

ORIGINAL ARTICLE

One-step synthesis of a mid-chain functional macrophotoinitiator of a polystyrene-poly(ϵ -caprolactone) diblock copolymer via simultaneous ATRP and ROP using a dual-functional photoinitiator

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A one-step synthesis of a well-defined mid-chain functional macrophotoinitiator of a polystyrene-poly(ϵ -caprolactone) diblock copolymer (PSt-PI-PCL) was successfully performed at 110 °C using a novel dual-functional photoinitiator via simultaneous atom transfer radical polymerization and ring-opening polymerization (ROP). This dual-functional photoinitiator (Br-PI-OH), possessing a bromine group on one end and a hydroxyl group on the other, was synthesized by the reaction of the photoinitiator 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (HO-PI-OH) with 2-bromopropanoyl bromide. The two distinct polymerization reactions initiated by Br-PI-OH proceeded in a controlled manner without mutual interference. Elemental analysis and $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ and Fourier transform infrared spectroscopy (FT-IR) spectroscopy were used to characterize the chemical structure of Br-PI-OH. Characterization of the macrophotoinitiator PSt-PI-PCL was achieved using $^1\text{H-NMR}$, FT-IR, gel permeation chromatography, UV-vis and fluorescence spectroscopy.

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INTRODUCTION

Structurally well-defined block copolymers are an important class of polymeric materials owing to their technological applications and extraordinary properties. Preparation of such block copolymers is generally achieved through sequential addition of monomers to a living polymerization, controlled/living polymerization systems or the transformation approach.¹ Among these, the use of a dual or heterofunctional initiator to combine two distinct controlled/living polymerization methods is the preferred technique because of the possibility of a one-step process and its applicability to a wide range of monomers.^{2–5} Dual initiators contain two functional groups that can initiate two mechanistically different polymerizations independently without any intermediate transformation steps. Recently, one-step processes using dual initiators successfully synthesized well-defined block copolymers through several combinations of polymerization techniques, such as nitroxide-mediated polymerization with ring-opening polymerization (ROP),^{6,7} atom transfer radical polymerization (ATRP) with nitroxide-mediated polymerization,⁶ reversible addition-fragmentation chain transfer polymerization with ROP,^{5,8–10} as well as ATRP with ROP.^{4,11}

Few studies have investigated the synthesis of well-defined block copolymers in a one-step process that combines ATRP with ROP. However, such a process was used by Mecerreyes *et al.*⁶ to synthesize PMMA-*b*-PCL, using 2,2,2-tribromoethanol as the dual initiator; Nasser-Eddine *et al.*⁴ to prepare PtMMA-*b*-PCL; and more recently,

Kryuchkov and co-workers¹¹ to synthesize amphiphilic diblock copolymers of lactide and 2-dimethylaminoethyl methacrylate in a one-pot approach. Using an approach that is distinct from those in the literature, in this study, we synthesized a polystyrene-poly(ϵ -caprolactone) diblock copolymer (PSt-PI-PCL) via simultaneous ATRP and ROP using a dual-functional photoinitiator in a one-step process. The resultant block copolymer contains a photofunctional group in the center of the polymer chain, and this polymer is known as a mid-chain functional macrophotoinitiator.

In recent years, there has been marked interest in the synthesis of macrophotoinitiators as they possess a combination of the properties of polymers and low molecular weight photoinitiators.^{12–15} The advantages expected from macrophotoinitiators in ultraviolet (UV) curing applications include good compatibility, high reactivity, low migration and low volatility, which should reduce the odor problems associated with low molar mass photoinitiators.^{16,17} Macrophotoinitiators are also used as precursors for block and graft copolymers.^{18–20} Two methods have been proposed for the preparation of well-defined macrophotoinitiators: (i) the introduction of photoactive groups into the polymer using photofunctional compounds as initiators in a controlled/living polymerization, such as ATRP or ROP; (ii) the functionalization of the final polymer prepared by these techniques (ATRP or ROP) using initiators with suitable functional and photoreactive groups.^{21–23} Many studies have aimed to synthesize well-defined end- or mid-chain functional macrophotoinitiators of

polystyrene (PSt),^{23–26} poly(methyl methacrylate) (PMMA)²⁷ and/or poly(ϵ -caprolactone) (PCL)^{28–30} using the above methods.

