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Preparation and Characterization of Linear and Miktoarm Star Side-Chain Liquid Crystalline block Copolymers with *p*-Methoxyazobenzene Moieties via a Combination of ATRP and ROP

Lei Zhang^a; Wei Zhang^a; Nianchen Zhou^a; Jian Zhu^a; Zhengbiao Zhang^a; Zhenping Cheng^a; Xiulin Zhu^a

^a Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, China

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Preparation and Characterization of Linear and Miktoarm Star Side-Chain Liquid Crystalline block Copolymers with *p*-Methoxyazobenzene Moieties via a Combination of ATRP and ROP

LEI ZHANG, WEI ZHANG, NIANCHEN ZHOU, JIAN ZHU, ZHENG BIAO ZHANG, ZHENGPING CHENG and XIULIN ZHU*

Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China

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One linear and two miktoarm star side-chain liquid crystalline (LC) block copolymers with *p*-methoxyazobenzene moieties were prepared by a combination of ring-opening polymerization (ROP) and atom transfer radical polymerization (ATRP) techniques. First, ROPs of ϵ -caprolactone (ϵ -CL) were carried out catalyzed by $\text{Sn}(\text{Oct})_2$ using three multifunctional initiators, hydroxyethyl 2-bromoisobutyrate (AB type), 3-hydroxy-2-(hydroxymethyl)-2-methylpropyl 2-bromo-2-methylpropanoate (A_2B type) and 2,2-bis(hydroxymethyl)propane-1,3-diyl bis(2-bromo-2-methylpropanoate) (A_2B_2 type), at 110°C in toluene, respectively. Second, the previously obtained poly(ϵ -caprolactone)s (PCLs) with bromine functionalities were used as the macroinitiators to conduct ATRP of 6-(4-methoxy-4-oxy-azobenzene) hexyl methacrylate (MMAZO) with $\text{CuBr}/\text{PMDETA}$ as the catalyst systems at 85°C in anisole to prepare the linear and miktoarm side-chain LC block copolymers (PCL-*b*-PMMAZO, (PCL)₂-(PMMAZO) and (PCL)₂-(PMMAZO)₂). The produced polymers were well-controlled with the controlled molecular weights and the relatively narrow molecular weight distributions ($M_w/M_n \leq 1.35$). The structures of the obtained polymers were all characterized by NMR, FT-IR and GPC analysis. Furthermore, the LC properties of the linear and miktoarm star block copolymers were also investigated by differential scanning calorimetry (DSC) and thermal polarized optical microscopy (POM).

Keywords: Liquid crystalline polymer, miktoarm star copolymer, atom transfer radical polymerization, ring-opening polymerization

1 Introduction

In recent years, azobenzene-containing polymers (azo polymers) have attracted considerable research interests due to their potential applications in many fields, such as optical data storage (1,2), liquid crystal displays (3), holographic surface relief gratings (4,5) etc. Their unique reversible photoisomerizations between the trans-to-cis isomers of the chromophores can induce large changes in its size, shape and polarity (6–8). In particular, azobenzene-containing side-chain liquid crystalline (LC) polymers are among the most interesting materials due to their combination of liquid crystalline behaviors and polymeric

properties (9–11). Meanwhile, poly(ϵ -caprolactone) (PCL) as one kind of aliphatic polyesters have also being paid much attention due to their biodegradability, biocompatibility, and high drug permeability (12), which made its homo- and copolymers having potential application in drug delivery (13), tissue engineering (13–15), surgical sutures (16), packing materials (17,18) etc.

More recently, miktoarm star block copolymers have generated a great deal of interests for their unique bulk and solution properties, such as crystalline, mechanical, lower solution and melt viscosities compared to their linear polymers (29–36). Previously, the well-defined star block copolymers were mainly prepared only by living anionic polymerization method, however, the relatively rigorous experimental conditions and finite range of polymerized monomers limited its further development. Fortunately, the emergence of the controlled/“living” radical polymerization (CRP) methods, such as nitroxide-mediated radical polymerization (NMRP) (19–21), atom transfer radical polymerization (ATRP) (22–23), and reversible

*Address correspondence to: Xiulin Zhu, Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China. Fax: 86-512-65112796; E-mail: xlzhu@suda.edu.cn

addition-fragmentation chain transfer (RAFT) (24,25) polymerization, realizes the preparation of miktoarm star block copolymers under relatively mild reaction conditions. Among them, ATRP has been proven to be a very powerful technique for preparation of homo-, block- and star polymers with designed structures, defined molecular weights and narrow molecular weight distributions (26–28). Although CRP methods have many advantages compared with living anionic polymerization and conventional radical polymerization methods, it is difficult to synthesize miktoarm star block copolymers via only one CRP technique. So combinations of different CRP methods have been used to prepare miktoarm star block copolymers (29–40). As to preparation of azobenzene-containing side-chain LC homo- and block polymers via CRP methods, ATRP and RAFT methods were mainly reported (41–46). Liao et al. reported (41) the successful preparation of amphiphilic side-chain LC diblock copolymers containing soft polyethylene oxide (PEO) blocks and polymethacrylate with azobenzene moieties (PMMAZO) via ATRP method. Our group also reported the preparation of amphiphilic azobenzene-containing side-chain block copolymers (poly{6-(4-phenylazophenoxy)hexylmethacrylate}-*b*-poly{2-(dimethylamino)ethyl methacrylate} (PAHMA-*b*-PDMAEMA)) via RAFT [42] and three-armed star azobenzene-containing side-chain block copolymers (PMMAZO-*b*-PMMA) by ATRP technique (43), respectively. Tang et al. (44) synthesized 4-arm star azobenzene-containing side-chain polymers with different terminal substituent via ATRP. However, as far as we are concerned, the preparations of miktoarm star azobenzene-containing side-chain LC polymers were rarely reported. He et al. prepared azobenzene-containing side-chain LC ABC (45) triblock copolymers and ABC₂ (46) type block copolymers via ATRP method.

In this article, we reported the synthesis of one linear and two miktoarm star side-chain LC block copolymers with *p*-methoxyazobenzene moieties ((PCL-*b*-PMMAZO, (PCL)₂-(PMMAZO) and (PCL)₂-(PMMAZO)₂)) via a combination of ROP and ATRP technique based on three novel miktifunctional initiators (AB, A₂B and A₂B₂ types). Meanwhile, the LC properties of the linear and miktoarm star block copolymers were also investigated.

2 Experiments

2.1 Materials

1,1,1-Tris(hydroxymethyl)ethane (99%, Aldrich), stannous octoate (Sn(Oct)₂, Aldrich), ϵ -caprolactone (99%, Aldrich). The 2-bis(hydroxymethyl)-1,3-propanediol (pentaerythritol, >95%, Shanghai Chemical Reagent) was dried under reduced pressure overnight prior to use. Copper bromide (98%; Aldrich) was stirred with acetic acid for 12 h, washed with ethanol and diethyl ether, and then dried in vacuum. Anisole and CHCl₃ were distilled before use. 1-Chloro-6-hydroxyhexane (Shanghai Chemical Reagent, 95%), and *N*,

N', *N''*, *N'''*-pentamethyldiethylenetriamine (PMDETA) (98%; Jiangsu Liyang Jiangdian Chemical Factory, Liyang, China) was dried with 4-Å molecular sieve and distilled in vacuum. Tetrahydrofuran (THF) was distilled from a purple sodium ketyl solution. *N,N*-Dimethylformamide (DMF) was dried over molecular sieves (4Å) and distilled before use. Other chemical reagents (Shanghai Chemical Reagent, analytical reagents) were used as received.

