

Synthesis and characterization of diblock copolymers based on crystallizable poly(ϵ -caprolactone) and mesogen-jacketed liquid crystalline polymer block

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Abstract

Diblock copolymers comprising crystallizable poly(ϵ -caprolactone) and poly{2,5-bis[(4-methoxyphenyl)oxycarbonyl]styrene} (PMPCS) were synthesized by ring-opening polymerization of ϵ -caprolactone and subsequent atom transfer radical polymerization (ATRP) of MPCPS. The molecular structure of the copolymers was confirmed by ^1H NMR spectroscopy and GPC. Kinetic study of ATRP showed that the polymerization proceeded in a controlled way up to high conversions. Three series of diblock copolymers were obtained with relatively narrow polydispersity indices ($\text{PDI} \leq 1.11$) and PCL blocks of 8000, 12,900, and 22,800 molecular weights, respectively. The existence of microphase separation was identified by differential scanning calorimetry (DSC) and directly observed through transmission electron microscopy (TEM). The melting behavior of PCL block was significantly affected by the length of PCL block and composition of PMPCS. The thermotropic liquid crystalline behavior was examined by polarized optical microscopy (POM) and DSC. The result showed that the diblock copolymer exhibited liquid crystalline behavior when the degree of polymerization (DP) of PMPCS block was not less than 44.

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1. Introduction

The self-assembly behavior of block copolymers has been extensively studied due to their abilities to self-organize into various phase morphologies, such as lamellae, double gyroid, cylinders, and spheres in bulk depending on the volume fraction of the block chains and the separation power denoted by χN (χ =Flory–Huggins interaction parameter, N =total chain length) [1,2]. If one or more of the blocks are crystallizable, the microphase separation behavior becomes more complicated [3–6]. The final morphology of the block copolymer is determined by the crystallization temperature of the crystallizable block (T_c), the glass transition temperature of the amorphous block (T_g) and the order–disorder temperature (ODT). Because the

competition between crystallization and microphase separation has important effect on the final morphology of the crystallizable block copolymers, extensive studies have been carried out to understand the effects of crystallization on the microphase separated morphology, as well as the effects of the microphase separation on the crystallization [7–13].

In recent years, many research groups have focused their interests on the synthesis and characterization of liquid crystalline (LC)-isotropic (I) block copolymers [14–18]. Because special functions can be introduced via the LC segment into the micro- or nanostructure of the block copolymers, these block copolymers are candidates for the development of new functional materials. The delicate competition between the liquid crystalline phase and microphase separated morphology is still under investigation by many scientists [16,18–21]. Considering the special effects of crystallizable segment and liquid crystalline segment on block copolymers, it is reasonable to suppose that diblock copolymer, which combine the crystalline segment and liquid crystalline segment, is greatly interesting because this kind of block copolymer

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may offer opportunities to modify the microphase separated structures and morphology through both crystallizable block and liquid crystalline block. As a result, the structure of ‘order-within-order’ would be generated. As we know, microphase separation of the diblock copolymers usually occurs on a scale of 10–100 nm, low ordered liquid crystalline phase formed by the liquid crystalline blocks is usually on a scale of a few nanometer, and crystallization of the crystalline blocks is on an atomic packing scheme of a few tenths of nanometer [12,21].

In the present study, we are specifically interested in the synthesis of series of crystalline–liquid crystalline diblock copolymers which based on crystallizable poly(ϵ -caprolactone) and mesogen-jacketed liquid crystalline polymers (MJLCPs). Different from the conventional side chain liquid crystalline polymers (SCLCPs) with long spacers, MJLCPs have no spacers between the backbones and mesogenic side chains. The spatial requirement of the bulky side chains leads to the extended and stiffened conformation of the backbones [22]. MJLCPs have unique properties different from the common SCLCPs such as stable nematic phase in a broad temperature range and stiff chains by strongly coupling of backbone and side chains [22,23]. The first MJLCP based diblock copolymer, poly(styrene-*block*-2,5-bis[(4-methoxyphenyl)oxycarbonyl]styrene) (PS-*b*-PMPCS), was successfully prepared via 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMP) mediated living-free radical polymerization [24]. The temperature-induced self-assemble behavior of this novel diblock copolymer was examined in *p*-xylene [25]. Meanwhile, the bulk phase behavior shows hierarchical assembly structure [26]. The PMPCS rigid column is formed due to the strong interaction between the side-chain mesogens and polymer backbone. The macromolecular columns possess orientational order, and parallel to the lamellar normal. Recently, we reported the preparation of PMPCS via ATRP in anisole [27]. It provided a new way to synthesize block copolymers from macro-initiators.

Copolymers containing poly(ϵ -caprolactone) (PCL) are especially interesting because they are miscible with a wide range of polymers, and they have features like crystallizability, lack of toxicity, ability to disperse pigments, low-temperature adhesiveness, and printability [28,29]. Different types of block copolymers that include amorphous–crystalline copolymers and double crystalline copolymers with PCL as crystalline block have been studied thoroughly [28,30–34]. In addition, PCL is one of biodegradable polymers which have been used to prepare functional materials [35,36]. The degradability of PCL may be used to investigate the morphology of block copolymer and may result in interesting materials.

The purpose of this paper is to synthesize three series of well-defined diblock copolymer, PCL-*b*-PMPCS, consist of different length of crystallizable segment PCL and liquid crystalline segment PMPCS by the ROP of ϵ -CL and subsequent ATRP of MPCS. Thermal properties and liquid crystalline behaviors of the diblock polymers have been

investigated depending on the composition of block copolymers. The microphase separations of block copolymers are also demonstrated by DSC and TEM.

