactions were conducted in a glove box at room temperature. ε-Caprolactone (ε-CL) (0.213 mL, 2 mmol, 40 equiv.) was mixed into acetonitrile ([ε-CL]$_0$ = 1.0 mol L^{-1}) using benzyl alcohol (5.2 μl, 0.05 mmol, 1 equiv.) as the initiator. DNBA (0.0124 g, 0.05mmol 1 equiv.) was then dissolved in the reaction solutions. After 4 h, the monomer conversion reached 95.2%, which was determined by ^{1}H NMR. At the end of the polymerization, an excess of triethylamine was added to stop the reaction. The polymer was dissolved in minimum of dichloromethane and separated out from cold methanol, then dried in vacuum drying oven. Conversion: 95.2%, yield, 61.0%. ^{1}H NMR ($CDCl_3$) : δ (ppm), 1.39 (m, 2H × *n*, (–$CH_2CH_2CH_2CH_2CH_2$–)$_n$), 1.63 (m, 2H × *n*, (–$CH_2CH_2CH_2O$–)$_n$), 1.68 (m, 2H × *n*, (–$COCH_2CH_2CH_2$–)$_n$), 2.31 (t, 2H × *n*, *J* = 7.3 Hz, (–$OCOCH_2CH_2$–)$_n$), 3.65(t, 2H, *J* = 6.6Hz, CH_2CH_2OH), 4.06 (t, 2H × n, *J* = 6.6 Hz, (–CH_2CH_2O–)$_n$), 5.12 (s, 2H, $ArCH_2O$), 7.23–7.39 (m, 5H, aromatic). $M_{n,NMR} \approx 4580$ g mol^{-1}, M_w/M_n = 1.16.

Block Copolymerization of ε-Caprolactone and δ-Valerolactone or Trimethylene Carbonate

All the reactions were conducted in a glove box and at room temperature. ε-Caprolactone (ε-CL) (0.213 mL, 2 mmol, 40 equiv.) was mixed into acetonitrile ([ε-CL]0 = 1.0 mol L^{-1}). Benzyl alcohol (5.2 μl, 0.05 mmol, 1 equiv.) was used as the initiator. DNBA (0.0124 g, 0.05mmol 1 equiv.) was then dissolved in the reaction solutions. After 6 hours (we extended the reaction time for full conversation of monomers), 40 equiv. of δ-VL (0.181 mL, 2 mmol) was then added to reaction chamber, and start the block copolymerization to obtain PCL-*b*-PVL under the same conditions. An excess of triethylamine were used to quench the reaction. The polymer was dissolved in a small quantity of CH_2Cl_2 and isolated by cold methanol. Yield, 53%. ^{1}H NMR ($CDCl_3$) : δ (ppm), 1.38 (m, 2H × *n*, (–

$CH_2CH_2CH_2CH_2CH_2–)n$), 1.63 (m, 2H × ($n+m$), (–$CH_2CH_2CH_2CH_2O–)n$), 1.68 (m, 2H × n, (–$COCH_2CH_2CH_2CH_2–)n$), 2.31 (t, 2H × ($n+m$), J = 7.3 Hz, (–$COCH_2CH_2–$)n), 3.65 (t, 2H, J = 6.5Hz, –CH_2CH_2OH), 4.07 (t, 2H × ($n+m$), J = 6.6 Hz, (–$CH_2CH_2O–$)n), 5.12 (s, 2H, $ArCH_2O$), 7.23–7.39 (m, 5H, aromatic). $M_{n,\ NMR} \approx 8140$ g mol^{-1}, $M_w/M_n = 1.16$.

Block Copolymerization of ε-caprolactone and trimethylene carbonate (PCL-*b*-PTMC) was carried out with the similar reaction conditions. Yield, 57.0%. ^{1}H NMR ($CDCl_3$): δ (ppm), 1.39 (m, 2H × n, (–$CH_2CH_2CH_2CH_2CH_2–)n$), 1.66 (m, 4H × n, (–$COCH_2CH_2CH_2–)n$), 1.93(n, 2H , (–OCH_2CH_2OH), 2.01 (m, 2H × m,(–$OCH_2CH_2–)m$), 2.31 (t, 2H × n, J = 6.8 Hz, (–$COCH_2–)n$), 3.75 (m, 2H, –CH_2OH), 4.07 (m, 2H × n, (–$OCH_2CH_2CH_2O–)n$), 4.25 (t, 4H × m, J = 6.4 Hz, (–$OCH_2CH_2CH_2O–)m$), 5.12 (s, 2H, ArCH2O), 7.24–7.38 (m, 5H, aromatic). SEC (THF): $M_{n,\ NMR} \approx 8480$ g mol^{-1}, $M_w/M_n = 1.15$.