2.2 Instrumentation

¹H-NMR spectra were recorded on an INOVA 400 MHz nuclear magnetic resonance (NMR) instrument, using CDCl₃ or dimethylsulfoxide-*d*₆ (DMSO-*d*₆) as the solvent and tetramethylsilane (TMS) as the internal standard at ambient temperature. FT-IR spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer. The elemental analyses for C, H, and N were tested by a LECO-CHNS microanalyzer. The molecular weights and molecular weight distributions of the polymers were determined with a Waters 1515 gel permeation chromatography (GPC) equipped with refractive index detector, using HR1, HR3, and HR4 column with molecular weight range 100–500,000 calibrated with PS standard samples. THF was used as the eluent at a flow rate of 1.0 mL min⁻¹ operated at 30°C. The conversions of the monomers were determined gravimetrically.

2.3 Synthesis of the Initiators

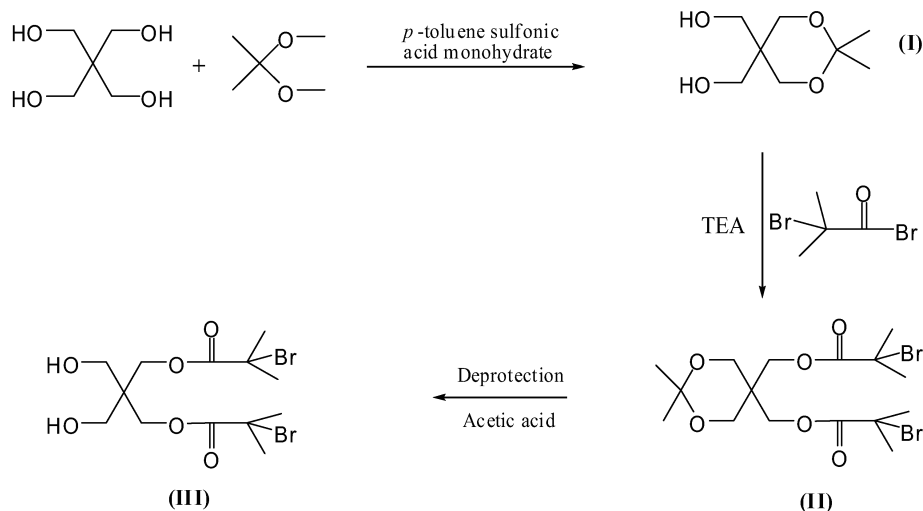
Hydroxyethyl 2-bromoisobutyrate (AB type) was synthesized according to the literature (47) and yield of 34%. ¹H-NMR (DMSO-*d*₆, δ): 1.89 ppm (s, 6H), 3.60–3.62 ppm (t, 2H), 4.12–4.15 ppm (t, 2H), 4.80 ppm (broad peak, s, 1H).

2.4 Synthesis of (2,2-dimethyl-1,3-dioxane-5,5-diyl)dimethanol (A₂B₂ type)

The synthesis of A₂B₂ type multifunctional initiator was performed following a literature procedure (48) and modified as follows (Scheme 1).

2.4.1. Synthesis of 2,2-dimethyl-5,5-bis(hydroxymethyl)-1,3-dioxane (I)

Pentaerythritol (1) (10 g, 73.53 mmol), *p*-toluene sulfonic acid monohydrate (0.122 g, 0.88 mmol) and 125 mL of DMF were added into a 250 mL round-bottom flask. The mixture was heated at 80°C until dissolution, and then was allowed to cool down. When the temperature reached 40°C, 8.52 mL (73.53 mmol) of 2,2-dimethoxypropane were added, then the solution was further cooled to room temperature and the reaction was allowed to proceed for 48 h. The solution was filtered and the solvent was evaporated under reduced pressure. The crude product was treated in a Soxhlet apparatus with petroleum ether (bp 30°C–60°C) for 12 h and then diethyl ether for 12 h, respectively. The



Sch. 1. The synthetic routes of (2, 2-dimethyl-1, 3-dioxane -5, 5-diyl)dimethanol.

final product was obtained as white crystals (4.60 g, 30% yield). $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, δ): 1.30 ppm (s, 6H), 3.35 ppm (d, 4H), 3.59 (s, 4H), 4.49 ppm (t, 2H). Elemental Analysis: Calculated (%): C 54.33, H 9.15; Found (%): C 53.97, H 9.18.

2.4.2. Synthesis of 2,2-dimethyl-5,5-bis(2-bromoisobutyrate)-1,3-dioxane (II)

2,2-Dimethyl-5,5-bis(hydroxymethyl)-1,3-dioxane (6 g, 34.1 mmol), triethylamine (9.40 mL, 68.2 mmol) and anhydrous THF (100 mL) were added to a 250 mL round-bottom flask which was immersed in an ice bath, and then 2-bromoisobutyryl bromide (4.22 mL, 34.1 mmol) was added dropwise into the solution while keeping syringe. The solution was stirred at room temperature for 24 h. The solution was filtered and the solvent was evaporated by rotary evaporation. The crude product was dissolved in dichloromethane and was treated with water at pH = 9 (12.25 g, 75% yield). $^1\text{H-NMR}$ (CDCl_3 , δ), 1.41 ppm (s, 6H), 1.98 ppm (s, 12H), 3.81 ppm (d, 4H), 4.24 ppm (s, 4H).

2.4.3. Deprotection (III)

2,2-Dimethyl-5,5-bis(2-bromoisobutyrate)-1,3-dioxane (2 g, 5 mmol), 150 mL CHCl_3 and 50 mL of 80% acetic acid were added to a 500 mL round-bottom flask. The solution was stirred at room temperature overnight. Then, additional 100 mL of 80% acetic acid were added and the mixture was refluxed for 1 h at 80°C . The crude product was recovered after evaporation of CHCl_3 and acetic acid under reduced pressure, and then was washed with water (pH 9), then was dried under a hood for 48 h. The crude product (III) was purified by preparative TLC (petroleum ether/ethyl acetate = 1/2, v/v) (0.95 g, 52% yield). $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, δ), 1.89 ppm (s, 6H), 3.50 (d, 4H), 3.59 (s, 4H), 4.49 (broad peak, s, 2H). Elemental Analysis: Calculated (%): C 35.97, H 5.11; Found (%): C 36.28, H 5.12.

