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ORIGINAL PAPER

Synthesis of A_2B_2 miktoarm star copolymers from a new heterobifunctional initiator by combination of ROP and ATRP

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Abstract A new heterobifunctional initiator, 2,3-bis(2-bromo-2-methylpropionyloxy) succinic acid, was synthesized and used in preparation of A_2B_2 miktoarm star copolymers, (polystyrene)$_2$(poly(ε-caprolactone))$_2$, by combination of atom transfer radical polymerization (ATRP) and Controlled ring-opening polymerization (ROP). The structures of products were confirmed by the ^{1}H NMR, ^{13}C NMR, FT–IR, elemental analysis, differential scanning calorimetry (DSC), and gel permeation chromatography (GPC). GPC traces show that the obtained polymers have a relatively narrow molecular weight distribution. The compositions of resulting miktoarm star copolymers were very close to theoretical.

Keywords Miktoarm · Star block copolymers · Polystyrene (PS) · Poly(ε-caprolactone) (PCL) · Controlled ring-opening polymerization · Atom transfer radical polymerization

Introduction

Block copolymers have attracted the interest of polymer chemists due to their feasible applications as adhesives, surfactants, compatibilizers, thermoplastic elastomers, and potential utility in many areas [1, 2]. Recently, there is a considerable focus on the nonlinear polymers. Among them, miktoarm star block copolymers have received great attention duo to their unique architectures and so unique properties regarding microphase separation in solid state as well as in solution [3–5]. There are two general strategies for synthesizing miktoarm star copolymers relies on living anionic polymerization; the first one is a chlorosilane

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approach, and the second one involves divinyl compounds [6–10]. However, these methods are limited to few monomers and required relatively rigorous polymerization conditions. Furthermore, both the precise arm numbers and the accurate architecture of the miktoarm star copolymers could not be controlled [10]. Designing a heteromultifunctional initiator which could initiate various polymerizations independently and sequentially is an efficient method for the construction of well-defined A_nB_m miktoarm star copolymers with exact arm numbers and length.

Until recently, controlled living polymerization methods (CLP), such as controlled ring-opening polymerization (ROP) [11], atom transfer radical polymerization (ATRP) [12–14], reversible addition-fragmentation chain transfer (RAFT) [15], and nitroxide-mediated radical polymerization (NMP) [16] have facilitated the synthesis of miktoarm star block copolymers with well-defined and complex macromolecular architectures due to the wide variety of feasible monomers and benign polymerization conditions. However, in some cases preparation of miktoarm star copolymers by only one polymerization method is difficult. So, various types of miktoarm star copolymers with different chemical compositions and molecular topologies have been synthesized by the combination of aforementioned methods [17–32].

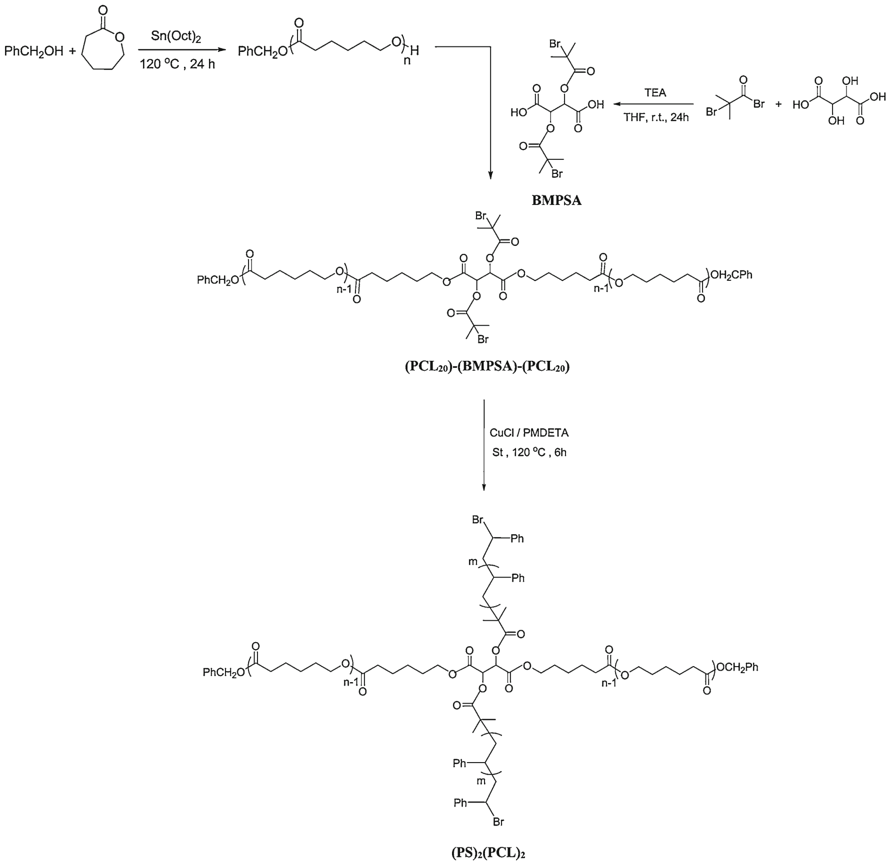
For the first time the A_2B_2 miktoarm copolymers were synthesized by Xie and Xia [33] using a chlorosilane method. Iatrou and Hadjichristidis [6] also obtained $(PS)_2(PB)_2$ using titration techniques monitored by size exclusion chromatography (SEC). Hadjichristidis and Dumas [34–36] used the combination of ROP of ε-caprolactone and ATRP of styrene or *tert*-butyl methacrylate to synthesize A_2B_2 miktoarm star polymers from a heterotetrafunctional initiator. Muller and Hadjichristidis [35] reported the synthesis, morphology, and basic calorimetric behavior of $(PCL)_2(PS)_2$ miktoarm star copolymers. In these methods, due to using inappropriate initiators for the preparation of miktoarm star copolymers, the utilizing of protection and deprotection procedures, or performing through more steps is necessary. Because of the mentioned reasons, some of the previous procedures are not easy to set, exactly.