We have previously synthesized well-defined macrophotoinitiators with mid- or end-chain photofunctional groups from bromine-functionalized photoinitiators with ATRP^{25,27} and hydroxyl-functionalized photoinitiators with ROP,^{28,29} as well as by functionalization of polymers obtained from ATRP or ROP using initiators with suitable functional and photoreactive groups.^{20,22,26,30} All of the macrophotoinitiators that we prepared using these methods were homopolymers. As part of our continuing interest in the synthesis (by various methods) and characterization of novel polymers possessing a photofunctional group in the middle or at the end of their chains, in this study, we combined ATRP and ROP in a one-step strategy. Many studies related to homopolymer-based macrophotoinitiators can be found in the literature, but there are no studies on the synthesis and characterization of copolymer-based macrophotoinitiators. To the best of our knowledge, in this study we provide the first reported synthesis of a well-defined block-type mid-chain macrophotoinitiator of PSt-PI-PCL via a combination of ATRP and ROP in a one-step process using a dual-functional photoinitiator containing a bromine group on one end and a hydroxyl group on the other.

EXPERIMENTAL PROCEDURE

Materials

ϵ -Caprolactone (ϵ -CL) (Sigma-Aldrich, Munich, Germany), styrene (St) (Sigma-Aldrich) and methyl methacrylate (MMA) (Sigma-Aldrich) were dried over CaH₂ followed by distillation under reduced pressure. The photoinitiator 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (HO-PI-OH, also known as Irgacure 2959) was purchased from Sigma-Aldrich and used without further purification. 2-Bromopropanoyl bromide (Sigma-Aldrich), CuBr (Sigma-Aldrich), 2,2'-bipyridine (Merck, Kenilworth, NJ, USA), pyridine (Lab-scan, Gliwice, Poland) and stannous 2-ethylhexanoate (Sn(Oct)₂) (Sigma-Aldrich) were also used as received. Dichloromethane (CH₂Cl₂) (Lab-scan) and tetrahydrofuran (THF) (Sigma-Aldrich) were dried and purified by previously reported methods. Methanol (Lab-scan) and all other chemicals were used as received.

Synthesis of the dual-functional photoinitiator (Br-PI-OH)

HO-PI-OH (1.12 g, 5 mmol), dry THF (30 ml) and pyridine (0.72 g, 10 mmol) were combined in a 250-ml three-necked round-bottom flask fitted with a condenser, a magnetic stirrer bead, a nitrogen inlet-outlet and an addition funnel containing 2-bromopropanoyl bromide (1.08 g, 5 mmol) and 30 ml of a dry THF mixture. The flask was placed in an ice-water bath. The solution of 2-bromopropanoyl bromide was added dropwise over a period of 45 min under nitrogen. Then, the mixture was allowed to reach room temperature and was stirred for 20 h. The resultant white precipitate was removed by filtration, and the solution was washed three times with 1 M HCl and twice with water. Then, the solution was dried with MgSO₄, and the solvent was removed by vacuum distillation. Finally, the remaining product was purified on a silica column and eluted with CH₂Cl₂/THF (3:1) to yield Br-PI-OH as a viscous orange–yellow liquid (yield: 1.47 g, 82%, after evaporation of the solvent). All steps were performed in the dark.

C₁₅H₁₉O₃Br: (359.22): Calcd. C 50.15%, H 5.33%; Found: C 50.02%, H 5.12%.