2.5 Synthesis of 3-hydroxy-2-(hydroxymethyl)-2-methylpropyl 2-bromo-2-methylpropanoate (A_2B type)

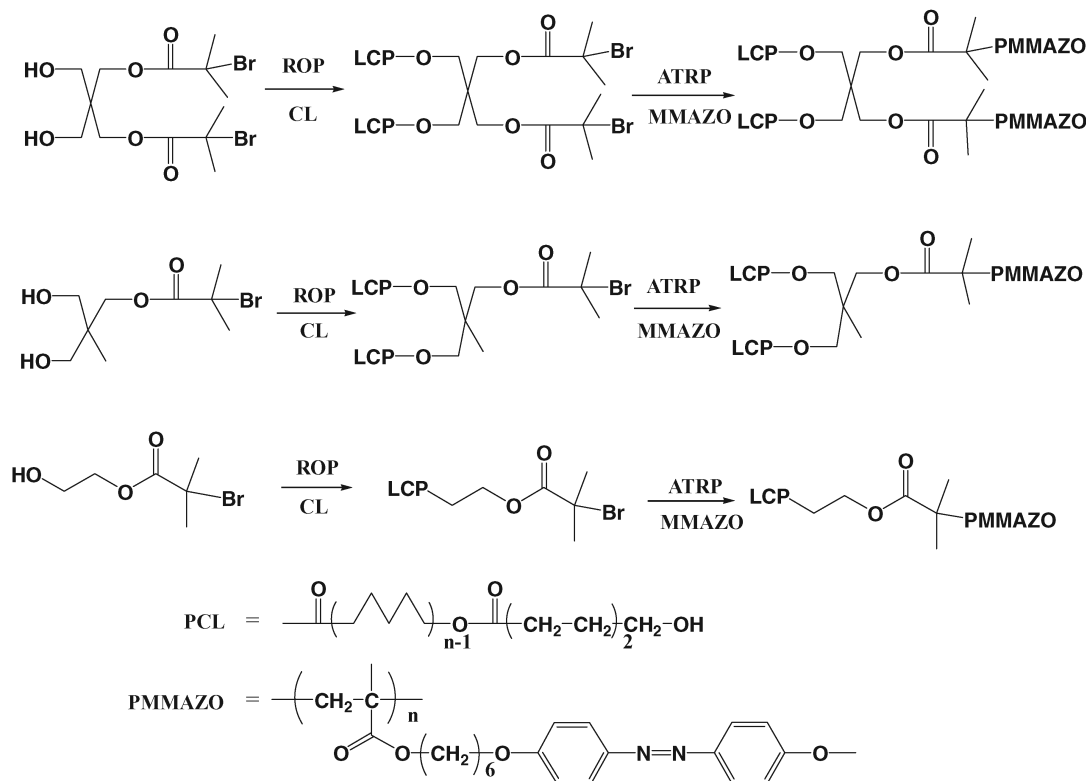
The synthetic procedures were similar to those of 2,2-bis(hydroxymethyl)propane-1,3-diyl bis(2-bromo-2-methylpropanoate) mentioned above. The final product was obtained as a white solid (12.28 g, 55% yield). $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, δ): 0.82 ppm (s, 3H), 1.89 ppm (s, 6H), 3.29 ppm (d, 4H), 3.97 ppm (s, 2H), 4.54 ppm (broad peak, s, 2H). Elemental Analysis: Calculated (%): C 40.26, H 6.37; Found (%): C 40.59, H 6.39.

2.6 Synthesis of PCL-based ATRP macroinitiators by ROP

The PCL-based ATRP macroinitiators (PCL-Br , $\text{PCL}_2\text{-Br}$ and $\text{PCL}_2\text{-Br}_2$) were prepared via the ROP of $\epsilon\text{-CL}$ with $\text{Sn}(\text{Oct})_2$ as the catalyst initiated by three types of initiators (AB , A_2B and A_2B_2 types) in bulk at 110°C for about 20 h, respectively. Taking PCL-Br as an example, typically, to a 50 mL of Schlenk tube equipped with a magnetic stirring bar were added hydroxyethyl 2-bromoisobutyrate (0.268 g, 1 mmol), a solution of $\text{Sn}(\text{Oct})_2$ 5 mL (0.005 g/mL in toluene) and $\epsilon\text{-CL}$ (12 mL, 112 mmol). The reaction mixture was purged with argon for approximately 15 min to eliminate the oxygen. At the designed time, the tube was cooled in ice water to stop the polymerization. The reaction mixture was concentrated, and then was precipitated into ether, filtered, and dried to provide a white powder. The synthetic procedures of $\text{PCL}_2\text{-Br}$ and $\text{PCL}_2\text{-Br}_2$ were similar to those of PCL-Br described above.

2.7 Synthesis of Linear and Miktoarm StarBlock Copolymers

The preparations of the linear and miktoarm star block copolymers, $\text{PCL-}b\text{-PMMAZO}$, $(\text{PCL})_2\text{-}(\text{PMMAZO})$ and $(\text{PCL})_2\text{-}(\text{PMMAZO})_2$, were accomplished by ATRP of MMAZO using CuBr/PMDETA as the catalyst



Sch. 2. The preparation of the linear and miktoarm star block copolymers.

(Scheme 2). PCL-Br, PCL₂-Br, PCL₂-Br₂ were employed as the macroinitiators to prepare PCL-*b*-PMMAZO, (PCL)₂-(PMMAZO) and (PCL)₂-(PMMAZO)₂, respectively. The typical synthetic procedures of (PCL)₂(PMMAZO) were described as following: a polymerization tube was charged with PCL₂-Br (0.12 g, 0.01 mmol, $M_{n(\text{GPC})} = 13700$ g/mol, $M_w/M_n = 1.26$), MMAZO (0.396 g, 1 mmol), CuBr (2.88 mg, 0.02 mmol), PMDETA (8.4 μL , 0.04 mmol) and 3 mL of anisole. After degassing with three freeze-thaw cycles, the tube was sealed under an argon atmosphere. The reaction was carried out at 85°C. After reaction (36 h), the polymerization tube was immersed into ice water and then opened. The sample was further diluted with 4 mL of THF, removed copper salts through a plugged column of neutral aluminum oxide, and precipitated in about 200 mL of methanol. The precipitation procedure was repeated two times. Finally, the polymer was filtered and dried in a vacuum oven at 30°C overnight. The conversion of monomer was determined gravimetrically. The PCL-*b*-PMMAZO and (PCL)₂-(PMMAZO)₂ were prepared following similar procedures described above.