Table 1 ROP of ε-Caprolactone (ε-CL) Catalyzed by 2,4-Dinitrobenzenesulfonic Acid (DNBA) with Benzyl Alcohol (BnOH) as the Initiator[a]

Run	[M]/[I]	Solvent	Time (h)	Conv.[b] (%)	$M_{n,\ calcd}$[c] (g mol^{-1})	$M_{n,NMR}$[b] (g mol^{-1})	M_w/M_n[d]	M_w[e] (g mol^{-1})
1	40	CH_2Cl_2	12	45.7	2190	-	-	
2	40	Toluene	12	0	-	-	-	
3	40	THF	12	0	-	-	-	
4[f]	40	Toluene	8	96.3	4500	4460	1.10	2509
5[g]	40	CH_2Cl_2	12	87.3	4100	4330	1.16	3472
6[h]	40	CH_2Cl_2	7	96.7	4520	4260	1.21	3978
7	40	CH_3CN	4	95.2	4450	4580	1.16	4231
8	80	CH_3CN	8	97.9	9050	9190	1.12	6673
9	100	CH_3CN	14	92.1	10620	11180	1.14	9979
10	160	CH_3CN	20	89.0	16360	16580	1.11	3978

[a] $[M]_0$ = 1.0 mol L^{-1}; room temperature. [b] Determined by ^{1}H NMR in $CDCl_3$. [c] Calculated from ($[M]_0/[BnOH]_0$) × conv. × (M_w of ε-CL) + (M_w of BnOH). [d] Determined by SEC in THF using polystyrene standards. [e] Determined by SEC in THF using polystyrene standards and correction factors.[30, 49, 50] [f] catalyzed by diphenyl phosphate (DPP); $[M]_0$ = 1.0 mol L^{-1}; room temperature; in Toluene; $[M]_0/[I]_0/[C]_0$ = 40/1/1. [g] catalyzed by Triflimide ($HNTf_2$); $[M]_0$ = 1.0 mol L^{-1}; in CH_2Cl_2; $[M]_0/[I]_0/[C]_0$ = 40/1/1. [h] catalyzed by trifluoromethanesulfonic acid (HOTf); $[M]_0$ = 1.0 mol L^{-1}; in CH_2Cl_2; $[M]_0/[I]_0/[C]_0$ = 40/1/1.

Results and discussion

Ring-Opening Polymerization of ε-Caprolactone Using Benzyl alcohol and 2,4-Dinitrobenzenesulfonic Acid. In order to evaluate the activity of 2,4-dinitrobenzenesulfonic acid, we used DNBA as the catalyst and benzyl alcohol as the initiator in the ROP of ε-caprolactone in CH_3CN (1.0 mol L^{-1}) at room temperature with [ε-CL]$_0$/[BnOH]$_0$/[DNBA]$_0$ = 40/1/1 (Table 1, Run 4). The monomer conversion reached 95.2% after 4h, which was determined from the ^{1}H NMR spectrum. To find the optimization of DNBA-catalyzed ROP of ε-CL reaction conditions, different solvents were carried out in DNBA-catalyzed ROP of ε-CL. (Table 1, Run 1–4). Toluene and THF were used as the solvent respectively, while no polymer was separate out, thus, they acted as poor solvents for DNBA-catalysed ROP of ε-CL; DNBA could partly soluble in CH_2Cl_2 (completely dissolved at the end of polymerization), thus with moderate monomer conversion (45.7% after 12 h). The results demonstrated that CH_3CN was suitable solvent for DNBA-catalyzed the ROP of ε-CL. In this paper, we provided the experiments for ROP of CL using other organocatalysts (diphenyl phosphate (DPP), Triflimide ($HNTf_2$) and trifluoromethanesulfonic acid (HOTf)) from other catalytic systems to compared catalytic performances, at room temperature with the $[M]_0/[I]_0/[C]_0$ ratio of 40/1/1 to afford poly(ε-caprolactone) (PCL), as shown in Table 1 (Run 4, Run 5, Run 6). All the results domestrated that 2,4-dinitrobenzenesulfonic acid (DNBA) with a better manner for the ROP of ε-CL.

According to ^{1}H NMR spectra of the obtained PCL (FIGURE 1), the peaks of initiator (BnOH) were observed, they appeared in the scope of 7.23-7.39 (A) ppm and 5.12 (B) ppm. The peaks for polymer chain (PCL) was observed in 2.31 (C), 1.62–1.70 (D+F), 1.39 (E), 4.05 (G) and 3.65 (H) ppm, respectively. Those results demonstrated that the obtained PCL was initiated from BnOH.