¹H-NMR (400 MHz, CDCl₃, δ /p.p.m.): 8.00 (d, 2H, –CO–aromatic), 6.89 (d, 2H, O–aromatic), 4.48 (t, 2H, –CH₂–O–aromatic), 4.34 (q, 1H, –CH–Br), 4.22 (t, 2H, –CH₂–O–CO–), 4.16 (broad peak, 1H, OH), 1.77 (d, 1H, –CH–CH₃) and 1.57 (s, 6H, CH₃–C–CH₃).

¹³C-NMR (400 MHz, CDCl₃, δ /p.p.m.): 202.48 (C=O, ketone), 170.07 (C=O, ester), 162.02, 132.31, 126.39 and 141.11 (aromatic carbons of benzene ring), 75.80 (C–OH), 65.59 (CH₂O–aromatic), 63.26 (CH₂O–CO–), 39.45 (CH), 28.56 (CH₃–C) and 21.45 (CH₃–CH).

Synthesis of the mid-chain functional macrophotoinitiator

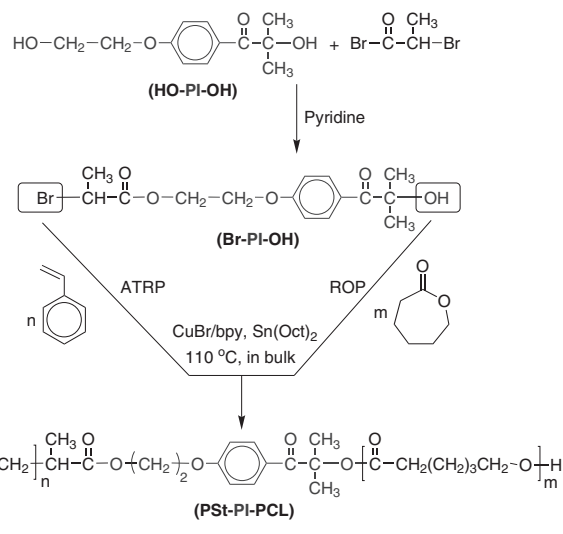
Polymerization was performed in a Schlenk tube equipped with a magnetic stirrer. The Schlenk tube was evacuated to a vacuum and then back-filled with nitrogen several times. The catalysts CuBr (0.093 g, 0.652 mmol) and stannous 2-ethylhexanoate (1.32 mg, 3.262 μ mol), the ligand 2,2'-bipyridine (0.305 g, 1.956 mmol), the dual-photoinitiator (Br-PI-OH) (0.234 g, 0.652 mmol) and the monomers ϵ -caprolactone (2.89 ml) and St (3 ml) were introduced into the tube under nitrogen atmosphere. The tube was warmed in an oil bath to 110 °C and stirred for 30 h at constant temperature. Following polymerization, the mixture was diluted with THF and passed through an alumina column to remove the complex salt. The polymer solution was concentrated and precipitated into 10-fold cold methanol. The polymer (PSt-PI-PCL) was collected after filtration and dried at room temperature in a vacuum. M_{nGPC} = 8700 g mol⁻¹ and M_w/M_n = 1.39, Conversion = 90% for St and 81% for ϵ -CL.

Photopolymerization

The photoinitiated free-radical polymerization of the monomer (MMA) in the presence of PSt-PI-PCL was performed in bulk at room temperature. MMA (1 ml) and PSt-PI-PCL (200 mg) were added to a Pyrex tube and degassed with nitrogen prior to irradiation by a 'merry-go-round-type' photoreactor equipped with 16 Philips 8 W/08 lamps (emitting light nominally at $\lambda > 300$ nm) and a cooling system. After 50 min of the photopolymerization, the polymer mixture obtained was diluted with CH₂Cl₂, precipitated into cold methanol and dried under vacuum at room temperature for 24 h. The conversion was calculated gravimetrically.