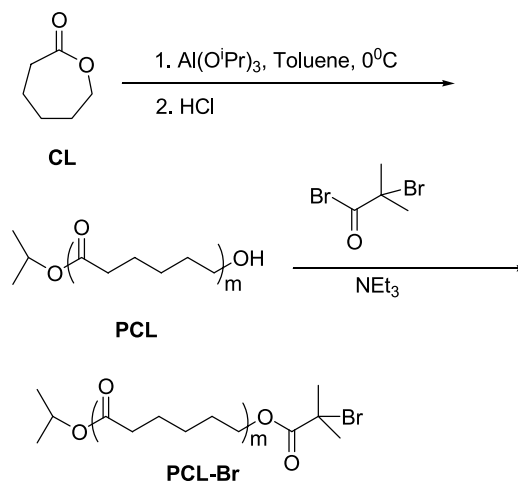
2. Experimental section

2.1. Materials

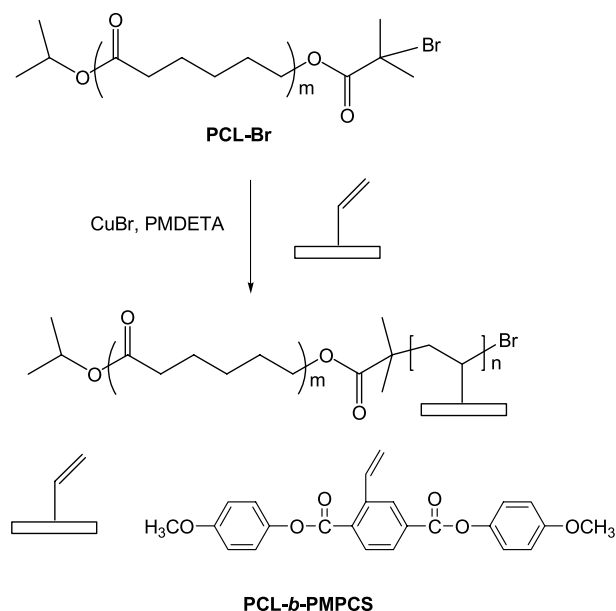
Toluene was dried by refluxing over Na metal and distilled under N₂ atmosphere just before use. ϵ -Caprolactone (CL) (99%, from Acros) was dried over calcium hydride at room temperature and distilled under reduced pressure. Aluminum iso-propoxide (Al(OⁱPr)₃) was purified by distilling under reduced pressure. Chlorobenzene was purified by washing with concentrated sulphuric acid to remove thiophene, followed by washing with water, being dried with anhydrous calcium chloride and being distilled. Cuprous bromide (CuBr) was synthesized from CuBr₂ and purified by stirring in acetic acid, washing with methanol and then dried in vacuum just before use. *N,N,N',N'',N''*-Pentamethyldiethylenetriamine (PMDETA) (99.5%, from TCI) and 2-bromo-2-methylpropionyl bromide (98%, from Acros) were used as obtained without further purification. MPCS was synthesized according to the literature [37].

2.2. Preparation of poly(ϵ -caprolactone) (PCL)

The synthetic procedures were listed in Schemes 1 and 2. Previously, glass reactor with a magnetic bar and rubber cap was flamed and purged nitrogen for three times. Toluene and CL were introduced into the reactor with a syringe. Then the initiator solution was added with a syringe. CL was polymerized at 0 °C under N₂ atmosphere. The reaction was stopped by adding an excess (relative to initiator) 2 N HCl solution. The reaction solution was washed with water to neutral pH and the polymer was recovered by precipitation



Scheme 1. Synthesis of the PCL macroinitiators.



Scheme 2. Synthesis of PCL-*b*-PMPCS diblock copolymers by ATRP.

in petrol ether. The polymer was dried under reduced pressure at room temperature until constant weight.

2.3. Fraction of PCL

To obtain relatively low polydispersity sample, PCL was fractioned by dropping petrol ether to THF solution of PCL slowly.

2.4. Preparation of PCL-Br

PCL was dissolved in dry THF, and 5-fold excess triethylamine (NEt₃) (relative to OH groups), 5-fold excess 2-bromo-2-methylpropionyl bromide was dropped slowly under ice bath. After the reaction solution stirred for two days at room temperature, the solution was filtrated to remove NEt₃HCl. The solution was evaporated and the product was dissolved in CH₂Cl₂, washed with 5% NaHCO₃ solution and water, respectively, dried over anhydrous Na₂SO₄, rotary evaporated most of the solvent and poured into methanol. The crude PCL-Br macroinitiator was reprecipitated in methanol several times and dried in vacuum.

2.5. Preparation of PCL-*b*-PMPCS

PCL-*b*-PMPCS diblock copolymer was synthesized by atom transfer radical polymerization in chlorobenzene. A tube was charged with MPCS, PCL-Br, CuBr, PMDETA (*n*/1/1/1) (in molar ratios) and chlorobenzene, then sealed after degassed in vacuum and flushed with N₂ for three times. Polymerization was carried out at 90 °C. Diluted with tetrahydrofuran (THF), the reaction solution was filtered over neutral aluminum oxide to remove catalyst complex, precipitated in methanol and dried in vacuum. The

conversion of polymerization was determined gravimetrically. The samples are abbreviated as 'PCL_{*x*}PMPCS_{*y*}', where *x* and *y* represents the DP of PCL and PMPCS, respectively, calculated from the ¹H NMR spectra.