3 Results and Discussion

3.1 Synthesis of the Multifunctional Initiators

More recently, the preparation of the target miktoarm star block copolymers via combinations of ATRP, NMRP, and RAFT with ring opening polymerization (ROP) method has been successfully carried out (23–34). Based

on these ideas, the miktofunctional initiators should be synthesized firstly. The synthetic routes of the miktoarm initiator were shown in Scheme 1. Selecting the most suitable protecting group of the hydroxyl groups is vital during the synthetic processes of the miktoarm initiators. In this work, the 2, 2-dimethoxypropane was chosen as reagent for the protecting group of the hydroxyl groups in the presence of *p*-toluenesulfonic acid leading to the diether as shown in Scheme 1. The unprotected hydroxyl groups reacted with 2-bromoisobutyryl bromide, and then the final miktoarm initiators were obtained after removal of the protective groups in the presence of acetic acid. The hydroxyethyl 2-bromoisobutyrate (AB type) was synthesized via esterification reaction of ethylene glycol with 0.02 equiv of 2-bromoisobutyrate (41). The ¹H-NMR spectra (Figure 1) of multifunctional initiators (AB, A₂B and A₂B₂ types) clearly showed signals that resulted from ATRP initiator ($\delta = 1.89$ ppm) and methylenes adjacent to hydroxyl groups ($\delta = 3.29$ – 3.62 ppm), along with other related peaks. Furthermore, the integral ratios between these peaks were very close the theoretical values. The elemental analysis also confirmed that the multifunctional initiator were successfully synthesized.

3.2 Synthesis of the Linear and Miktoarm Star Block Copolymers

As stated previously in the introduction, we aimed to synthesize the linear and miktoarm side-chain liquid crystalline (LC) block copolymers containing PCL

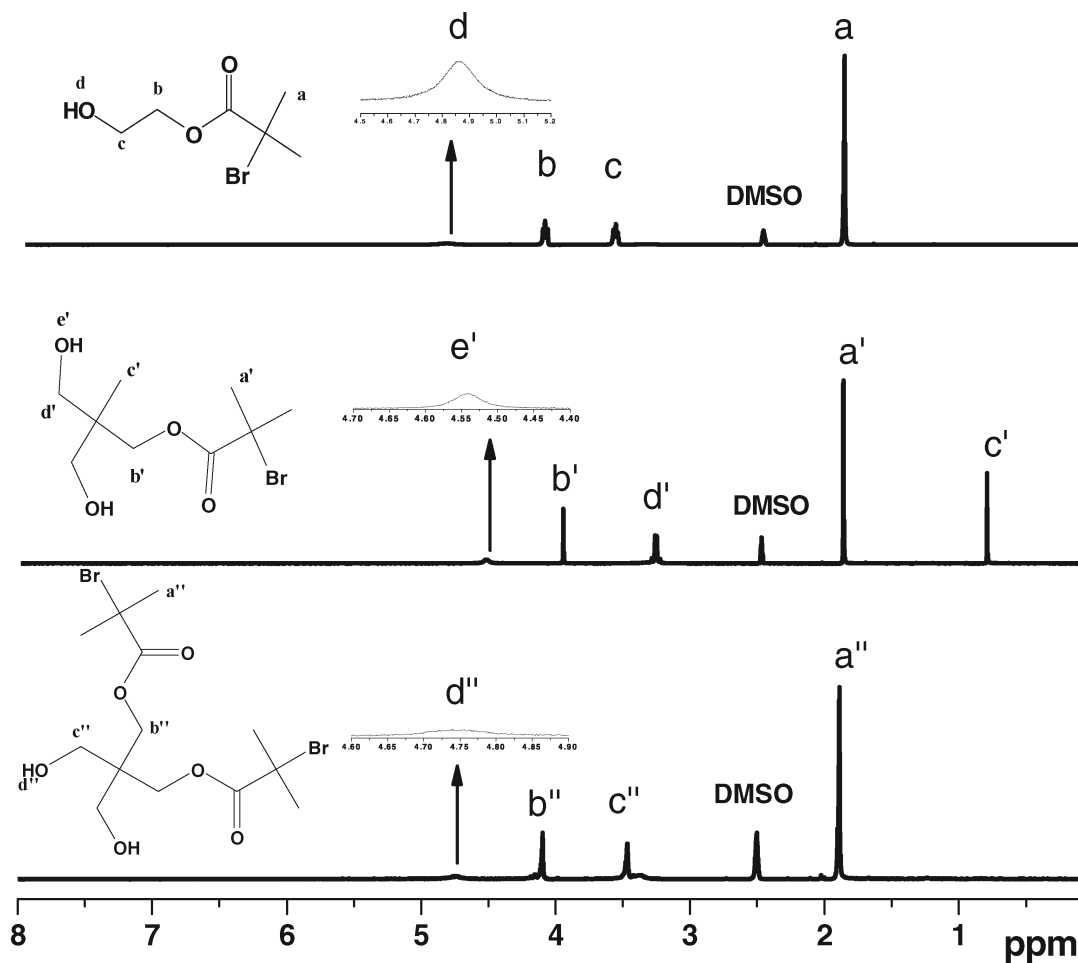


Fig. 1. The ^1H -NMR spectra of multifunctional initiators.

and PMMAZO blocks ($\text{PCL-}b\text{-PMMAZO}$, $(\text{PCL})_2\text{-PMMAZO}$ and $(\text{PCL})_2\text{-(PMMAZO)}_2$) via combinations of ATRP and ROP techniques with multifunctional initiators (AB , A_2B and A_2B_2 types). Firstly, the corresponding PCL-based ATRP macroinitiators were synthesized via ROP of $\epsilon\text{-CL}$ from the hydroxyl groups of different initiators catalyzed by $\text{Sn}(\text{Oct})_2$ at 110°C as presented in Scheme

2 and the results were shown in Table 1 and Figures 2 and 3. The $\epsilon\text{-CL}$ conversions for PCL-Br , $(\text{MPCL})_2\text{-Br}$ and $(\text{MPCL})_2\text{-Br}_2$ were 80%, 85% and 82%, respectively. From Table 1 (entries 1–3), we can see that the ROPs of $\epsilon\text{-CL}$ initiated by multifunctional initiators (AB , A_2B and A_2B_2 types) were all well-controlled. The molecular weight distributions (M_w/M_n) of the obtained PCLs obtained were

Table 1. Characterization and thermal transitions data of copolymers

Entry	$M_n(\text{GPC})$ (g mol^{-1})	$M_n(\text{NMR})$ (g mol^{-1})	$M_n(\text{th})$ (g mol^{-1})	M_w/M_n	Composition (%)	Phase Transition Temperature ($^\circ\text{C}$)
PCL-Br	14700	10100	10470	1.13	100% PCL	K60 I
$(\text{PCL})_2\text{-Br}$	13700	12000	11170	1.26	100% PCL	K62 I
$(\text{PCL})_2\text{-Br}_2$	16800	9900	10950	1.17	100% PCL	K62 I
PCL- <i>b</i> -PMMAZO	31200	34000	38590	1.32	34% PCL, 66% PMMAZO	g52 S96 N133 I
$(\text{PCL})_2\text{-PMMAZO}$	32800	31000	38890	1.35	38% PCL, 62% PMMAZO	g52 S95 N132 I
$(\text{PCL})_2\text{-(PMMAZO)}_1$	21700	29000	29170	1.26	34% PCL, 66% PMMAZO	g47 S86 N112 I
$(\text{PCL})_2\text{-(PMMAZO)}_2$	27700	33000	38670	1.26	30% PCL, 70% PMMAZO	g48 S92 N124 I
$(\text{PCL})_2\text{-(PMMAZO)}_3$	32500	42000	46590	1.25	23% PCL, 77% PMMAZO	g44 S94 N127 I

g = glassy phase; S = smectic phase; N = nematic phase; I = isotropic phase; K = crystalline phase.