RSC Advances RSCPublishing

Paper

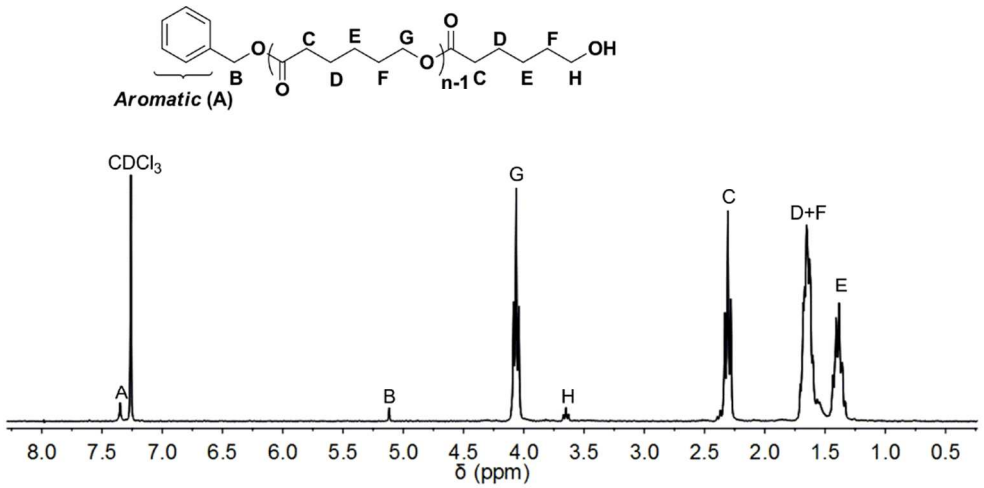


Fig. 1 ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of Poly(ε-caprolactone) ([ε-CL]$_0$/[BnOH]$_0$/[DNBA]$_0$ = 40/1/1) CH_3CN, rt, [M]$_0$ = 1.0 mol L^{-1}, 4 h.

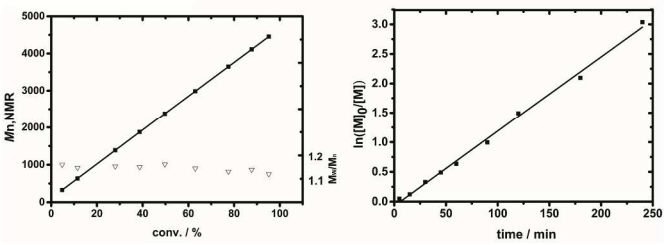


Fig. 2 (A) Molecular weight (M_n) and polydispersity (M_w/M_n) versus the monomer conversion of ε-CL (Theoretical M_n (solid line) calculated from 108.13 (M_w of BnOH) + conv. × ([M]/[I]) × 114.07 (M_w of ε-CL)) and (B) kinetic plots for the polymerization of ε-CL ([ε-CL]$_0$/[BnOH]$_0$/[DNBA]$_0$ = 40/1/1).

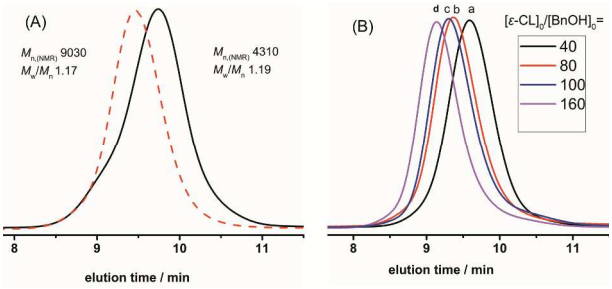


Fig. 3 (A) SEC traces of first PCL sequence (solid line) and postpolymerization (dashed line). (B) SEC traces of PCLs with various [M]$_0$/[I]$_0$ ratios of 40 (a), 80 (b), 100 (c), 160 (d). (eluant, THF; flow rate, 0.7 mL min^{-1}).

TABLE 2 Syntheses of End-Functionalized and a,ω-Dihydroxy Telechelic Poly(ε-caprolactone) by the DNBA-Catalyzed ROP of ε-CL Using various Initiators.[a]

Run	Initiator	Conv.[b] (%)	$M_{n,\ calcd}$[c] (g mol^{-1})	$M_{n,NMR}$[b] (g mol^{-1})	M_w/M_n[d]	M_w[e]
1	propargyl alcohol	96.7	4510	4390	1.11	2497
2	5-hexen-1-ol	97.2	4540	4250	1.13	2531
3	HEMA[f]	98.1	4610	4410	1.15	4119
4	Pentaerythritol	98.3	4190	4490	1.17	3763
5	1,3-Propanediol	90.1	4620	4460	1.10	2508

RSC Advances RSCPublishing

Paper

[a] at room temperature; solvent, CH_3CN; time, 10 h; $[M]_0/[I]_0/[DNBA]_0$=40/1/1; $[M]_0$ = 1.0 mol L^{-1}. [b] Determined by ^1H NMR in $CDCl_3$. [c] Calculated from $([M]_0/[I]_0)\times$ conv. × (M_w of ε-CL) + (M_w of Initiator). [d] Determined by SEC in THF using polystyrene standards. [e] Determined by SEC in THF using polystyrene standards and correction factors.[30, 49, 50] [f] HEMA = 2-hydroxyethyl methacrylate

Moreover, in order to certify the controlled/living nature of the polymerizations, we carried out ROPs of ε-CL by varying $[\varepsilon\text{-CL}]_0/[BnOH]_0$ ratio from 40 to 160 (Table 1, Run 4–7), the results showed that the obtained PCLs of predicted $M_{n\ (NMR)}$ agreed with calculated ones by the initial ratio of $[\varepsilon\text{-CL}]_0/[BnOH]_0$ and the monomer conversions. For example, in the 40-mer (Table 1, Run 4), the values of 4580 g mol^{-1} detected by ^{1}HNMR was nicely agreed with calculate values of 4450 g mol^{-1}. In addition, molecular weights of the polymers can be higher than 16000 g mol^{-1}, simultaneously, the polydispersity (M_w/M_n) values of PCLs range from 1.19–1.12 by SEC analysis.