In this article, we describe the synthesis of well-defined $[(PS)_2(PCL)_2]$ miktoarm star block copolymers, involving just four steps, starting from BMPSA as a new heterobifunctional initiator, bearing two bromine for preparation of PS arms via ATRP and two carboxyl groups for coupling reactions of poly(ε-caprolactone) prepared by the anionic coordinated ROP (Scheme 1).

Experimental

Materials

ε-Caprolactone (Cl, 99%) and styrene (99%) were purchased from Aldrich and dried with calcium hydride for 48 h and distilled under high vacuum before use. Triethylamine (TEA), dichloromethane (CH_2Cl_2), Tetrahydrofuran (THF), methanol (MeOH), toluene, and *N,N*-dimethylformamide (DMF) also were supplied by Merck Company and dried before use. Pentamethyl diethylene triamine (PMDETA)



Scheme 1 The synthesis of $(PS)_2(PCL)_2$ miktoarm star copolymers

was received from Aldrich. All other chemicals were purchased either from Across and used without further purification.

Characterization

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 25 °C with a BRUKER DRX-300 AVANCE spectrometer at 300.13 MHz. IR spectra were recorded on a Bomem MB-Series FT–IR spectrophotometer using the KBr disk method. The gel permeation chromatographic (GPC) system was used to determine the number-average molecular weights (M_n) of polymers. The GPC system was equipped with Waters 2690D separations module, Waters 2410 refractive index detector. THF was introduced as the eluent at a flow rate of 0.3 mL min^{-1}. Waters millennium module software was used to calculate molecular weight on the basis of a universal calibration curve generated by polystyrene standard with narrow molecular weight distribution. The thermal stability of the samples was determined using a thermogravimetric analyzer (TGA/DTA BAHR: STA 503) under air and a heating rate of 10 °C min^{-1} from 0 to 200 °C. The weight percentages of X (where X = carbon or hydrogen atoms) were assessed by elemental analysis at Elementar Analysensysteme GmbH.

Synthesis of heterobifunctional initiator (BMPSA)

In a three-neck round bottom flask equipped with a magnetic stirrer, L-tartaric acid (5.55 g, 37 mmol) was dissolved in anhydrous THF (80 mL). Triethylamine (12.6 mL, 90 mmol) was added by syringe. After cooling the flask to 0 °C in an ice-salt bath, a solution of 2-bromoisobutyryl bromide (11.1 mL, 90 mmol) in THF was added dropwise. The mixture was stirred at room temperature overnight. The salt was filtered off and the solvent was completely evaporated under vacuum. A clearly viscous liquid (19.36 gr, 90%) was obtained and used without further purification. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.8 (*s*, 2H, COOH), 3.7 (*s*, 2H, CH), and 1.9 (*s*, 6H, CH_3).^{13}C NMR ($CDCl_3$, 300 MHz) δ (ppm): 175.67 (C^c, C^e), 67.77 (C^d), 30.54 (C^b), and 25.41 (C^a).

Synthesis of hydroxyl-terminated PCL, (PCL-OH)

Typically, ε-caprolactone (1.03 g, 9.04 mmol), benzyl alcohol (46 µL, 0.45 mmol) and $Sn(Oct)_2$ (0.00366 g, 2 µmol) as a catalyst were added into a round-bottomed flask. The solution was heated up to 120 °C under stirring for 24 h. After completion of the reaction, the mixture was cooled to room temperature. The crude product was dissolved in 5 mL dichloromethane (CH_2Cl_2). Then the polymer was precipitated in an excess of cold methanol to remove residual CL monomers. The polymer was then dried in a vacuum oven until it achieved a constant mass (PCL_{20}-OH, 0.95 gr, 92.2% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.35 (*br. s*, Ph^aCH_2), 5.11 (*s*, $PhCH_2^b$), 4.05 (*t*, CH_2^fOCO), 3.64 (*t*, $CH_2^{f'}OH$), 2.30 (*t*, $COCH_2^c$), 1.60 (*m*, $COCH_2CH_2^dCH_2CH_2^dCH_2OCO$), and 1.37 (*m*, $COCH_2CH_2CH_2^eCH_2CH_2$ OCO). ^{13}C NMR ($CDCl_3$, 300 MHz) δ (ppm): 173.56 (C^c), 128.17 (C^a), 64.13 (C^b, C^h), 34.09 (C^d), 28.13 (C^g), 25.50 (C^f), and 24.55 (C^e).