Characterization

¹H-NMR and ¹³C-NMR spectra were obtained using an Agilent 400 MHz NMR instrument with CDCl₃ as the solvent. Fourier transform infrared (FT-IR) spectra were measured with a Perkin-Elmer Spectrum Two FT-IR spectrophotometer. UV-vis spectra were obtained in a CH₂Cl₂ solution with a Shimadzu 1601 spectrophotometer. Fluorescence spectra were registered in a CH₂Cl₂ solution with a Jasco FP-6300 spectrofluorometer. The molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) using a Viscotek GPCmax Autosampler system consisting of a pump, three Viscotek GPC columns (G2000HHR, G3000HHR and G4000HHR), a Viscotek UV detector and a Viscotek differential refractive index detector with a THF flow rate of 1.0 ml min⁻¹ at



Scheme 1 One-step synthesis of the mid-chain functional macrophotoinitiator of the polystyrene-poly(ϵ -caprolactone) diblock copolymer using Br-PI-OH as the dual-functional photoinitiator. A full color version of this scheme is available at *Polymer Journal* online.

30 °C. GPC was calibrated using PSt standards with a narrow molecular weight distribution. The data were analyzed using Viscotek OmniSEC Omni-01 software.

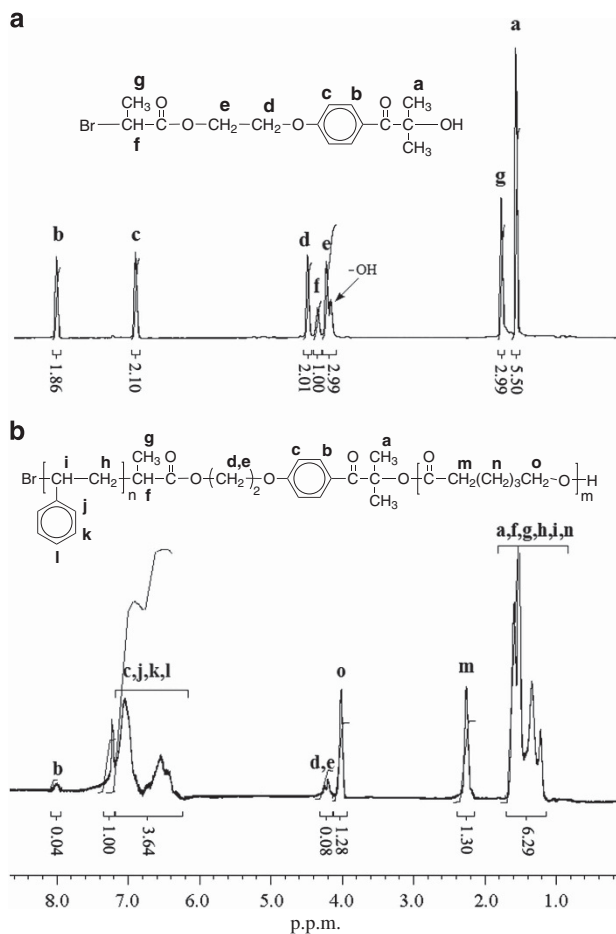


Figure 1 ¹H-NMR spectra of the dual-functional photoinitiator Br-PI-OH (a) and the diblock macrophotoinitiator PSt-PI-PCL (b).

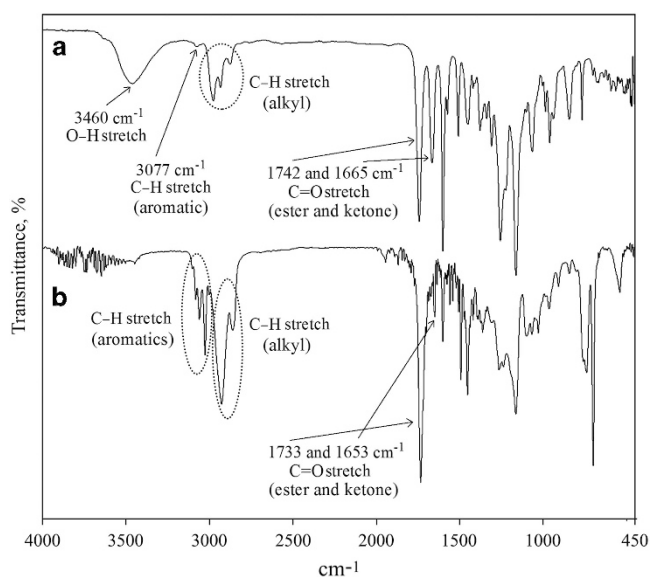


Figure 2 FT-IR spectra of the dual-functional photoinitiator Br-PI-OH (a) and the diblock macrophotoinitiator PSt-PI-PCL (b).