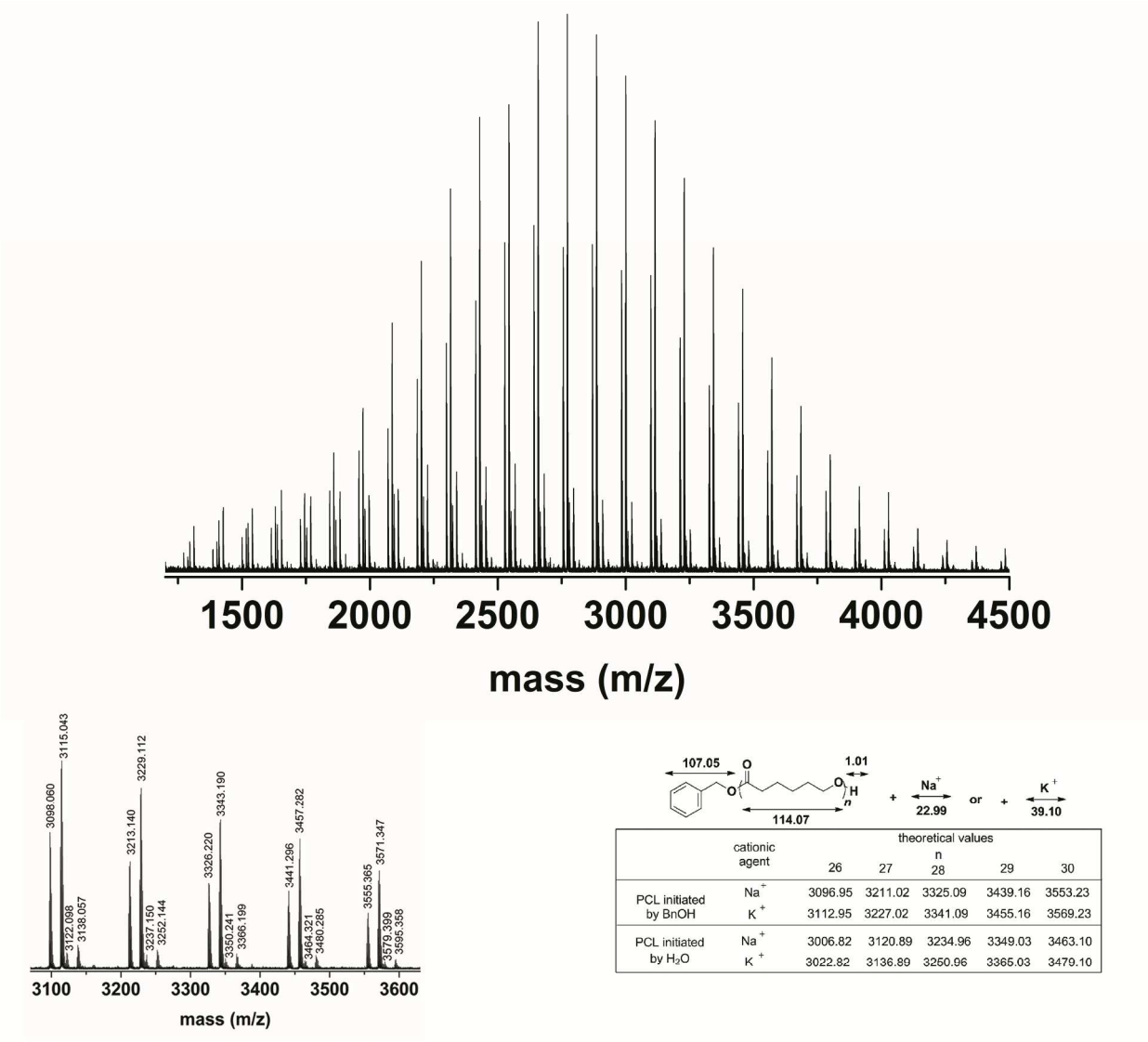
Furthermore, the kinetics and postpolymerization experiments were provided forceful evidences of DNBA-catalyzed ROP of ε-CL with controlled/living nature. As shown in Fig. 2, we explored $[\varepsilon\text{-CL}]_0$ = 1.0 mol L^{-1} and $[\varepsilon\text{-CL}]_0/[BnOH]_0/[DNBA]_0$ = 40/1/1, a liner relationship between monomer conversion and molecule mass values of PCLs was observed (Fig. 2(A)). The plots of $\ln([M]_0/[M])$ *vs*. reaction time also fitted strict linear relationship (Fig. 2(B)). Fig. 3(A) shows the SEC traces for chain extension experiments, the first polymerization proceed with $[\varepsilon\text{-CL}]_0/[BnOH]_0/[DNBA]_0$ = 40/1/1 in CH_3CN at room temperature without quench, the monomer conversion reached 97% after 6 h, and PCL with $M_{n,\ NMR}$ = 4310 g mol^{-1}, M_w/M_n = 1.19. Additional ε-CL (40 equiv.) was added to performed the second polymerization, and obtained PCL with $M_{n,\ NMR}$ = 9030 g mol^{-1}, M_w/M_n = 1.17, indicating that the chain end group of PCL with living nature. Besides, Fig. 3(B) shows the SEC traces of varying $[\varepsilon\text{-CL}]_0/[BnOH]_0$ from 40 to 160, and the PCLs were with low polydispersities. All the results implied the polymerizations featured with characteristics of controlled/living nature.