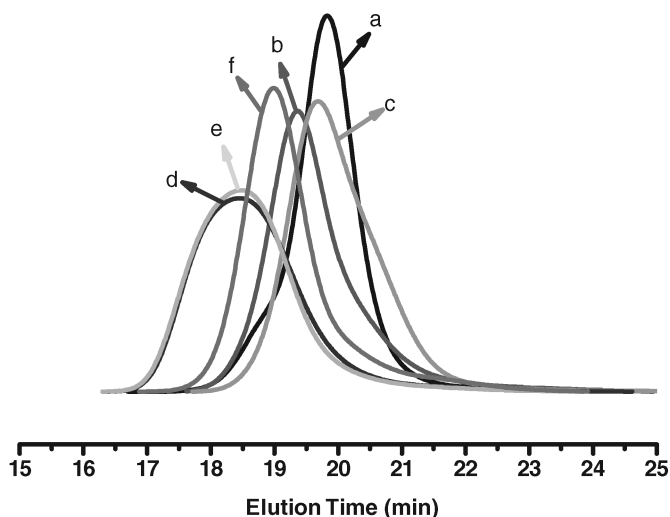


Fig. 2. GPC curves of the PCL-based ATRP macroinitiators and the corresponding linear and miktoarm block copolymers. (a) PCL-Br ($M_{n(\text{GPC})} = 14700$ g/mol, $M_w/M_n = 1.13$); (b) (PCL)₂-Br ($M_{n(\text{GPC})} = 13700$ g/mol, $M_w/M_n = 1.26$); (c) (PCL)₂-Br₂ ($M_{n(\text{GPC})} = 16800$ g/mol, $M_w/M_n = 1.17$); (d) PCL-*b*-PMMAZO ($M_{n(\text{GPC})} = 31200$ g/mol, $M_w/M_n = 1.32$); (e) (PCL)₂-PMMAZO ($M_{n(\text{GPC})} = 32800$ g/mol, $M_w/M_n = 1.35$); (f) (PCL)₂-(PMMAZO)₃ ($M_{n(\text{GPC})} = 32500$ g/mol, $M_w/M_n = 1.25$).

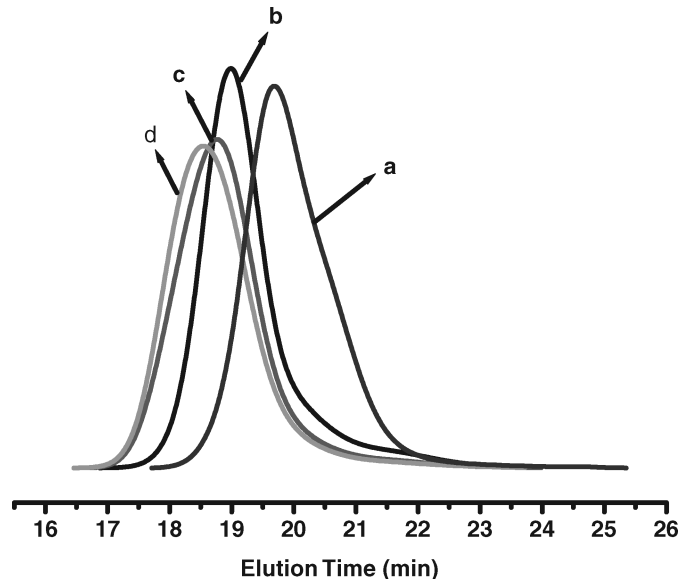


Fig. 3. GPC curves of the PCL-based ATRP macroinitiator and the corresponding A₂B₂ type copolymers. (a) (PCL)₂-Br₂ ($M_{n(\text{GPC})} = 16800$ g/mol, $M_w/M_n = 1.17$); (b) (PCL)₂-(PMMAZO)₁ ($M_{n(\text{GPC})} = 21700$ g/mol, $M_w/M_n = 1.26$); (c) (PCL)₂-(PMMAZO)₂ ($M_{n(\text{GPC})} = 27700$ g/mol, $M_w/M_n = 1.26$); (d) (PCL)₂-(PMMAZO)₃ ($M_{n(\text{GPC})} = 32500$ g/mol, $M_w/M_n = 1.25$).

relatively narrow ($M_w/M_n \leq 1.26$) and the GPC curves of them also followed mono-distributions as shown in Figure 2. Moreover, the molecular weights of the obtained PCLs derived from ¹H NMR spectra ($M_{n(\text{NMR})}$ s) were also

close to those corresponding theoretical values ($M_{n(\text{th})}$ s) ($M_{n(\text{th})} = ([M]_0/[I]_0) \times M_M \times \text{Conversion} + M_I$, where $[M]_0$ and $[I]_0$ are initial concentrations of monomer and initiator, respectively, and M_M and M_I are the molecular weight

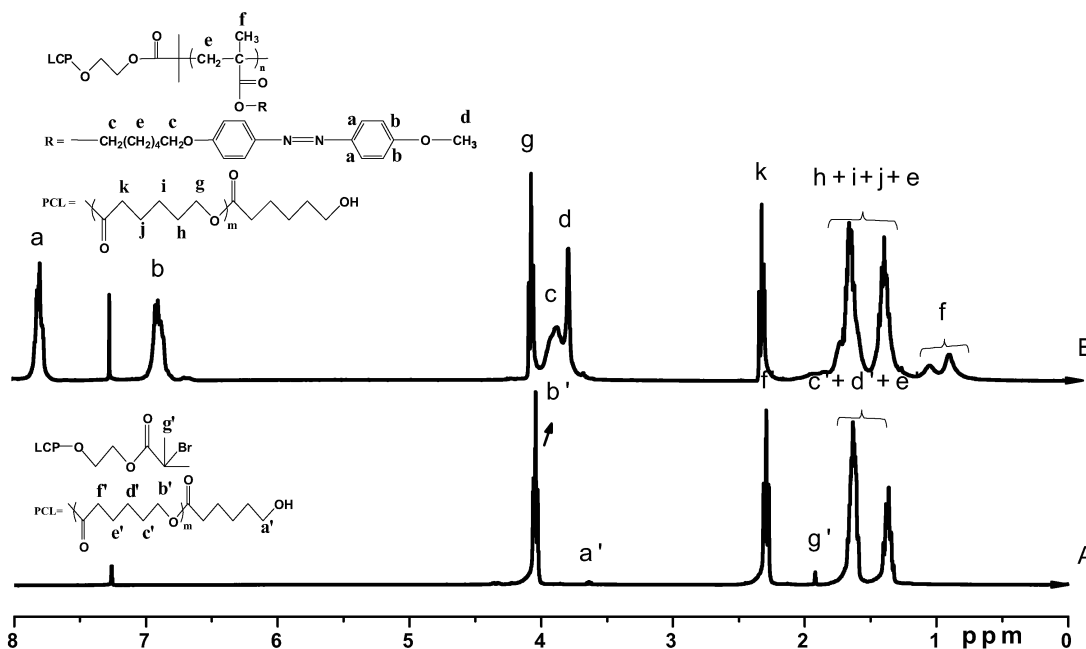


Fig. 4. ¹H-NMR spectra of PCL-Br ($M_{n(\text{GPC})} = 14700$ g/mol, $M_w/M_n = 1.13$) (A) and PCL-*b*-PMMAZO ($M_{n(\text{GPC})} = 31200$ g/mol, $M_w/M_n = 1.32$) (B).