RESULTS AND DISCUSSION

In the present study, a well-defined mid-chain functional macrophotoinitiator of PSt-PI-PCL was successfully prepared by combining ATRP with ROP in a one-step process using a dual-functional photoinitiator. The dual-functional photoinitiator, Br-PI-OH, was synthesized by a condensation reaction of HO-PI-OH with 2-bromopropanoyl bromide, as shown in Scheme 1 (Reaction 1). The synthesis was performed in an ice-water bath using dry THF as the solvent. The dual-functionalized photoinitiator contains a bromine group that initiates the ATRP of vinyl monomers, such as St, and a hydroxyl functionality, which is the initiation center for the ROP of cyclic lactides or lactones, such as ε-CL.

The successful synthesis of Br-PI-OH was confirmed by characterization with elemental analysis and spectroscopic investigations. The ¹H-NMR spectrum (Figure 1a) exhibited the typical proton signals attributed to aromatic protons at 8.00 and 6.89 p.p.m., a methine

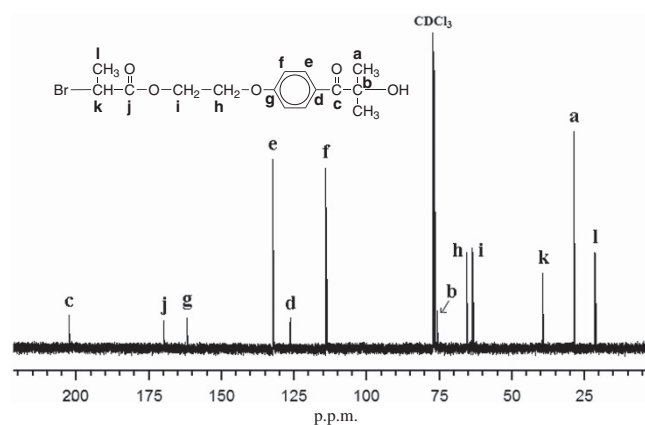


Figure 3 ¹³C-NMR spectrum of the dual-functional photoinitiator Br-PI-OH.

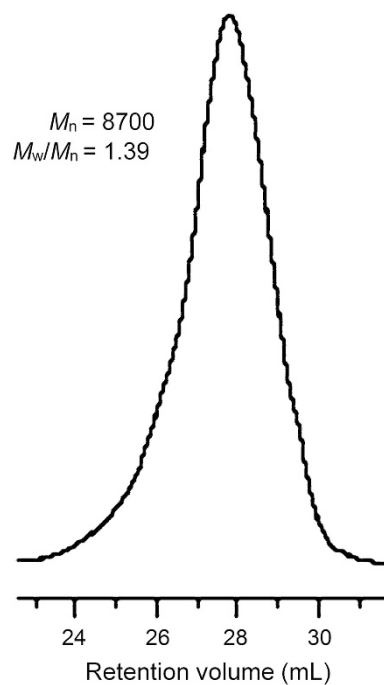


Figure 4 GPC trace of the diblock macrophotoinitiator PSt-PI-PCL.

(-CH) proton at 4.34 p.p.m., methylene (-CH₂) protons at 4.48 and 4.22 p.p.m. and methyl (-CH₃) protons at 1.77 and 1.57 p.p.m. The infrared absorption spectrum (Figure 2a) contained the characteristic OH alcohol, C=O ester and C=O keto stretching vibrations at 3460 cm⁻¹, 1742 cm⁻¹ and 1665 cm⁻¹, respectively, which also verified the formation of the dual-functional photoinitiator.