2.6. Measurements

Gel permeation chromatography (GPC) measurements were carried out in THF on a Waters 2410 instrument equipped with three Waters μ-Styrigel columns (10³, 10⁴, and 10⁵ Å) at 35 °C, with a Waters 2410 RI detector. Calibration was based on low polydispersity polystyrene standards. The number-averaged molecular weight (*M_n*) of PCL was calibrated by reference to a universal calibration curve and polystyrene standards in THF at 35 °C (*K_{PS}* = 1.25 × 10⁻⁴ dL/g, α_{PS} = 0.707; *K_{PCL}* = 1.09 × 10⁻³ dL/g, α_{PCL} = 0.600 in the [η] = *KM^α*, a Mark-Houwink relationship) [34]. A Bruker ARX 400 MHz spectrometer was used for the ¹H NMR measurements with CDCl₃ as the solvent and tetramethylsilane (TMS) as internal reference. The thermogravimetric analysis (TGA) was performed on a TA SDT 2960 instrument at a heating rate of 10 °C/min in a nitrogen atmosphere. DSC measurements were made on a Thermal Analysis company Q-100 instrument with Universal Analysis software under a dynamic atmosphere of N₂. The DSC cooling thermograms were obtained at a rate of -10 °C/min from 200 to -90 °C, after the samples were heated at 10 °C/min, and the melting thermograms of all sample were obtained from the second heating run at 10 °C/min to 200 °C. The crystallinity of PCL *X_c* was calculated from the heat of fusion Δ*H* (J/g) by *X_c* = Δ*H* / (Δ*H₀f_w*), where *f_w* is the weight fraction of PCL block in PCL-*b*-PMPCS and Δ*H₀* is heat of fusion for perfect PCL crystals (Δ*H₀* = 137.5 J/g) [30]. Transmission electron microscopy (TEM) experiments were carried out on a Hitachi H-800 electron microscopy. After the samples were annealing at 150 °C, ultrathin sections were cut on a cryoultramicrotome. The sections were stained using RuO₄ vapor at room temperature for 30 min. The regions of PMPCS block and amorphous PCL block were preferentially stained by RuO₄ [30,38]. Polarized optical microscopy (POM) observation was conducted on a Leitz Laborlux 12 microscope with a Leitz 350 hot stage.

3. Results and discussion

3.1. Synthesis of macroinitiator

Ring-opening polymerization of CL in the presence of Al(O^{*i*}Pr)₃ in toluene was carried out at 0 °C according to the other papers [39,40] (Scheme 1). Three different molecular weight poly(ε-caprolactones) (PCLs) were synthesized. The GPC curves were symmetrically monomodal with molecular weight distribution of 1.22–1.26. To get lower polydispersity PCLs, PCLs were fractioned successfully.

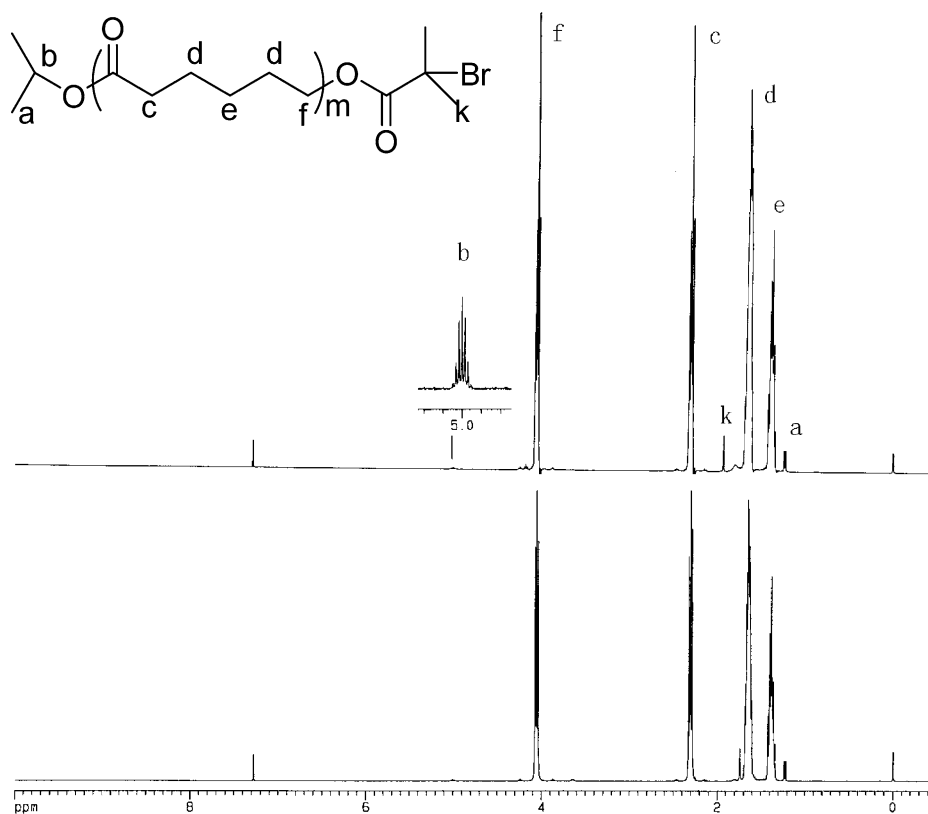


Fig. 1. ^1H NMR spectra of PCL₁₁₃ (down) and macroinitiator PCL₁₁₃-Br (up) (in CDCl₃, 400 MHz).

PCL macroinitiators were prepared by end capping of living PCL with an excess of 2-bromo-2-methylpropionyl bromide [35]. Fig. 1 shows the ^1H NMR spectra of a typical PCL and resulting PCL-Br macroinitiator with the tertiary halide end group. After reaction, the two methyl protons of the 2-bromoisobutyl moiety (*k*) appeared. From the relative intensity of the peak (*b*) and the peak (*c*), the molecular weight of PCL was calculated. The degree of end functionalization was obtained by comparison of the intensity of the peak (*b*) and the peak (*k*). The result showed that esterification was complete. The specifications of three macroinitiators are presented in Table 1. The difference between molecular weights obtained by GPC and those calculated from ^1H NMR is ascribed to the difference of hydrodynamic volume of PCL-Br vs. polystyrene standards [41]. The molecular weights

determined by means of ^1H NMR spectroscopy are taken as actual molecular weights.