Synthesis of macroinitiator (PCL_{20})-(BMPSA)-(PCL_{20})

In a 50-mL flask with a magnetic stirring bar, hydroxyl-terminated PCL (PCL-OH) (M_n = 2393.42 g mol^{-1}, 0.955 g, 0.4 mmol) was dissolved in anhydrous dichloromethane (9.0 ml). 4-dimethylaminopyridine (DMAP, 0.036 g, 0.3 mmol) and BMPSA (0.145 g, 0.25 mmol) were added subsequently. Then, the flask was cooled to 0 °C, a diluted solution of *N,N′*-dicyclohexyl carbodiimide (DCC, 0.051 g, 0.25 mmol) was added dropwise over 2 h. The reaction mixture was warmed to room temperature and stirred for 48 h. After filtration of dicyclohexylurea (DCU), the crude product was precipitated into methanol and collected by vacuum filtration. After redissolving the solid in CH_2Cl_2, the precipitation cycle was repeated two more times followed by re-precipitation in methanol. The solid product was dried in a vacuum oven at room temperature for 24 h to obtain the macroinitiator (PCL_{20})-(BMPSA)-(PCL_{20}) (1.00 gr, 91.6% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm):

7.35 (*br. s*, $Ph^{a}CH_2$), 5.12 (*s*, $PhCH^{b}_{2}$), 4.06 (*t*, $CH^{f}_{2}OCO$), 3.7 (CH^{g}), 2.28 (*t*, $COCH^{c}_{2}$), 1.93 (*s*, $CH(CH_3)^{h}_{2}$), 1.63 (*m*, $COCH_2CH^{d}_{2}CH_2CH^{d}_{2}CH_2OCO$), and 1.38 (*m*, $COCH_2CH_2CH^{e}_{2}CH_2CH_2OCO$). ^{13}C NMR ($CDCl_3$, 300 MHz) δ (ppm): 173.56 (C^{c},C^{i},C^{k}), 128.18 (C^{a}), 64.14 (C^{b}, C^{h}, C^{j}), 34.10 ($C^{d,}$ C^{l}), 28.32 (C^{g}), 25.66 (C^{m}), 25.51(C^{f}), and 24.56 (C^{e}). Elemental analysis: C, 61.59; H, 8.68; (calcd): C, 61.52; H, 8.25.

Synthesis of miktoarm star copolymer $(PS)_2(PCL)_2$

This step consist of the growth of two polystyrene chains by ATRP from the two centered bromoisobutyryl groups of the (PCL_{20})-(BMPSA)-(PCL_{20}) macroinitiator.

The (PCL_{20})-(BMPSA)-(PCL_{20}) macroinitiator ($M_n = 5575$ g mol^{-1}, 0.557 g, 0.1 mmol) was added into the polymerization apparatus contains anhydrous toluene followed by the addition of styrene (2.5, 6.0, and 14.0 mmol). The PMDETA (0.4 mmol) was injected into the reaction flask under stirring. After the introduction of CuCl (0.2 mmol) the apparatus was deoxygenized and the polymerization was allowed to proceed at 120 °C. The reaction led to the dark green and viscous solution; the reaction was terminated by exposure to air followed by dilution in THF immediately. The solution was purified through a column containing silica gel to remove the copper catalyst and obtain a colorless solution. Then the solvent was evaporated under reduced pressure and the miktoarm copolymer was precipitated in an excess of cold methanol. After redissolving the solid in THF, the precipitation cycle were repeated two other times followed by re-precipitation in methanol. The resulting product was dried under vacuum at room temperature overnight and after achieving constant weight, obtained the miktoarm star copolymers $(PS)_2(PCL)_2$ weighed for the determination of the polymer conversion. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.36 (br. s, $Ph^{a}CH_2$), 6.59 and 7.09 (br. s, $Ph^{j+i}CHCH_2$), 5.12 (*s*, $PhCH^{b}_{2}$), 4.07 (*t*, $CH^{f}_{2}OCO$), 2.32 (*t*, $COCH^{c}_{2}$), 1.64–1.89 (br. s, $COCH_2CH^{d}_{2}CH_2CH^{d}_{2}CH_2OCO$, $PhCH^{h}CH_2$), and 1.41–1.46 (*m*, 2H, $COCH_2CH_2CH^{e}_{2}CH_2CH_2OCO$, $PhCHCH^{g}_{2}$). ^{13}C NMR ($CDCl_3$, 300 MHz) δ (ppm): 173.57 (C^{c},C^{i},C^{k}), 128.20–127.57 (C^{a},C^{n}), 64.15 (C^{b}, C^{h}, C^{j}), 34.12 (C^{d}, C^{l}, C^{p}), 28.34 (C^{g}, C^{o}), 25.53 (C^{m},C^{f}), and 24.57 (C^{e}). Elemental analysis: C, 80.02; H, 8.175; (calcd): C, 83.16; H, 7.85.