The ¹³C-NMR spectrum (Figure 3) also showed the characteristic carbon peaks expected from Br-PI-OH, which also confirmed the formation of the dual-functional photoinitiator.

The synthesized Br-PI-OH was used as a dual-functional initiator in the one-step polymerization of St and ε-CL monomers to prepare a mid-chain functional macrophotoinitiator of PSt-PI-PCL. During this one-step synthesis, the ATRP of St occurs simultaneously with the ROP of ε-CL to yield the diblock copolymer with a photofunctional group at the mid-point of the polymer chain. The reaction pathway for this process is shown in Scheme 1 (Reaction 2).

The obtained macrophotoinitiator (PSt-PI-PCL) was characterized by ¹H-NMR, FT-IR, GPC, UV-vis and fluorescence spectroscopy. In the ¹H-NMR spectrum of PSt-PI-PCL (Figure 1b), along with the

typical proton signals of PSt and PCL segments, proton signals corresponding to the mid-chain group of the macrophotoinitiator (PI) were observed: the peaks appearing at 4.21–4.17 p.p.m. were assigned to the PI methylene (-CH₂) protons. The characteristic aromatic protons of PSt and the methylene (-CH₂) protons (**m** protons) of the PCL segments were observed at ~7.20–6.25 and 2.35–2.29 p.p.m., respectively. The related corresponding assignments are given in Figure 1(b). The structure of PSt-PI-PCL was further supported by the FT-IR observations. The FT-IR spectrum contained the characteristic C=O ester band of the PCL unit, the aromatic bands of the PSt unit and the C=O keto group of the photoinitiator moiety, as shown in Figure 2(b).

The relative molecular weight and the molecular weight distribution of the synthesized PSt-PI-PCL were determined from GPC measurements. As shown in Figure 4, the GPC trace of the PSt-PI-PCL was unimodal and symmetrical ($M_n = 8700 \text{ g mol}^{-1}$ and $M_w/M_n = 1.39$). The conversion of the two monomers, the absolute molecular weight and the composition of the block copolymer were determined by the ¹H-NMR measurement shown in Figure 1(b). The conversions of St and ε-CL monomers were calculated as 90 and 81%, respectively, using the characteristic peak intensity of the photoinitiator residue (**b** protons) located at the junction of the two blocks. The kinetic profile of the one-step polymerization is shown in Figure 5. A decrease in the ATRP rate and an increase in the maximum conversion (~80%) of ε-CL were observed. The two polymerization rates were similar until the ROP plateaued at ~80% conversion of each monomer.

The block copolymer composition was determined as 52.55% PSt and 47.45% PCL, in per cent by mole, by comparing the integration ratio of the methylene (**m** protons) peak in the PCL (2.35–2.29 p.p.m.) and the aromatic peaks in the PSt block (7.20–6.25 p.p.m.). The absolute molecular weight ($M_{n, \text{H NMR}}$) was calculated as 7820 g mol⁻¹ ($M_{n, \text{H NMR}} = 7820$) using the following equation (1):

$$M_{n, \text{H NMR}} = (I_m/I_b) \times M_{\epsilon\text{-CL}} + (2I_{Ar}/5I_b) \times M_{\text{St}} + M_{\text{PI}} \quad (1)$$

where $M_{n, \text{H NMR}}$ is the ¹H-NMR molecular weight of PSt-PI-PCL; I_m , I_b and I_{Ar} are the integral values of the signals at 2.35–2.29 p.p.m. (CH₂ protons in the PCL segment), at 8.06–7.98 p.p.m. (aromatic 2