3.2. Synthesis of PCL-*b*-PMPCS diblock copolymer

The macroinitiator (PCL-Br) was used to initiate MPSCS in chlorobenzene for synthesis of PCL-*b*-PMPCS block copolymer by ATRP with effective and cheap PMDETA [42] (Scheme 2). Fig. 2 shows the GPC curves of a macroinitiator PCL₁₁₃-Br as well as a block copolymer

Table 1
Molecular properties of PCL macroinitiators

Sample	$M_n \times 10^{-4}$			PDI ^a
	GPC ^a	NMR ^b	Calcd ^c	
PCL ₇₀ -Br	1.58	0.80	0.78	1.08
PCL ₁₁₃ -Br	2.26	1.29	1.14	1.11
PCL ₂₀₀ -Br	3.50	2.28	1.82	1.10

^a Calibrated by PS standards.

^b Measured by ^1H NMR.

^c Calculated according to the calibration equation: $M_{\text{PCL}} = 0.258M_{\text{PSt}}^{1.067}$, which is deduced from the Mark–Houwink relationship (Section 2).

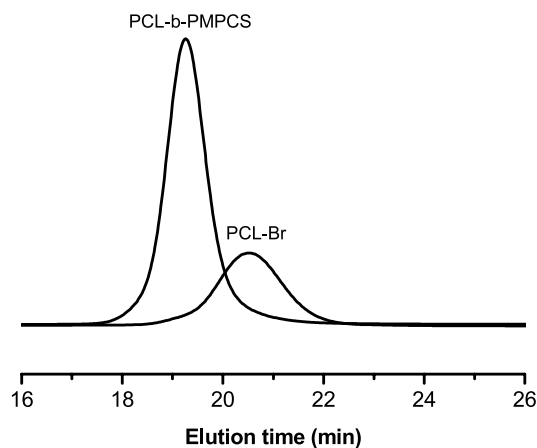


Fig. 2. GPC curves of macroinitiator PCL₁₁₃-Br and diblock copolymer PCL₁₁₃-PMPCS₁₀₃.

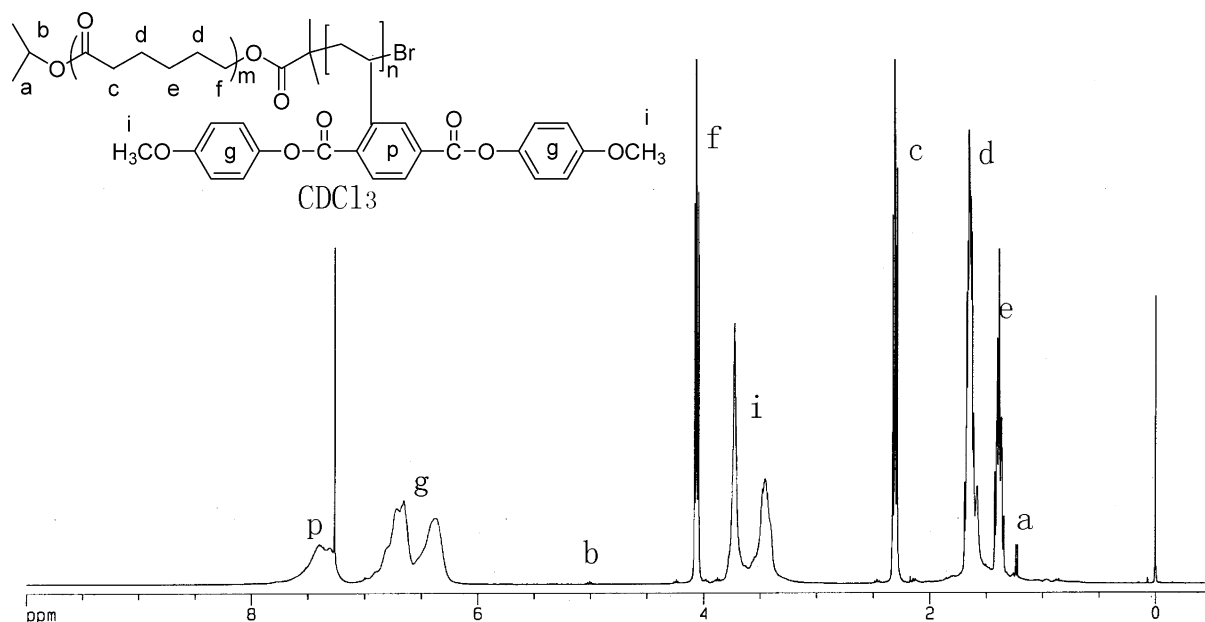


Fig. 3. ^1H NMR spectrum of $\text{PCL}_{113}\text{PMPCS}_{103}$ (in CDCl_3 , 400 MHz).

produced from it. It was found that the molecular weight of the copolymer increased and the GPC curve of the copolymer was symmetrically single modal. This indicated the high initiating efficient of initiator and a low degree of permanent termination by any side reaction. The successful preparation of $\text{PCL-}b\text{-PMPCS}$ was proven by ^1H NMR spectrum illustrated in Fig. 3. The composition in terms of block weight fraction was calculated base on the ratio of the peak (i) and peak (f). The spectrum was further used to calculate the number molecular weight of diblock copolymer.