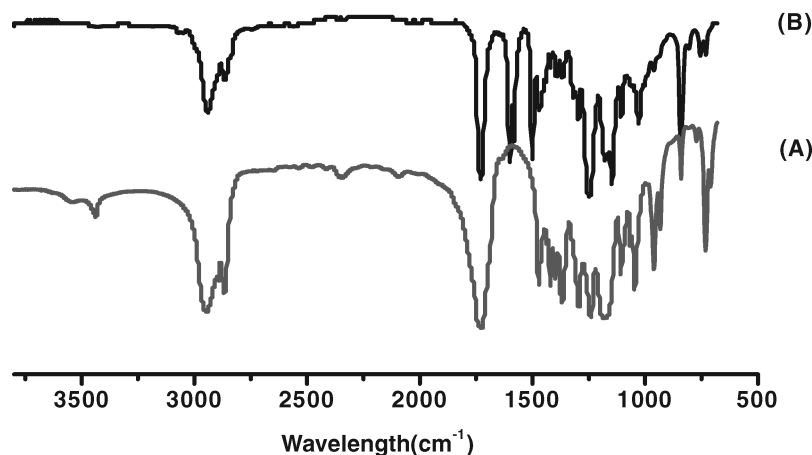


Fig. 5. IR spectra of PCL-Br ($M_{n(\text{GPC})} = 14700$ g/mol, $M_w/M_n = 1.13$) (A) and PCL-*b*-PMMAZO ($M_{n(\text{GPC})} = 31200$ g/mol, $M_w/M_n = 1.32$) (B).

of ϵ -CL and the initiator, respectively). $M_{n(\text{NMR})}$ was determined from the ratio of the peak areas of the initiator peaks around the 1.89 ppm and the $-\text{CH}_2\text{OCO}$ group of PCL around 3.90 ppm.

Then the obtained PCLs (PCL-Br, (PCL)₂-Br and (PCL)₂-Br₂) with activated bromide groups were used as the macroinitiators for ATRP of MMAZO to prepare the linear and miktoarm side-chain LC block copolymers (PCL-*b*-PMMAZO, (PCL)₂-PMMAZO and (PCL)₂-(PMMAZO)₂), respectively. The characteristic results were presented in Table 1. The MMAZO conversions for PCL-*b*-PMMAZO, (PCL)₂-PMMAZO and (PCL)₂-(PMMAZO)₂ were 71%, 70% and 70%, respec-

tively. From Table 1 (entries 4–8), we can see that the molecular weight distributions of the obtained linear and miktoarm star block copolymers were still kept narrow ($M_w/M_n \leq 1.35$). Meanwhile, the $M_{n(\text{th})}$ s were also close to the $M_{n(\text{NMR})}$ s. $M_{n(\text{th})}$ of the obtained block copolymer was calculated according to $M_{n(\text{th})} = ([M]_0/[I]_0) \times \text{Conversion} \times 396 + M_{n(\text{NMR})}$ of the PCL macroinitiator, and $M_{n(\text{NMR})}$ of the obtained block copolymer was determined accordingly from the integration of the signals at range of 6.5–7.0 ppm and those at 3.90 ppm. The difference between $M_{n(\text{NMR})}$ s and the values measured by GPC ($M_{n(\text{GPC})}$ s) may be attributed to linear PS used as standard samples [49,50]. As also can be seen from Table 1 (entries 6–8), the $M_{n(\text{GPC})}$

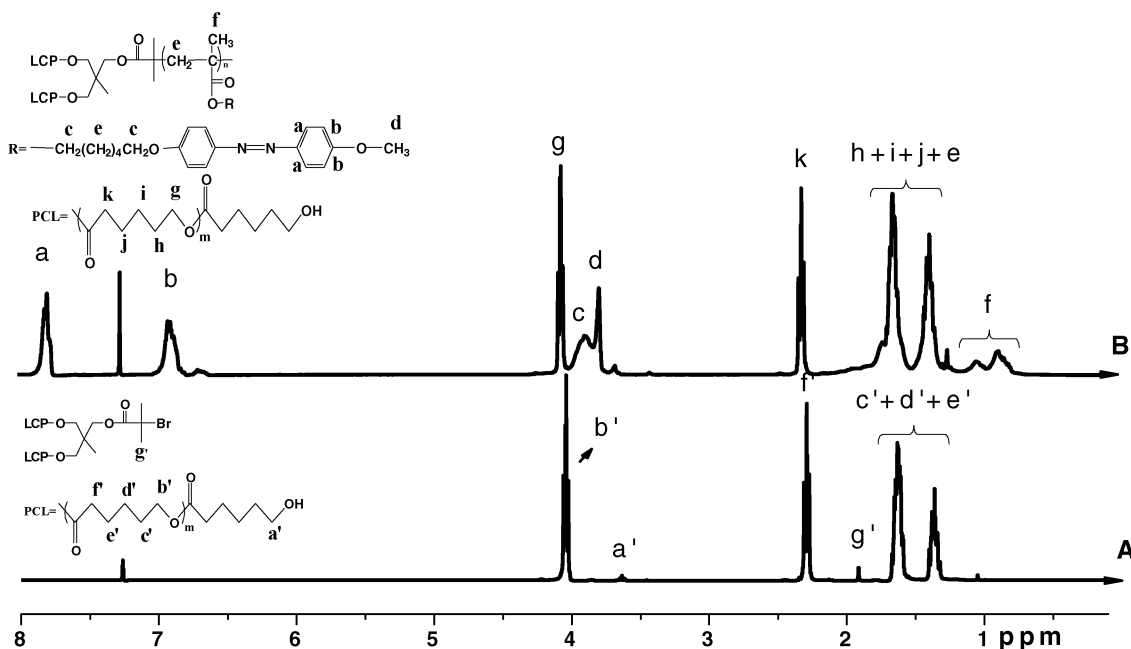


Fig. 6. ¹H-NMR spectra of (PCL)₂-Br ($M_{n(\text{GPC})} = 13700$ g/mol, $M_w/M_n = 1.26$) (A) and (PCL)₂-PMMAZO ($M_{n(\text{GPC})} = 32800$ g/mol, $M_w/M_n = 1.35$) (B).