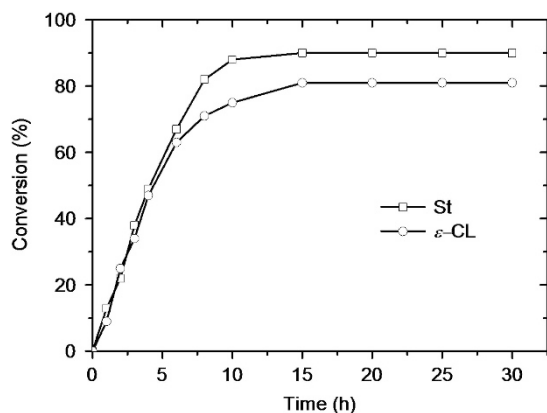
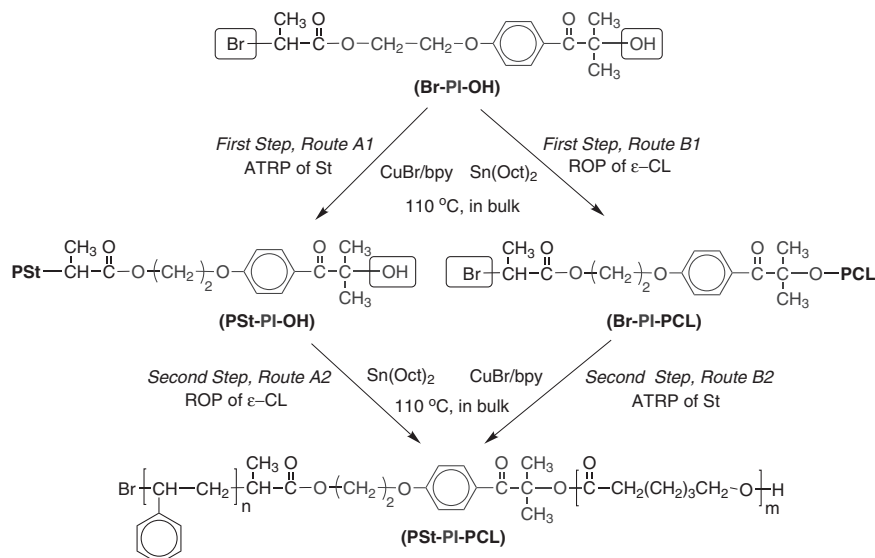


Figure 5 Kinetic study of the one-step polymerization.



Scheme 2 Two-step synthesis of the mid-chain functional macrophotoinitiator of the polystyrene-poly(ε-caprolactone) diblock copolymer. A full color version of this scheme is available at *Polymer Journal* online.

Table 1 Synthesis and properties of the mid-chain functional macrophotoinitiator of the polystyrene-poly(ϵ -caprolactone) diblock copolymer (PSt-PI-PCL) via a combination of ATRP^a and ROP^b

Polymer	Initiator (I)	Monomer	Time (h)	Conv. ^c (%)	M_n theo ^d	M_n H NMR ^e	M_n GPC ^f	M_w/M_n
Route A1, A2								
PSt-PI-OH	Br-PI-OH	St	7	82	3775	3750	3700	1.12
PSt-PI-PCL	PSt-PI-OH	ϵ -CL	35	90	7884	7990	7900	1.25
Route B1, B2								
Br-PI-PCL	Br-PI-OH	ϵ -CL	30	93	4246	4500	4400	1.43
PSt-PI-PCL	Br-PI-PCL	St	8	75	7370	7700	7500	1.35

Abbreviations: ATRP, atom transfer radical polymerization; GPC, gel permeation chromatography; ROP, ring-opening polymerization.

^aTemperature = 110 °C, [St]₀ = 8.75 the mol ratio of [St]₀/[I]/[CuBr]/[Bpy] = 40/1/1/3.^bTemperature = 110 °C, [ϵ -CL]₀ = 9.02 mol l⁻¹ (in bulk), the mol ratio of [ϵ -CL]₀/[I] = 40/1 and [I]/[Sn(Oct)₂] = 400/1.^cThe conversions were calculated as gravimetrically.^d M_n theo = $[M]_0/[I]_0 \times M_{monomer} \times Conv. + M_{initiator}$.^eDetermined from ¹H-NMR data.^fDetermined by GPC according PSt standards.