In order to provide further evidence, the MALDI-ToF MS measurements were applied to prove that the DNBA-catalyzed ROP of ε-CL was initiated by BnOH. As shown in Fig. 4, the MALDI-ToF MS analyses obtained PCL with monomers to initiator ratios of 40, in which PCL with molecular formula of molar mass M = 108.13 (M_w of BnOH) + n × 114.07 (M_w of ε-CL) + 23 (Na^+) or M = 108.13 (M_w of BnOH) + n × 114.07 (M_w of ε-CL) +39 (K^+), indicating that BnOH residue at the chain end. In addition, the mass differences between two adjacent peaks were a ε-CL unit. Those results strongly implied that BnOH initiated the polymerization, and emerged as a living manner without backbiting, transesterification or other undesirable side reactions. In addition, though the monomer (ε-CL), the catalyst (2,4-dinitrobenzenesulfonic acid), the initiator (BnOH) and the solvent (acetonitrile) was through rigorous drying process before use, there also concomitant loss of H_2O. From the MALDI-ToF MS spectrum, another two series of undesired peaks were initiated by H_2O. Obviously, measured values of wather initiated were equal to theoretical values (as shown in figure 4). According to the report of Penczek and co-workers, the mechanism of Brønsted acid-catalyzed ROP of cyclic esters were activated monomer mechanism (AM), leading to well-defined polyesters,[51] we proposed a similar AM mechanism as shown in scheme 2.

RSC Advances

RSCPublishing

Paper

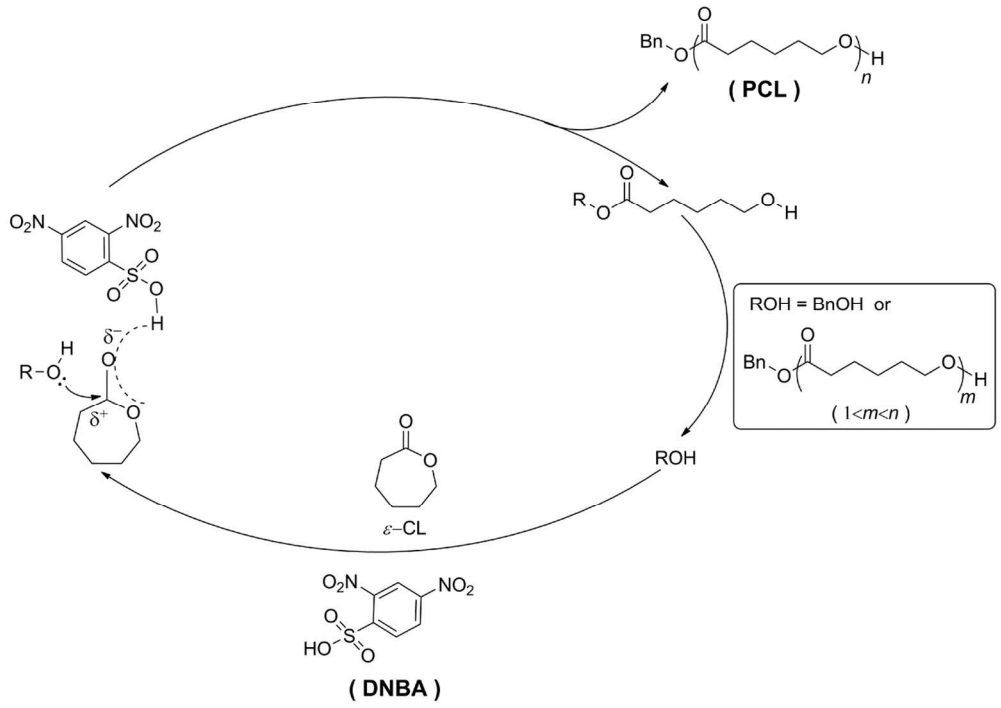


	cationic agent	theoretical values n 26	27	28	29	30
PCL initiated by BnOH	Na^+	3096.95	3211.02	3325.09	3439.16	3553.23
	K^+	3112.95	3227.02	3341.09	3455.16	3569.23
PCL initiated by H_2O	Na^+	3006.82	3120.89	3234.96	3349.03	3463.10
	K^+	3022.82	3136.89	3250.96	3365.03	3479.10

Fig. 4 MALDI-ToF MS spectra of the obtained PCL ([ε-CL]$_0$/[BnOH]$_0$/[DNBA]$_0$ = 40/1/1, conversion = 95.2%, $M_{n,NMR}$ = 4580 g mol^{-1}, M_w/M_n = 1.16).