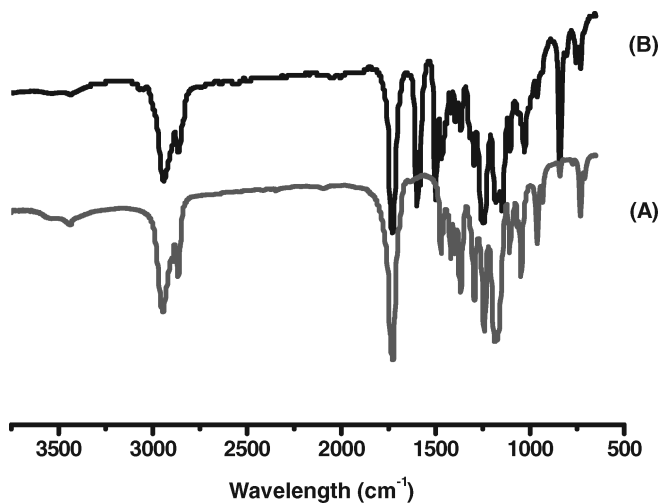


Fig. 7. FT-IR spectra of (PCL)₂-Br ($M_{n(\text{GPC})} = 13700$ g/mol, $M_w/M_n = 1.26$) (A) and (PCL)₂-PMMAZO ($M_{n(\text{GPC})} = 32800$ g/mol, $M_w/M_n = 1.35$) (B).

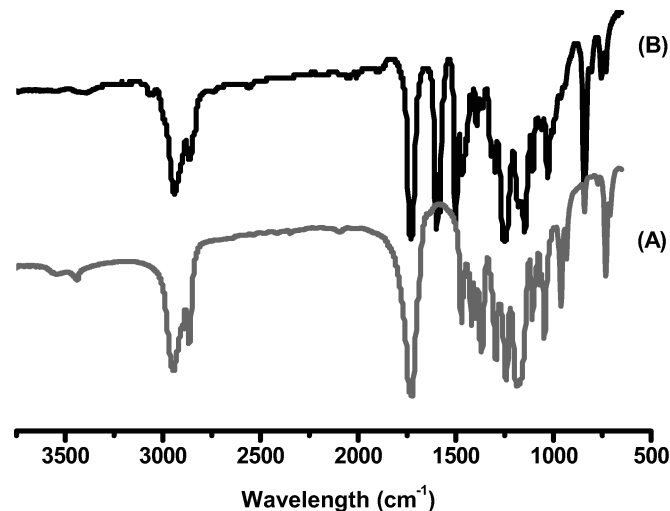


Fig. 9. FT-IR spectra of (PCL)₂-Br₂ ($M_{n(\text{GPC})} = 16800$ g/mol, $M_w/M_n = 1.17$) (A) and (PCL)₂-(PMMAZO)₂ ($M_{n(\text{GPC})} = 32500$ g/mol, $M_w/M_n = 1.25$) (B).

of (PCL)₂-(PMMAZO)₂ also increased with the monomer conversion from 21700 g/mol to 27700 g/mol, and to 32500 g/mol, when the monomer conversion was 46%, 70% and 90%, which confirmed that the polymerization proceeded via an ATRP process. Moreover, the disappearance of the PCL macroinitiators in the GPC curves as shown in Figure 2 and 3 also confirmed the successful introductions of the PMMAZO blocks.

The obtained linear and miktoarm star block copolymers were also characterized by ¹H-NMR and FT-IR spectra

as presented in Figures 4–9. The appearance of chemical shifts at 7.80 ppm and 6.90 ppm in Figures 4(B), 6(B) and 8(B) as compared with their corresponding PCL macroinitiators confirmed the incorporation of MMAZO blocks into the linear and miktoarm block copolymers. In the IR spectra (Figures 5(B), 7(B) and 9(B)), we also can see that the four peaks at 1450 cm⁻¹, 1500 cm⁻¹, 1581 cm⁻¹, 1610 cm⁻¹ (N=N group) were belong to the azophenyl group and the peak at 1730 cm⁻¹ was the vibration of the C=O group (51), which also proved the successful preparation

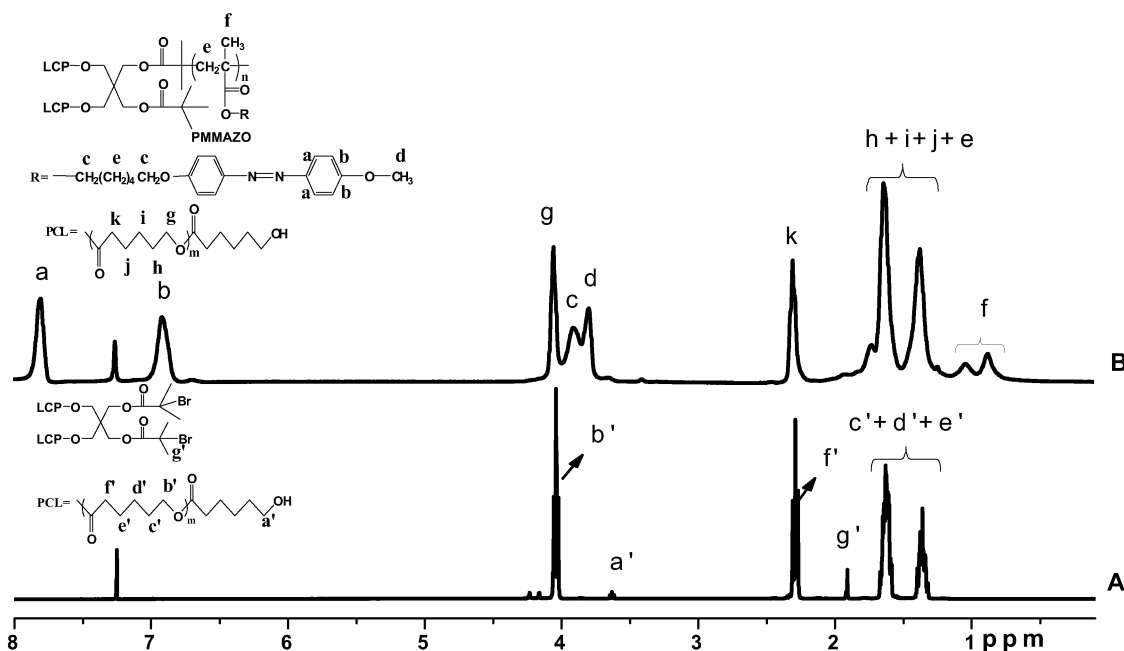


Fig. 8. ¹H-NMR of (PCL)₂-Br₂ ($M_{n(\text{GPC})} = 16800$ g/mol, $M_w/M_n = 1.17$) (A) and (PCL)₂-(PMMAZO)₂ ($M_{n(\text{GPC})} = 32500$ g/mol, $M_w/M_n = 1.25$) (B).