Results and discussion

As mentioned before, because of high importance of miktoarm star copolymers, various types of these compounds with different chemical compositions and molecular topologies have been synthesized by the combination of the several polymerization methods. Therefore, we designed a new synthetic route for the synthesis of miktoarm star copolymers using heteromultifunctional initiator which has been presented in Scheme 1. The first step is synthesis of bifunctional initiator with two bromoisobutyryl groups and two carboxyl groups. Subsequently, $(PCL_{20}$-OH) was prepared by ring-opening polymerization of CL. Then (PCL_{20})-(BMPSA)-(PCL_{20}) was obtained by the coupling reaction of them and used as macroinitiator for ATRP of St. Finally, miktoarm star copolymers $(PS)_2(PCL)_2$ were synthesized.

Synthesis of heterobifunctional initiator (BMPSA)

This heterobifunctional initiator was synthesized by the reaction of L-tartaric acid and 2-bromoisobutyryl bromide in a 90% yield and was characterized by ^{1}H and ^{13}C NMR. The ^{1}H NMR spectrum of BMPSA (Fig. 1A) showed no signal corresponding to the OH proton of L-tartaric acid (appeared at 5.33 ppm). The signals at 1.9 and 3.7 ppm are attributed to protons of methyl (a) and methene (b) groups, respectively. Other signal at 8.8 ppm refers to the COOH protons (c). The obtained ^{1}H NMR spectrum in the $CDCl_3$ and D_2O confirmed it (Fig. 1A′). Moreover the ^{13}C (Fig. 2A) NMR spectrum also conformed to BMPSA.

Synthesis of hydroxyl-terminated PCL, (PCL_{20}-OH)

Linear PCL with one hydroxyl terminal group was synthesized by the controlled ring-opening polymerization (ROP) of ε-caprolactone using benzyl alcohol as initiator and stannous octoate as catalyst at 120 °C. The obtained (PCL-OH) was characterized by ^{1}H and ^{13}C NMR and FT–IR. The ^{1}H NMR and ^{13}C NMR

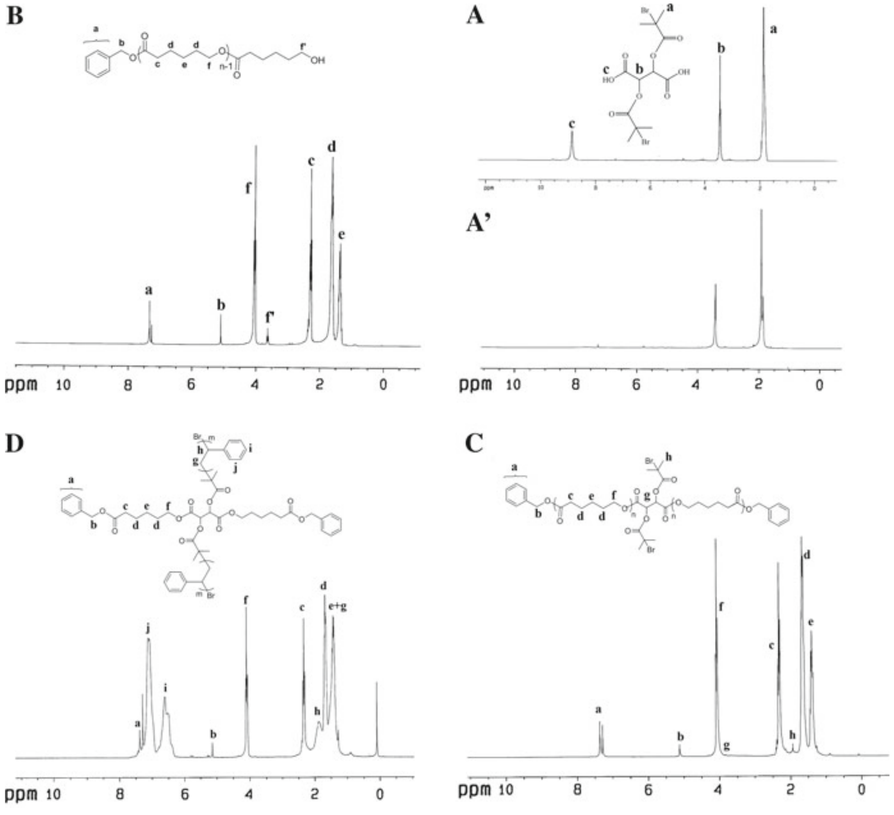


Fig. 1 ^{1}H NMR spectra of **A** BMPSA ($CDCl_3$), **A′** BMPSA (D_2O), **B** PCL_{20}-OH, **C** (PCL_{20})-(BMPSA)-(PCL_{20}), and **D** $(PS)_2(PCL)_2$