RSC Advances RSCPublishing

Paper



Scheme 2 An Activated Monomer Mechanism for the DNBA-Catalyzed ROP of ε-CL Using BnOH as the initiator.

Syntheses of End-Functionalized and *a,ω*-Dihydroxy Telechelic Poly(*ε*-caprolactone). For the purpose of evaluating DNBA-catalyzed polymerizations with characteristic of controlled/living nature, we utilized DNBA-catalyzed ROP of ε-CL with propargyl alcohol, 5-hexen-1-ol, 2-hydroxyethyl methacrylate, 1,3-propanediol, and pentaerythritol as initiators for provide end-functionalized and *a,ω*-dihydroxy telechelic polymers, which were confirmed by ^{1}H NMR spectra, (Figures S1-S5). The obtained polymers with alkyne group could serve for click reaction,[52, 53] and polymers with methacrylate group as macromonomers, and polymers along with alkene could use for further modifications.[52, 54] Table 2 lists the results for obtained poly(ε-caprolactone), for the PCLs initiated by propargyl alcohol, 5-hexen-1-ol, 2-hydroxyethyl methacrylate, pentaerythritol, and 1,3-propanediol, the values of $M_{n,NMR}$ of 4390, 4250, 4410, 4490 and 4460 g mol^{-1} correspond to the $M_{n,calcd}$ of 4510, 4540, 4610, 4190 and 4620 g mol^{-1}, respectively. Meanwhile, the M_w/M_n was at the range of 1.10–1.17 (Table 2), showed narrow distributions. Thus, we revealed that DNBA was an efficient organo-catalyst to syntheses well-defined macromolecular architectures.

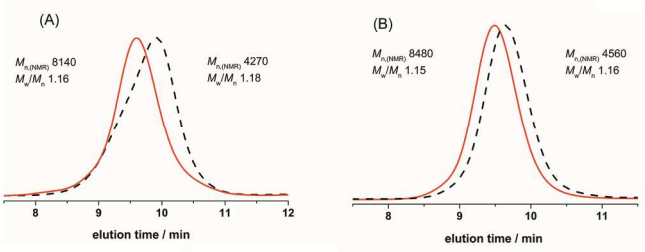


Fig. 5 (A) SEC traces of first sequence of poly(ε-caprolactone) (PCL; dashed line) and poly(ε-caprolactone)-*block*-poly(δ-valerolactone) (PCL-*b*-PVL, solid line), (B) SEC traces of first sequence of poly(ε-caprolactone) (PCL; dashed line) and poly(ε-caprolactone)-*block*-poly(trimethylene carbonate) (PCL-*b*-PTMC, solid line).

Synthesis Diblock Copolymers of ε-Caprolactone and δ-Valerolactone or Trimethylene Carbonate. According to the chain extension experiments, we concluded that the chain end of obtained PCL has a living nature. Indeed, we also explored the copolymerization of ε-CL with two different monomers (δ-

VL and TMC) producing PCL-*b*-PVL and PCL-*b*-PTMC which were versatile as biodegradable materials, and it also illustrated that hydroxyl group at the chain end with further polymerization ability. We carried out first polymerization with $[\varepsilon\text{-CL}]_0/[\text{BnOH}]_0/[\text{DNBA}]_0$ = 40/1/1, after the monomer was consumed completely without quenching, then added another monomer (δ-VL, 40 equiv.) for second polymerization. Besides, TMC (40 equiv.) was as the second monomer to synthesize diblock copolymers (PCL-*b*-PTMC) carried out with the same method. The obtained copolymers were determined by ^{1}H NMR spectra (Supporting information Figures S6, S7). Then, the SEC traces illustrated the molar mass of the obtained PCL-*b*-PVL shifted from 4270 to 8140 g mol^{-1}, and the polydispersity was slightly narrowed from 1.18 to 1.16; and the molar mass of PCL-*b*-PTMC shifted from 4560 to 8480 g mol^{-1}, and the polydispersity was varied from 1.16 to 1.15, as shown in fig. 5. All the results indicated DNBA was an efficient catalyst in synthesis of well-defined diblock copolymers of ε-CL with δ-VL and TMC.

Conclusions

In this work, we used DNBA as an efficient Brønsted Acid organocatalyst for ROP of ε- caprolactone (ε-CL) and BnOH as the initiator to product well-defined poly(ε-caprolactone)s (PCLs). The polymerization proceeded in a controlled/living nature, and the obtained polymers featured with narrow polydispersity even at high molecular weights. Moreover, we utilized various initiators (propargyl alcohol, 5-hexen-1-ol, 2-hydroxyethyl methacrylate, 1,3-propanediol, pentaerythritol) to produce end-functionalized and *a,ω*-dihydroxy telechelic poly(ε-caprolactone)s. We also synthesized well-defined block copolymers of PCL-*b*-PVL and PCL-*b*-PTMC. DNBA as commercial available, inexpensive and shelf-stable acidic catalyst may hopefully applicable in wider range of ring-opening polymerizations, and we will extend DNBA catalysis in diversity of cyclic esters.