3.3. Kinetics of ATRP polymerization

ATRP of MPCS initiated by PCL-Br combined with CuBr , complexed by PMDETA , was carried out in chlorobenzene at 90°C . To investigate the living character of ATRP, a kinetic study was conducted with $\text{PCL}_{113}\text{-Br}$ as macroinitiator. The polymerization condition was $[\text{PCL}_{113}\text{-Br}]:[\text{MPCS}]:[\text{CuBr}]:[\text{PMDETA}]=1:113:1:1$ (in molar ratios) at 40 wt% concentration. Fig. 4 shows the time dependence of $\ln([M]_0/[M]_t)$ and the conversion. Each data point represents a single experiment. The linear behavior of $\ln([M]_0/[M]_t)$ was consistent with a controlled polymerization that was first order in monomer concentration indicating absence of termination. The plots of molecular weight and polydispersity vs. conversion are illustrated in Fig. 5. Both the M_n calculated from ^1H NMR and that valued by GPC were found to increase in direct proportion to the monomer conversion. It must be noted that the M_n (GPC) was lower than M_n (NMR) at low conversion, then higher than M_n (NMR) at high conversion. This may be caused by the difference of the hydrodynamic volume of PCL segment

and PMPCS segment in copolymers vs. polystyrene standards. The corresponding molecular weight distributions were narrow throughout the polymerization ($\text{PDI} \leq 1.11$). We can conclude that the macromolecular initiator PCL-Br combined with CuBr , complexed by PMDETA induced a living polymerization of MPCS.

3.4. Characterization and thermal behaviors of $\text{PCL-}b\text{-PMPCS}$

Table 2 summarized molecular characteristics of three series of block copolymers with PCL blocks of 8000, 12,900, and 22,800 molecular weights, respectively. For all block copolymers, the final molecular weight distributions are relatively narrow ($\text{PDI} \leq 1.11$).

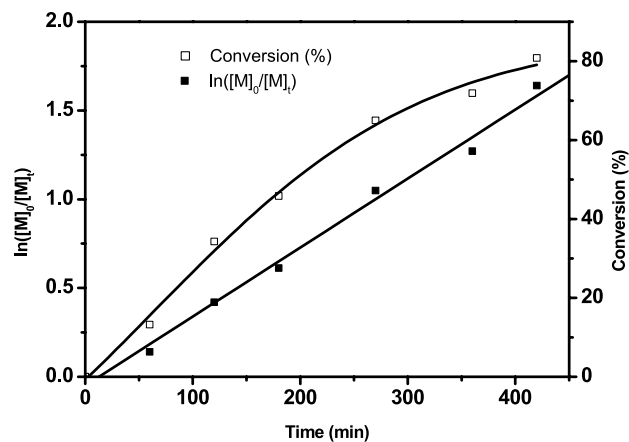


Fig. 4. The relationships of the conversion and $\ln([M]_0/[M]_t)$ with the polymerization time for MPCS polymerization in chlorobenzene at 90°C using macroinitiator $\text{PCL}_{113}\text{-Br}$.

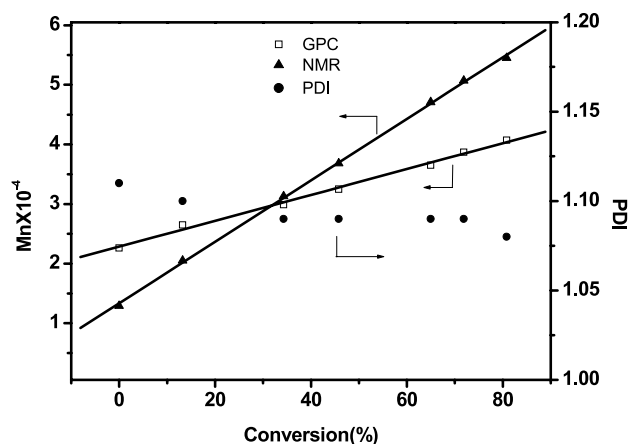


Fig. 5. Dependence of molecular weight and PDI on the conversion for MPCS polymerization in chlorobenzene at 90 °C using macroinitiator PCL₁₁₃-Br.

3.4.1. Thermal stability

The thermal stabilities of the diblock copolymers were evaluated using thermogravimetric analysis (TGA). Perseaire et al. [43] have studied the thermal stability of PCL prepared with the method as this work. Two-stage thermal degradation mechanism has been proposed. The first stage implies statistical rupture of PCL chains via pyrolysis reaction. The second stage involves formation of ϵ -caprolactone as result of the unzipping degradation process. It was also found that acetylation of hydroxyl end group can

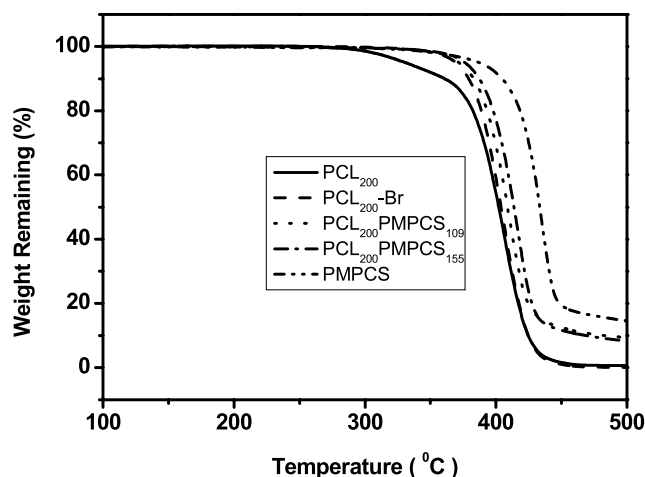


Fig. 6. TGA curves obtained at heating rate of 10 °C/min under a nitrogen atmosphere for PCL, PCL-Br, diblock copolymers and homo-PMPCS prepared by ATRP ($M_{n,GPC}$ = 20,600, PDI = 1.07).

limited the degradation by depolymerization. Fig. 6 shows the weight loss curves for typical diblock copolymers with PCL, PCL-Br and homo-PMPCS. It is not surprising that the initial decomposition temperature of macroinitiator (PCL-Br) improve obviously as compared with corresponding precursor PCL. The temperatures at 5% weight loss for selected samples are listed in Table 3. The results show that the block copolymers have good thermal stabilities below 350 °C.