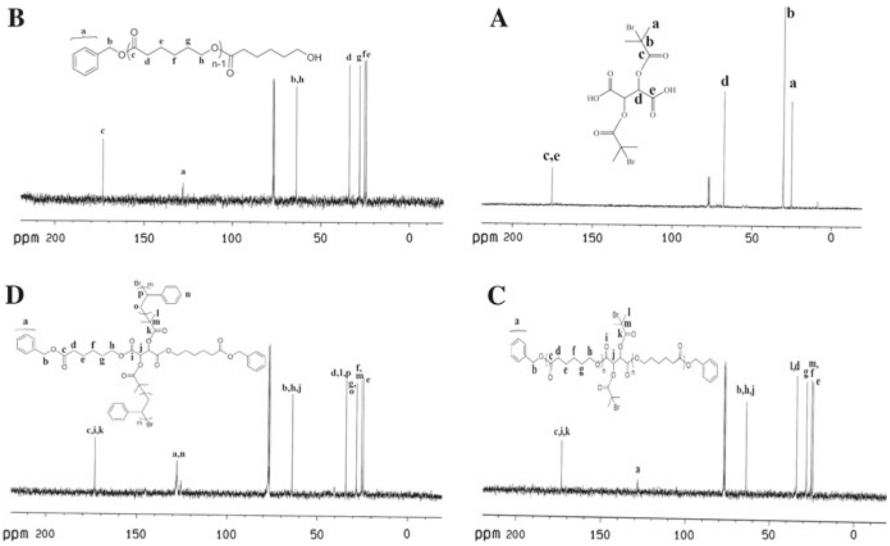


Fig. 2 ^{13}C NMR spectra of **A** BMPSA, **B** PCL$_{20}$-OH, **C** (PCL$_{20}$)-(BMPSA)-(PCL$_{20}$), and **D** (PS)$_2$(PCL)$_2$

spectrum of (PCL-OH), respectively, presented in Figs. 1B and 2B, confirm the preparation of PCL chains. From the integration ratio (I_f and I_b) which are, respectively, ascribed to the PCL and the initiator characteristics resonance signals, the number-average molecular weight, M_n(NMR) can be obtained. The M_n(NMR) is 2393.42 g mol^{-1} which agrees well with the M_n(Conv.) (calculated from the molar ratio of the ε-caprolactone and benzyl alcohol). The IR spectrum of the PCL-OH is shown in Fig. 3a. The IR spectrum of the PCL had a band characteristic for the ester carbonyl at 1723 cm^{-1} and a band for hydroxyl at 3540–3438 cm^{-1}. There is only one hydroxyl group per PCL chain, so the intensity of the hydroxyl band was low, reflecting the low content of –OH in the sample. (PCL$_{20}$-OH) shows a single melting peak $T_m = 60.9$ °C (Fig. 5a).

Synthesis of macroinitiator (PCL$_{20}$)-(BMPSA)-(PCL$_{20}$)

BMPSA was reacted with PCL$_{20}$-OH in the presence of DCC and DMAP at room temperature for 48 h to produce (PCL$_{20}$)-(BMPSA)-(PCL$_{20}$). The obtained product was characterized by ^{1}H NMR (Fig. 1C), ^{13}C NMR (Fig. 2C), and FT–IR (Fig. 3b). All of the spectra demonstrate that (PCL$_{20}$)-(BMPSA)-(PCL$_{20}$) has been formed successfully. The IR spectrum of the (PCL$_{20}$)-(BMPSA)-(PCL$_{20}$) macroinitiator had a characteristic band for the ester carbonyl at 1724 cm^{-1} and a band for hydroxyl at 3543–3441 cm^{-1}. By ^{1}H NMR, the peak assigned to the methylene (Fig. 1B, (f′)) protons of the PCL block at 3.65 ppm disappeared, while novel signals corresponding to methyl (g) protons and methyn (h) protons of BMPSAs appeared at 1.93 and 3.7 ppm, indicating that all the terminal hydroxyl groups have been reacted completely. The number-average molecular weight, M_n(NMR) (5575.56 g mol^{-1}) is in good agreement with the M_n(GPC) (5383.5 g mol^{-1}). Moreover, the GPC trace