Acknowledgements

This work was supported by the National High Technology Research and Development Program of China (2011AA02A202), the Doctoral Program of Higher Education of China (20123221110009), and a Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions. We would like to thank Dr. Hailong Liu of Nanjing Normal University for conducting the MALDI-TOF MS experiments and Dr. Zhe Song of China Pharmaceutical University for NMR analyses.

Notes and references

1. N. E. Kamber, W. Jeong, R. M. Waymouth, R. C. Pratt, B. G. G. Lohmeijer and J. L. Hedrick, *Chem. Rev.*, 2007, **107**, 5813-5840.
2. D. G. Barrett and M. N. Yousaf, *Molecules*, 2009, **14**, 4022-4050.
3. P. Lecomte and C. Jerome, in *Synthetic Biodegradable Polymers*, eds. B. Rieger, A. Kunkel, G. W. Coates, R. Reichardt, E. Dinjus and T. A. Zevaco, 2012, vol. 245, pp. 173-217.
4. H. R. Kricheldorf, *Chem. Rev.*, 2009, **109**, 5579-5594.
5. A. P. Dove, *Chem. Commun.*, 2008, 6446-6470.
6. H. R. Kricheldorf, I. Kreiser-Saunders and A. Stricker, *Macromolecules*, 2000, **33**, 702-709.
7. O. Dechy-Cabaret, B. Martin-Vaca and D. Bourissou, *Chem. Rev.*, 2004, **104**, 6147-6176.
8. A. C. Albertsson and I. K. Varma, *Biomacromolecules*, 2003, **4**, 1466-1486.
9. J. C. Wu, T. L. Yu, C. T. Chen and C. C. Lin, *COORDIN CHEM REV*, 2006, **250**, 602-626.
10. C. A. Wheaton, P. G. Hayes and B. J. Ireland, *Dalton Trans.*, 2009, 4832-4846.
11. A. Sauer, A. Kapelski, C. Fliedel, S. Dagorne, M. Kol and J. Okuda, *Dalton Trans.*, 2013, **42**, 9007-9023.
12. D. Bourissou, S. Moebs-Sanchez and B. Martin-Vaca, *C. R.Chim.*, 2007, **10**, 775-794.
13. F. Nederberg, E. F. Connor, M. Moller, T. Glauser and J. L. Hedrick, *Angew. Chem. Int. Ed.*, 2001, **40**, 2712-2715.
14. E. F. Connor, G. W. Nyce, M. Myers, A. Mock and J. L. Hedrick, *J. Am. Chem. Soc.*, 2002, **124**, 914-915.
15. G. W. Nyce, T. Glauser, E. F. Connor, A. Mock, R. M. Waymouth and J. L. Hedrick, *J. Am. Chem. Soc.*, 2003, **125**, 3046-3056.
16. A. P. Dove, H. Li, R. C. Pratt, B. G. G. Lohmeijer, D. A. Culkin, R. M. Waymouth and J. L. Hedrick, *Chem. Commun.*, 2006, 2881-2883.
17. N. E. Kamber, W. Jeong, S. Gonzalez, J. L. Hedrick and R. M. Waymouth, *Macromolecules*, 2009, **42**, 1634-1639.
18. A. P. Dove, R. C. Pratt, B. G. G. Lohmeijer, R. M. Waymouth and J. L. Hedrick, *J. Am. Chem. Soc.*, 2005, **127**, 13798-13799.
19. R. C. Pratt, B. G. G. Lohmeijer, D. A. Long, P. N. P. Lundberg, A. P. Dove, H. Li, C. G. Wade, R. M. Waymouth and J. L. Hedrick, *Macromolecules*, 2006, **39**, 7863-7871.
20. L. Zhang, R. C. Pratt, F. Nederberg, H. W. Horn, J. E. Rice, R. M. Waymouth, C. G. Wade and J. L. Hedrick, *Macromolecules*, 2010, **43**, 1660-1664.
21. L. Zhang, F. Nederberg, J. M. Messman, R. C. Pratt, J. L. Hedrick and C. G. Wade, *J. Am. Chem. Soc.*, 2007, **129**, 12610-+.
22. L. Zhang, F. Nederberg, R. C. Pratt, R. M. Waymouth, J. L. Hedrick and C. G. Wade, *Macromolecules*, 2007, **40**, 4154-4158.
23. R. C. Pratt, B. G. G. Lohmeijer, D. A. Long, R. M. Waymouth and J. L. Hedrick, *J. Am. Chem. Soc.*, 2006, **128**, 4556-4557.
24. A. Chuma, H. W. Horn, W. C. Swope, R. C. Pratt, L. Zhang, B. G. G. Lohmeijer, C. G. Wade, R. M. Waymouth, J. L. Hedrick and J. E. Rice, *J. Am. Chem. Soc.*, 2008, **130**, 6749-6754.
25. B. G. G. Lohmeijer, R. C. Pratt, F. Leibfarth, J. W. Logan, D. A. Long, A. P. Dove, F. Nederberg, J. Choi, C. Wade, R. M. Waymouth and J. L. Hedrick, *Macromolecules*, 2006, **39**, 8574-8583.
26. H. A. Brown, A. G. De Crisci, J. L. Hedrick and R. M. Waymouth, *ACS Macro Lett.*, 2012, **1**, 1113-1115.
27. Y. Shibasaki, H. Sanada, M. Yokoi, F. Sanda and T. Endo, *Macromolecules*, 2000, **33**, 4316-4320.