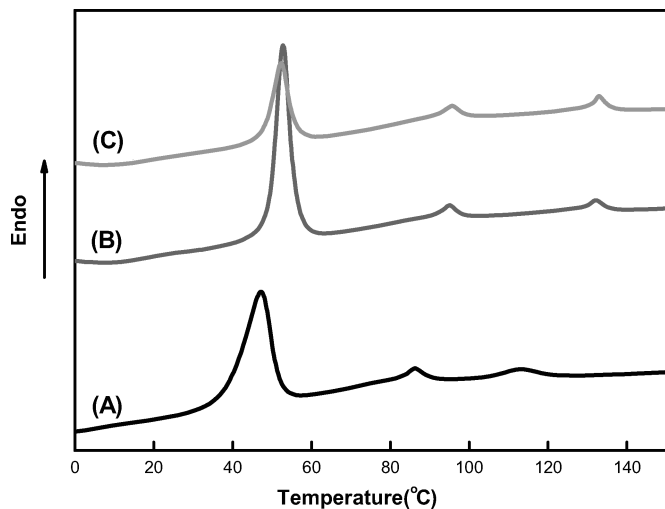


Fig. 10. The DSC curves of the linear and miktoarm star block copolymers. (A): $(\text{PCL})_2\text{-}(\text{PMMAZO}_2)_2$ ($M_{n(\text{GPC})} = 21700$ g/mol, $M_w/M_n = 1.26$) (B): $(\text{PCL})_2\text{-PMMAZO}$ ($M_{n(\text{GPC})} = 32800$ g/mol, $M_w/M_n = 1.35$); (C): $\text{PCL-}b\text{-PMMAZO}$ ($M_{n(\text{GPC})} = 31200$ g/mol, $M_w/M_n = 1.32$).

of the linear and miktoarm block copolymers containing PCL and PMMAZO chains.

3.3 Thermal Properties and Morphologies

Thermal properties of the linear and miktoarm star block copolymers were characterized by differential scanning calorimetry (DSC) and polarized optical microscope (POM). The phase transition temperatures of all samples were obtained from the second heating, and the data were summarized in Table 1 and Figures 10 and 11. From Table 1 and Figures 10 and 11, we can see that the DSC curves of the resulting linear and miktoarm star block copolymers containing PCL and PMMAZO chains showed three endothermic peaks, which can be assigned to the crystalline phase (K) transition, T_{s-n} (the smectic-to-nematic transition temperature) and T_{n-i} (the nematic-to-isotropic tran-

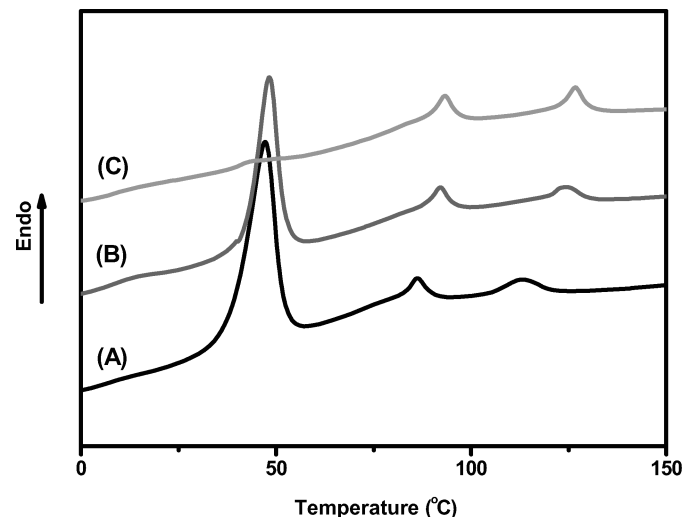


Fig. 11. The DSC curves of the miktoarm star block copolymers with different MMAZO contents. (A): $(\text{PCL})_2\text{-}(\text{PMMAZO}_1)_2$ ($M_{n(\text{GPC})} = 21700$ g/mol, $M_w/M_n = 1.26$); (B): $(\text{PCL})_2\text{-}(\text{PMMAZO}_2)_2$ ($M_{n(\text{GPC})} = 27700$ g/mol, $M_w/M_n = 1.26$); (C) $(\text{PCL})_2\text{-}(\text{PMMAZO}_3)_2$ ($M_{n(\text{GPC})} = 32500$ g/mol, $M_w/M_n = 1.25$).

sition temperature), respectively. As can be observed from Figure 10 and Table 1 (entries 4 and 7), the T_{s-n} changed from 92°C to 96°C , and the T_{n-i} changed from 124°C to 133°C when the molecular weights and PMMAZO segment contents were almost same, which may be due to the influence of polymer structures.

Furthermore, Figure 11 and Table 1 (entries 6-8) results showed that the phase transition temperature increased with the lengths of PMMAZO chains, and the T_{s-n} changed from 86°C to 92°C and to 94°C , and the T_{n-i} changed from 112°C to 124°C and to 127°C , when the MMAZO contents were 66%, 70% and 77%, respectively.

In order to investigate the liquid crystalline behaviors of the linear and miktoarm star block copolymers, polarized optical microscope (POM) was used and the results were given in Figure 12. From Figure 12, we can see that the

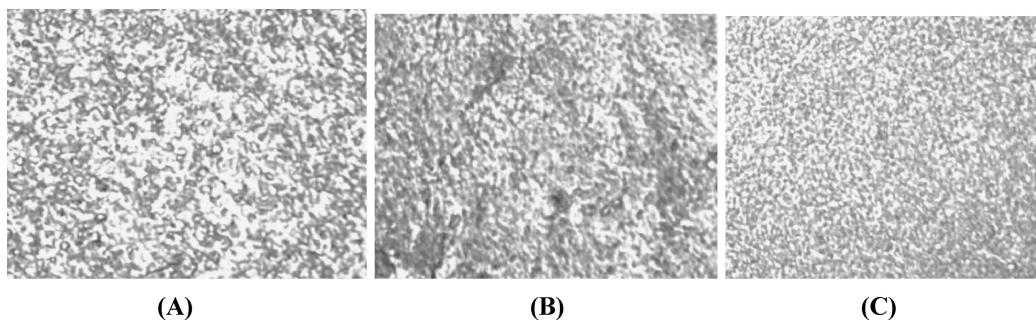


Fig. 12. Polarizing optical micrograph for the linear and miktoarm star block copolymers. (A): $\text{PCL-}b\text{-PMMAZO}$ (130°C , $500\times$) ($M_{n(\text{GPC})} = 31200$ g/mol, $M_w/M_n = 1.32$); (B): $(\text{PCL})_2\text{-PMMAZO}$ (131°C , $500\times$) ($M_{n(\text{GPC})} = 32800$ g/mol, $M_w/M_n = 1.35$); (C): $(\text{PCL})_2\text{-}(\text{PMMAZO}_3)_2$ (127°C , $500\times$) ($M_{n(\text{GPC})} = 32500$ g/mol, $M_w/M_n = 1.25$).

polymer structure had a slight effect on the mesophases of the polymers.

4 Conclusions

The one novel linear and two miktoarm star liquid crystalline block copolymers containing PCL and PMMAZO blocks were successfully prepared via combinations of ATRP and ROP techniques. The obtained block copolymers were well controlled with the designed molecular structures and narrow molecular weight distributions. DSC study revealed that the phase transition temperature of T_{S-N} and T_{N-I} increased with the increasing molecular weight of PMMAZO block. The polymer structure had a slight effect on the mesophases of the polymers.

Acknowledgments

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