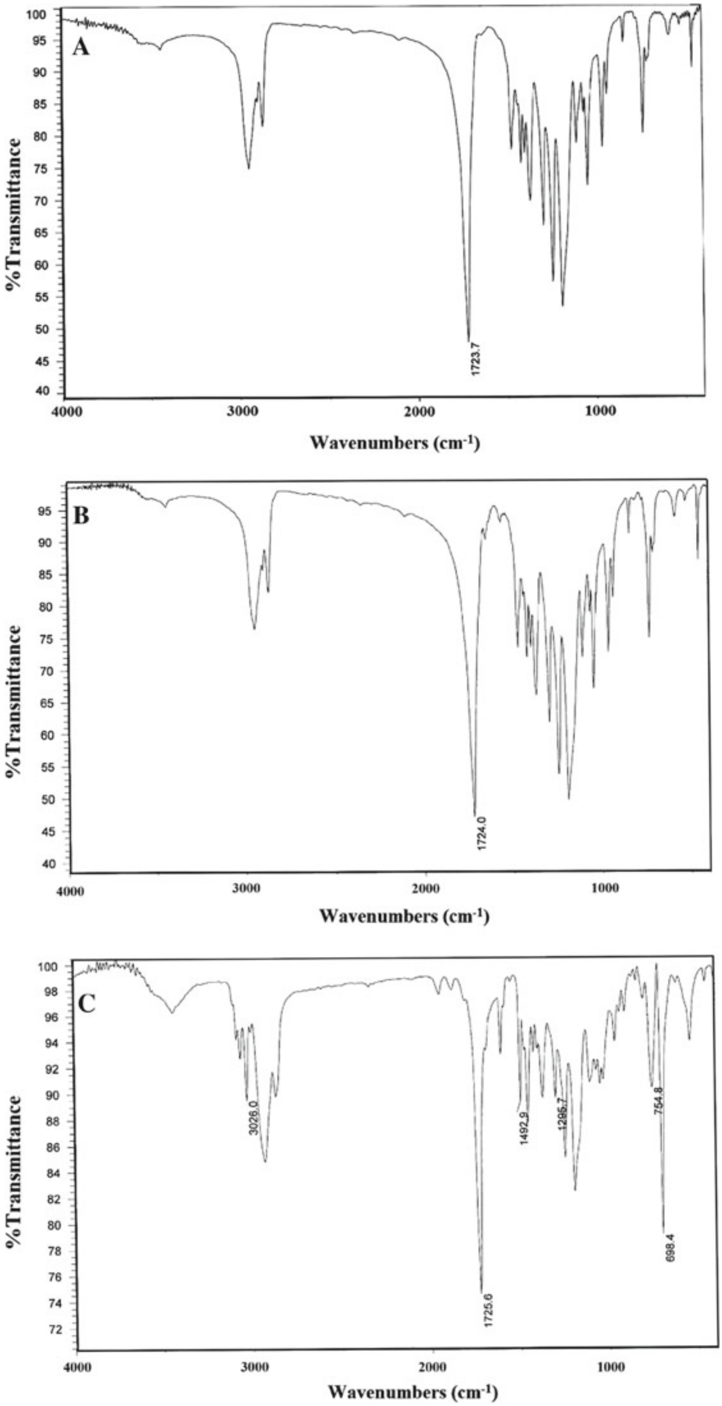


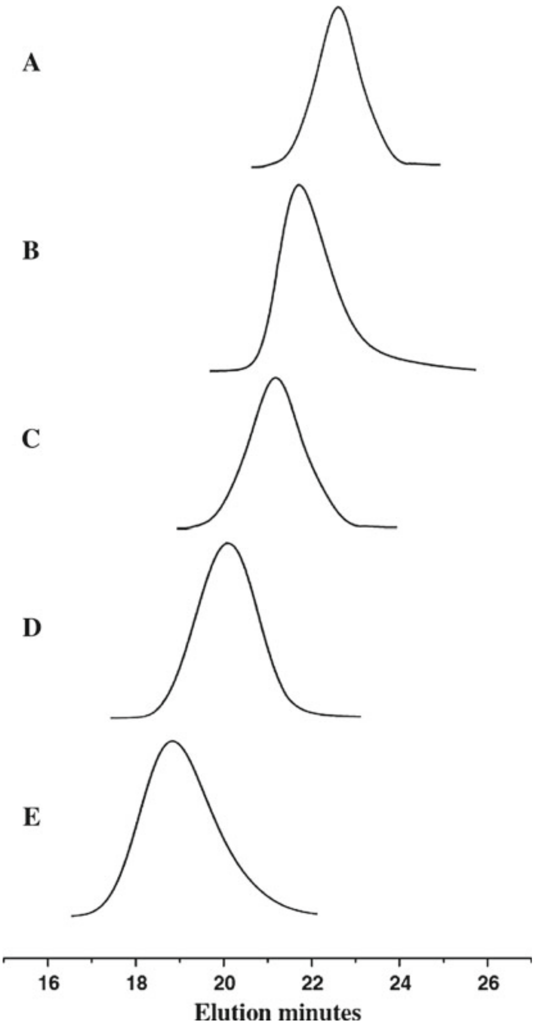
Fig. 3 FT–IR spectra of **a** PCL_{20}-OH, **b** (PCL_{20})-(BMPSA)-(PCL_{20}), and **c** $(PS)_2(PCL)_2$

has been presented in Fig. 4B. The (PCL_{20})-(BMPSA)-(PCL_{20}) homopolymer exhibits a peak melting temperature (T_m) of 61.5 °C (Fig. 5b).