Table 2

Characterization data of molecular weight, polydispersities, and composition of three series of PCL and PCL-*b*-PMPCS

Sample	$M_n \times 10^{-4}$		PMPCS ^a		PDI ^b	Liquid crystallinity ^c
	GPC ^b	NMR ^d	Wt%	Mol%		
PCL ₇₀ -Br	1.58	0.80	–	–	1.08	–
PCL ₇₀ PMPCS ₁₈	1.89	1.52	47.6	20.3	1.06	No
PCL ₇₀ PMPCS ₄₄	2.33	2.59	69.0	38.6	1.06	Yes
PCL ₇₀ PMPCS ₅₉	2.58	3.19	75.0	45.7	1.07	Yes
PCL ₇₀ PMPCS ₁₀₃	3.22	4.97	83.9	59.5	1.07	Yes
PCL ₇₀ PMPCS ₁₇₂	4.17	7.74	89.6	71.0	1.06	Yes
PCL ₁₁₃ -Br	2.26	1.29	–	–	1.11	–
PCL ₁₁₃ PMPCS ₂₅	2.84	2.30	43.9	18.1	1.09	No
PCL ₁₁₃ PMPCS ₄₆	2.99	3.13	58.9	28.8	1.09	Yes
PCL ₁₁₃ PMPCS ₅₉	3.25	3.68	64.8	34.3	1.09	Yes
PCL ₁₁₃ PMPCS ₁₀₃	4.07	5.45	76.3	47.7	1.08	Yes
PCL ₁₁₃ PMPCS ₁₆₆	4.99	7.98	83.8	59.4	1.08	Yes
PCL ₁₁₃ PMPCS ₂₂₆	5.83	10.41	87.6	66.6	1.08	Yes
PCL ₂₀₀ -Br	3.50	2.28	–	–	1.10	–
PCL ₂₀₀ PMPCS ₁₆	3.91	2.93	22.1	7.6	1.09	No
PCL ₂₀₀ PMPCS ₆₂	4.16	4.77	52.2	23.5	1.10	Yes
PCL ₂₀₀ PMPCS ₁₀₉	4.83	6.68	66.0	35.3	1.08	Yes
PCL ₂₀₀ PMPCS ₁₄₃	4.98	8.06	71.7	41.7	1.10	Yes
PCL ₂₀₀ PMPCS ₁₅₅	5.70	8.57	73.4	43.7	1.09	Yes
PMPCS ^e	2.06	–	–	–	1.07	Yes

^a Determined from the M_n (PCL-Br) and M_n (PCL-*b*-PMPCS) by ¹H NMR analysis.

^b Determined from GPC, calibrated by PS standards.

^c Examined by POM.

^d Calculated based on ¹H NMR analysis of the PCL-Br and PCL-*b*-PMPCS.

^e Prepared by ATRP for comparison.

Table 3
Thermal data from TGA and DSC measurements for homopolymers and diblock copolymers^a

Sample	T_d (°C) ^b	$T_{g,PCL}$ (°C)	$T_{m,PCL}$ (°C)	X_c (%)	$T_{g,PMPCS}$ (°C)
PCL ₇₀ -Br	329.7	-59.3	55.2	58.9	-
PCL ₇₀ PMPCS ₁₈	348.6	-55.7	51.6	37.6	-
PCL ₇₀ PMPCS ₄₄	-	-59.7	37.7	0.8	79.1
PCL ₇₀ PMPCS ₅₉	365.9	-63.3	40.7	7.7	110.2
PCL ₇₀ PMPCS ₁₀₃	-	-62.1	40.5	8.4	117.4
PCL ₇₀ PMPCS ₁₇₂	379.2	-64.2	42.8	10.9	120.6
PCL ₁₁₃ -Br	368.2	-61.2	55.2	57.3	-
PCL ₁₁₃ PMPCS ₂₅	363.9	-	52.8	44.2	-
PCL ₁₁₃ PMPCS ₄₆	-	-	51.9	46.9	97.9
PCL ₁₁₃ PMPCS ₅₉	367.3	-	51.9	49.9	113.8
PCL ₁₁₃ PMPCS ₁₀₃	-	-	50.4	43.3	117.6
PCL ₁₁₃ PMPCS ₁₆₆	378.8	-	48.9	37.2	118.4
PCL ₁₁₃ PMPCS ₂₂₆	-	-	47.0	32.6	120.0
PCL ₂₀₀ -Br	368.0	-63.7	55.2	57.8	-
PCL ₂₀₀ PMPCS ₁₆	368.0	-57.8	55.3	49.6	-
PCL ₂₀₀ PMPCS ₆₂	-	-59.5	55.6	49.5	110.9
PCL ₂₀₀ PMPCS ₁₀₉	371.4	-59.8	53.9	47.3	117.2
PCL ₂₀₀ PMPCS ₁₄₃	-	-61.5	53.9	43.8	118.5
PCL ₂₀₀ PMPCS ₁₅₅	376.3	-62.8	53.3	41.9	117.8
PMPCS	387.1	-	-	-	120.7

^a Data of DSC are determined from the second heating rate of 10 °C/min after cooling at 10 °C/min.