28. F. Sanda, H. Sanada, Y. Shibasaki and T. Endo, *Macromolecules*, 2002, **35**, 680-683.
29. S. Gazeau-Bureau, D. Delcroix, B. Martin-Vaca, D. Bonrissou, C. Navarro and S. Magnet, *Macromolecules*, 2008, **41**, 3782-3784.
30. D. Delcroix, B. Martin-Vaca, D. Bourissou and C. Navarro, *Macromolecules*, 2010, **43**, 8828-8835.
31. D. Bourissou, B. Martin-Vaca, A. Dumitrescu, M. Graullier and F. Lacombe, *Macromolecules*, 2005, **38**, 9993-9998.
32. K. Makiguchi, T. Satoh and T. Kakuchi, *Macromolecules*, 2011, **44**, 1999-2005.
33. K. Makiguchi, Y. Ogasawara, S. Kikuchi, T. Satoh and T. Kakuchi, *Macromolecules*, 2013, **46**, 1772-1782.
34. D. Delcroix, A. Couffin, N. Susperregui, C. Navarro, L. Maron, B. Martin-Vaca and D. Bourissou, *polym.chem.*, 2011, **2**, 2249-2256.
35. R. Kakuchi, Y. Tsuji, K. Chiba, K. Fuchise, R. Sakai, T. Satoh and T. Kakuchi, *Macromolecules*, 2010, **43**, 7090-7094.
36. K. Makiguchi, S. Kikuchi, T. Satoh and T. Kakuchi, *J. Polym. Sci.Part A: Polym. Chem.*, 2013, **51**, 2455-2463.
37. S. Kan, Y. Jin, X. He, J. Chen, H. Wu, P. Ouyang, K. Guo and Z. Li, *polym.chem.*, 2013, **4**, 5432.
38. J. Chen, S. Kan, H. Xia, F. Zhou, X. Chen, X. Jiang, K. Guo and Z. Li, *Polymer*, 2013, **54**, 4177-4182.
39. X. He, Y. Ji, Y. Jin, S. Kan, H. Xia, J. Chen, B. Liang, H. Wu, K. Guo and Z. Li, *J. Polym. Sci.Part A: Polym. Chem.*, 2014, **52**, 1009-1019.
40. Y. Jin, Y. Ji, X. He, S. Kan, H. Xia, B. Liang, J. Chen, H. Wu, K. Guo and Z. Li, *polym.chem.*, 2014, **5**, 3098-3106.
41. D. Kampen, A. Ladepeche, G. Classen and B. List, *Adv. Synth. Catal.*, 2008, **350**, 962-966.
42. D. Kampen and B. List, *Synlett*, 2006, 2589-2592.
43. R. Sanz, A. Martinez, V. Guilarte, J. M. Alvarez-Gutierrez and F. Rodriguez, *European Journal Of Organic Chemistry*, 2007, 4642-4645.
44. W. Zhou, L.-W. Xu, L. Li, L. Yang and C.-G. Xia, *European Journal Of Organic Chemistry*, 2006, 5225-5227.
45. E. M. Beck, A. M. Hyde and E. N. Jacobsen, *Organic Letters*, 2011, **13**, 4260-4263.
46. J. Casas, P. V. Persson, T. Iversen and A. Cordova, *Adv. Synth. Catal.*, 2004, **346**, 1087-1089.
47. C. H. Cheon and H. Yamamoto, *Chem. Commun.*, 2011, **47**, 3043-3056.
48. J. Matsuo, K. Aoki, F. Sanda and T. Endo, *Macromolecules*, 1998, **31**, 4432-4438.
49. M. Save, M. Schappacher and A. Soum, *Macromolecular Chemistry And Physics*, 2002, **203**, 889-899.
50. I. Palard, M. Schappacher, B. Belloncle, A. Soum and S. M. Guillaume, *Chemistry-a European Journal*, 2007, **13**, 1511-1521.
51. S. Penczek, *J. Polym. Sci.Part A: Polym. Chem.*, 2000, **38**, 1919-1933.
52. H. Misaka, R. Kakuchi, C. Zhang, R. Sakai, T. Satoh and T. Kakuchi, *Macromolecules*, 2009, **42**, 5091-5096.
53. J. N. Hoskins and S. M. Grayson, *Macromolecules*, 2009, **42**, 6406-6413.
54. M. Xie, J. Shi, L. Ding, J. Li, H. Han and Y. Zhang, *J. Polym. Sci.Part A: Polym. Chem.*, 2009, **47**, 3022-3033.