Synthesis of miktoarm star copolymers $(PS)_2(PCL)_2$

The resulting (PCL_{20})-(BMPSA)-(PCL_{20}) was subsequently used as the macroinitiator in the ATRP of St for preparation of miktoarm star copolymers with three different molecular weight, $(PS)_2(PCL)_2$. The obtained miktoarm star copolymer, $(PS)_2(PCL)_2$, was characterized by ^{1}H NMR, ^{13}C NMR, FT–IR, and GPC. In the ^{1}H NMR of $(PS_{10})_2(PCL_{20})_2$ (Fig. 1D), in addition to the characteristic signals of (PCL_{20})-(BMPSA)-(PCL_{20}) at 7.36 (a), 5.12 (b), 4.07 (f), 2.32 (c), 1.66 (d), 1.41 (e) ppm, we can find the signals at 7.09 (j), 6.59 (i), 1.87 (h), and 1.41–146 (e + g) ppm ascribed to protons of the aromatic ring, methylene and methyn in PS arms.

Fig. 4 GPC traces of (*A*) PCL_{20}-OH, (*B*) (PCL_{20})-(BMPSA)-(PCL_{20}), (*C*) $(PS_{10})_2(PCL_{20})_2$, (*D*) $(PS_{19})_2(PCL_{20})_2$, (*E*) $(PS_{59})_2(PCL_{20})_2$



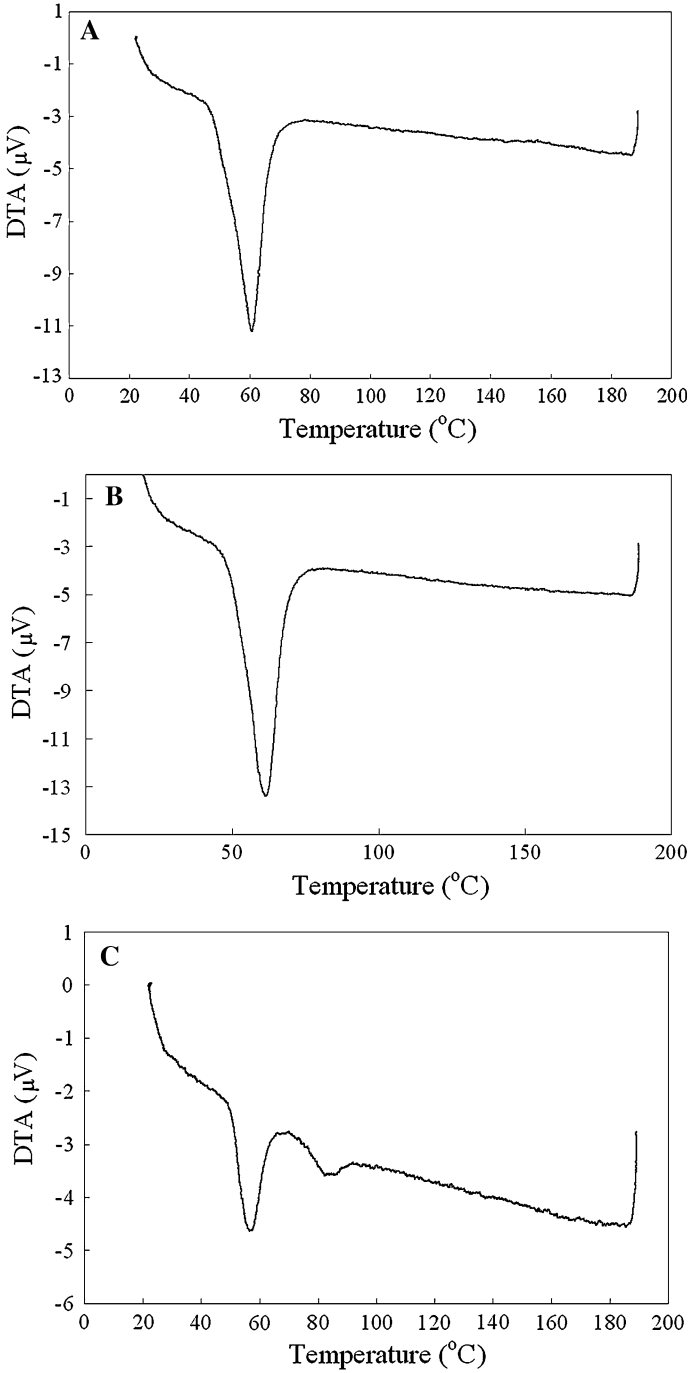


Fig. 5 DSC traces of **a** PCL_{20}-OH, **b** (PCL_{20})-(BMPSA)-(PCL_{20}), **c** $(PS_{59})_2(PCL_{20})_2$