^b Temperature at 5% weight loss, determined from the TGA at heating rate of 10 °C/min under atmosphere of N₂.

3.4.2. Liquid crystalline behavior

PMPCS is known to be nematic liquid crystalline polymer above its T_g and no clearing point is detected until decomposition. The liquid crystalline behavior of the diblock copolymers was investigated by POM. As shown in Table 2, when DP of PMPCS segment is not less than 44, the block copolymer exhibits liquid crystallinity. No relationship between the liquid crystallinity and length of the PCL block was found in three series of diblock copolymers. Chen et al. have studied the liquid crystalline behavior of different molecular weights PMPCS [23]. Based on Flory's estimation, the critical DP of 39–42 for stabilizing the LC phase was calculated. The value is corresponding to our result of 44. Representative LC texture of block copolymer is shown in Fig. 7.

3.4.3. Solid state behavior

When the question of immiscibility of diblock copolymers is addressed, it is usually to measure the glass transitions or melting points of each component [44,45].

At first, the diblock copolymers with longer length PCL were investigated. Fig. 8 presents the typical thermograms of diblock copolymer based on the PCL₂₀₀-Br including PCL₂₀₀-Br and homo-PMPCS at second heating run. As shown in Fig. 8, T_g of PCL was detected unambiguously for this block copolymer like PCL homopolymer. A similar trend was observed for copolymers based on PCL₂₀₀-Br. The values of transitions and crystallinities are summarized in Table 3. When the DP of PMPCS was over 16, the T_g of the PMPCS block was observed. These features demonstrated the multiphase of block copolymers. With an increasing of the PMPCS block, the block copolymer

showed a melting endotherm of the PCL block between 55 and 53 °C and crystallinity was changed modestly from 50 to 42%. This indicated that the crystallization of PCL block was affected by PMPCS block but the effect was not very pronounced.

Similar to the diblock copolymer based on PCL₂₀₀-Br, broadening T_g of PCL was observed for the PCL₁₁₃-Br diblock copolymer with DP of PMPCS lower than 103. Representative DSC curve is shown in Fig. 9. When the DP of the PMPCS increased (over 103), the T_g of PCL was puzzling due to low content as well as the high crystallinity of PCL. The experiment in order to prevent the PCL from crystallization was failed by quenching PCL₁₁₃PMPCS₂₂₆ to -90 °C and equilibrated for 2 min. It was found that the crystallization was not depressed. As a result, T_g of PCL block was not shown clearly in the subsequently heating curve. However, T_g s of PMPCS block were clearly observed

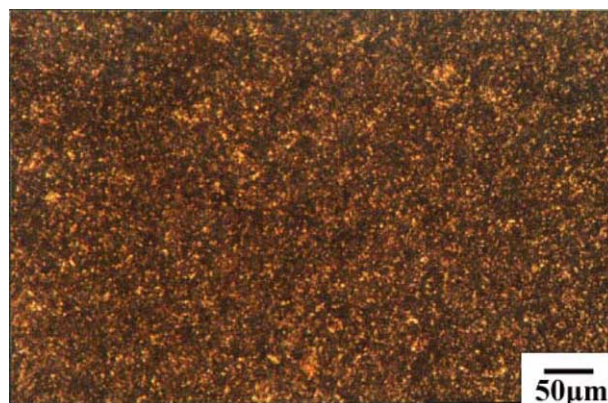


Fig. 7. LC texture of PCL₇₀PMPCS₄₄ at 200 °C.

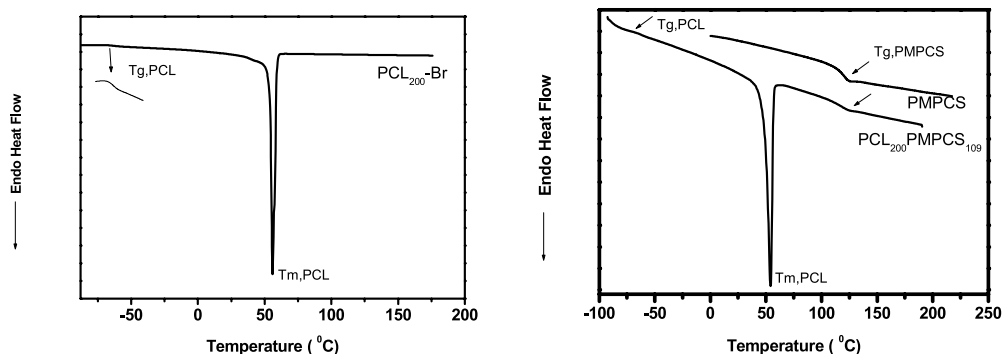


Fig. 8. DSC curves of PCL₂₀₀-Br and diblock copolymer based on PCL₂₀₀-Br at heating rate of 10 °C/min under a nitrogen atmosphere. The DSC curve of a LC PMPCS prepared by ATRP is included for comparison ($M_{n,GPC}=20,600$, PDI=1.07).

for all block copolymers with the exception of PCL₁₁₃-PMPCS₂₅ which had low DP of PMPCS (Table 3). This demonstrated that the block copolymers remained micro-phase separations. With an increase of content of the PMPCS, the crystallization and melting temperature of PCL block decreased. This indicated that the PMPCS block had obviously effect on the crystallinity of PCL block.

The diblock copolymers based on PCL₇₀-Br exhibited thermal behavior significantly different from the other two series of diblock copolymers. Fig. 10 presents the thermogram of PCL₇₀PMPCS₅₉. The T_g s of PMPCS block were clearly observed for copolymers which had higher DP of PMPCS (over 18). The T_g s of PCL block for all copolymers were observed even the content of PCL were lower than 10 wt%. This may due to lower crystallinity of PCL block. As shown in Table 3, the crystallinities of diblock copolymers were depressed notably and affected by content of PMPCS strongly. In agreement with the literature [46,47], the intensity and position of glass transition of the PCL depend on the crystallinity of the PCL.