Table 1 Synthesis and properties of $(PS)_2(PCL)_2$ miktoarm star copolymers by combination of ROP and ATRP

Sample	Conv.[a] (%)	$M_{n(\mathrm{GPC})}$	$M_{n(\mathrm{NMR})}$	$M_{n(\mathrm{Conv.})}$	M_w/M_n
PCL_{20}-OH[b]	98	2280.0	2393.42	2342.4	1.27
(PCL_{20})-(BMPSA)-(PCL_{20})	–	5383.5	5575.56	–	1.28
$(PSt_{10})_2(PCL_{20})_2$[c]	40	7463.1	7527.29	7269.8	1.31
$(PSt_{19})_2(PCL_{20})_2$[c]	33.4	9297.5	9438.60	9433.0	1.33
$(PSt_{59})_2(PCL_{20})_2$[c]	43	17649.0	17805.34	17711.4	1.39

[a] Gravimetric result

[b] [Benzyl alcohol]:[ε-Caprolactone] = 1:20, 120 °C, 24 h

$M_{n(\mathrm{NMR})} = [(I_f/I_b) \times 114] + 108 + 114$

$M_{n(\mathrm{conv.})} = [([\varepsilon\text{-Caprolactone}]/[\text{Benzyl alcohol}]) \times \text{Conv.} \times 114] + 108$

[c] $[(PCL_{20})\text{-(BMPSA)-}(PCL_{20})]$:[Styrene]:[CuCl]:[PMDETA] = 1:(25, 60, and 140):0/02:0/04, 120 °C, 6 h

$M_{n(\mathrm{NMR})} = 2(2I_{j+i}/5I_b) \times 104 + M_{n,(\mathrm{PCL20})\text{-}(\mathrm{BMPSA})\text{-}(\mathrm{PCL20})}$

$M_{n(\mathrm{conv.})} = [2([\text{Styrene}]/[(PCL_{20})\text{-(BMPSA)-}(PCL_{20})]) \times \text{Conv.} \times 104] + M_{n,(\mathrm{PCL20})\text{-}(\mathrm{BMPSA})\text{-}(\mathrm{PCL20})}$

From the integral values of the PS and the macroinitiator (PCL_{20})-(BMPSA)-(PCL_{20}) characteristics resonance signals (I_{j+i} and I_b, respectively), the number–average molecular weight, M_n(NMR) can be calculated. M_n(Conv.) can be calculated from the molar ratio of the styrene and the macroinitiator. The results are summarized in Table 1. The results show that the molecular weights increase with the addition of molar ratio of styrene. The M_n(NMR) is close to M_n(Conv.) that proves high initiation efficiency of Br in ATRP of St. As seen in Table 1, the M_n(NMR)s are less than M_n(GPC)s due to their different hydrodynamic volume from monodispersed polystyrenes standards. The molecular weight distributions are narrow (M_w/M_n = 1.31–1.39). The GPC traces of the $(PS)_2(PCL)_2$ miktoarm star copolymers presented in Fig. 4C–E are symmetrical and monomodal, which confirm that all the Br groups are involved in the ATRP of St. By comparison of a typical IR spectrum of $(PS_{10})_2(PCL_{20})_2$ with (PCL_{20})-(BMPSA)-(PCL_{20}), the characteristic absorption peaks of PS at 3026, 1492, 754, 798 cm^{-1} are observed in Fig. 3c, which confirm the formation of PS arms. The DSC analysis of the miktoarm star copolymers $(PS)_2(PCL)_2$ (Fig. 5c) showed two peaks, one at 56.6 °C, corresponding to T_m of the PCL chains, and another at 82.3 °C, attributed to T_g of the PS domains. The melting temperature (T_m) of the PCL block in $(PS_{59})_2(PCL_{20})_2$ decreased in comparison with that of (PCL_{20})-(BMPSA)-(PCL_{20}) when the morphological confinement increased as result of increasing the PS block content into the miktoarm star copolymers $(PS_{59})_2(PCL_{20})_2$ [35]; however, the melting temperature varied a few degrees, from 61.5 to 56.6 °C.

Conclusion

In this study, we have developed a new and feasible strategy for the preparation of well-defined A_2B_2 miktoarm star copolymers, which are composed of two PCL chains with benzyl group at its end and two PS chains. $(PS)_2(PCL)_2$ has been synthesized successfully in just four steps by the combination of coupling reaction of chain prepared by controlled ring-opening polymerization (ROP) and atom transfer radical polymerization (ATRP) with controlled molecular weight and narrow molecular weight distribution.

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