A detailed consideration of the data given in Table 3 showed that the diblock copolymer displayed a lower T_g and the wider T_g range of PMPCS with the decrease of PMPCS

length. The lower T_g of PMPCS was not caused by the molecular weight of PMPCS block because previously result showed that the T_g would not vary when M_n up to 1.0×10^4 [27]. This probably resulted from the partial miscibility of the short length PMPCS and PCL blocks above the melting temperature of PCL as a consequence of the direct chemical interlinkage between the two components. This interpretation would be consistent with higher T_g of PCL block in block copolymer with low DP of PMPCS (less than 44). Miscible and partially miscible block copolymers were found in polystyrene-*b*-poly(ϵ -caprolactone) copolymer system when the molecular weight of polystyrene was short ($M_n=6000$) [47]. Considering multiphase structure which was identified for diblock copolymer with short length PCL (PCL₇₀ series) in our work, it was more appropriate to say that both the lower T_g of PMPCS and the wider T_g range may be the result of size and interface effects of the PMPCS layers being located between molten PCL layers [12,47].

Though the main thermal transitions exhibited by PCL-*b*-PMPCS block copolymers unambiguously concluded to their multiphase character, this structural feature would be further confirmed by the direct observation of the phase morphology by TEM [48,49].

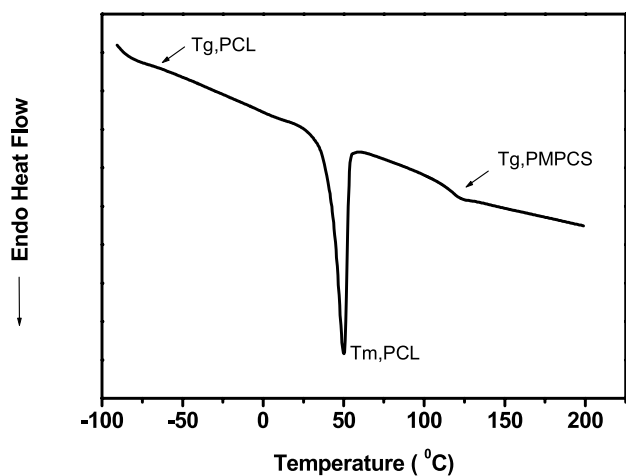


Fig. 9. Representative DSC curve of PCL₁₁₃PMPCS₁₀₃ at heating rate of 10 °C/min.

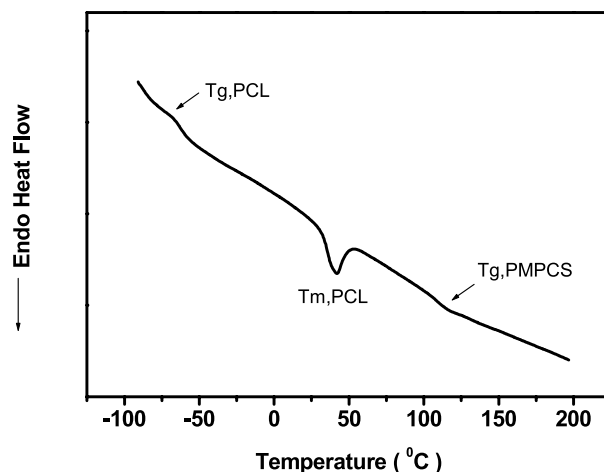


Fig. 10. DSC curve of PCL₇₀PMPCS₅₉ at heating rate of 10 °C/min.



Fig. 11. The TEM image of a thin section of PCL₂₀₀PMPCS₆₂. The sample was sectioned followed by RuO₄ staining for 30 min. The dark regions are PMPCS and amorphous PCL domains, which were stained by RuO₄.

The samples for TEM were obtained by solution-casting films (thickness over 1 mm) from THF solutions. The solvent is allowed to evaporate at room temperature for 5 days. Residual solvent was removed under vacuum, and the sample was then annealed at 150 °C under vacuum. A typical TEM image of PCL₂₀₀PMPCS₆₂ is shown in Fig. 11. The black parts are ascribed to PMPCS segments and amorphous PCL. From the image, alternating black and white strips were easily discernible. Thus, the microphase separated structures with a long-range order was directly confirmed for the sample. We must advise that above morphological result are preliminary and presented just for validating a nanophase separated system. Comprehensive investigations of the microphase separated structure with different content are in progress and will be the subject of the forthcoming paper.

4. Conclusion

Three series of crystalline and liquid crystalline diblock copolymers, PCL-*b*-PMPCS, are synthesized with PCL blocks of 8000, 12,900, and 22,800 molecular weights, respectively. Kinetic study of ATRP shows that the polymerization proceeded in a controlled way up to high conversions. All obtained block copolymers have relatively narrow polydispersity indices (PDI < 1.11). Microphase separation of diblock copolymers is confirmed by DSC

and directly observed through TEM. With a decrease of PMPCS length in diblock copolymer, the partial miscibility is proposed due to chemical interlinkage of short length PCL and PMPCS. Crystallinity of PCL is greatly affected by the length of the PCL block and composition of PMPCS in copolymer. The liquid crystallinity is investigated by POM. The result shows that the PMPCS block exhibit liquid crystalline behavior when the DP of PMPCS is higher than 44. The length of PCL block has no remarkable effect on the liquid crystallinity of PMPCS block. The fact that these block copolymers contain crystallizable and liquid crystalline blocks, i.e. PCL and PMPCS, made them very interesting from a structural point of view.

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