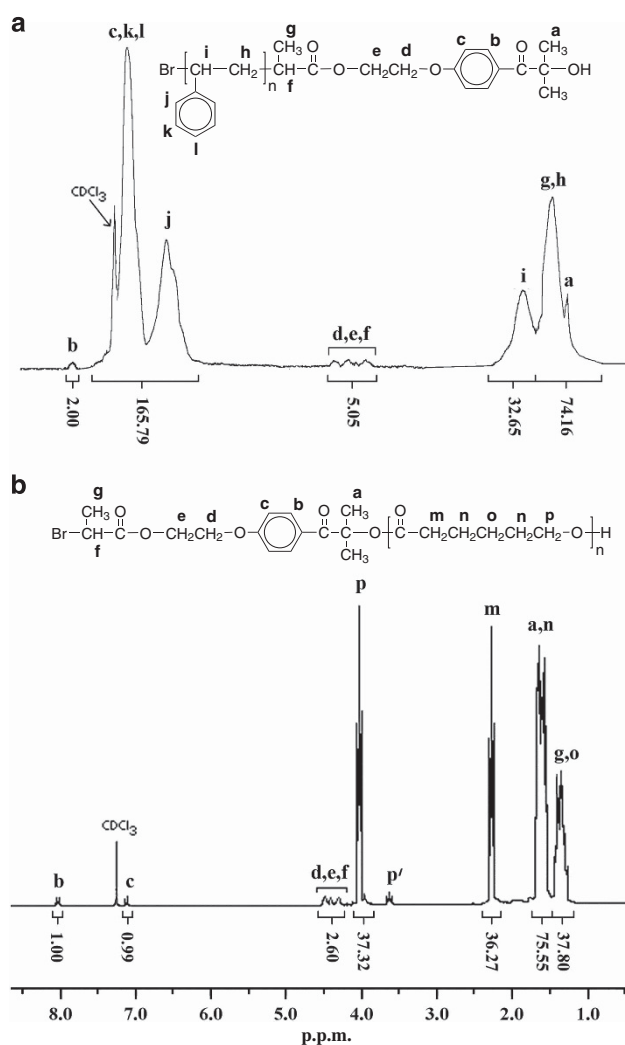
CH protons of the PI unit) and at 7.20–6.25 p.p.m. (aromatic CH protons in the PSt segment); $M_{\epsilon\text{-CL}}$, M_{St} and M_{PI} are the molecular weights of ϵ -CL, St and Br-PI-OH, respectively. The strong agreement between the M_n data from GPC and the ¹H-NMR measurements suggested that each block copolymer chain contained one photoinitiator group (PI) at the mid-point and that the one-step polymerization reaction proceeded in a controlled manner without mutual interference.

To demonstrate the efficiency of the dual initiator and the controllability of the polymerization reactions, the macrophotoinitiator of PSt-PI-PCL was also synthesized in two steps by a combination of ATRP of St and ROP of ϵ -CL. As shown in Scheme 2, two routes, ATRP followed by ROP (named route A1 and A2) and ROP followed by ATRP (named route B1 and B2), were attempted to obtain PSt-PI-PCL using Br-PI-OH as a dual-functional initiator. The experimental conditions and results are given in Table 1.

¹H-NMR and GPC measurements confirmed the resultant polymer structures. The ¹H-NMR spectra of the samples showed not only specific signals of polymers but also absorptions belonging to the PI moiety. For example, Figure 6 shows the ¹H-NMR spectra of the PSt-PI-OH and Br-PI-PCL precursors in CDCl₃.

As shown in Table 1, the measured and calculated M_n values were in good agreement, indicating that the photoinitiator added to the solution generated macrophotoinitiators with one growing end and one functional end (PSt-PI-OH and Br-PI-PCL), as well as a mid-chain functional macrophotoinitiator of PSt-PI-PCL, with low polydispersities. In all cases, the GPC traces of the polymers were unimodal and narrow, indicating that no side reactions occurred during the polymerization, and well-defined macrophotoinitiators were obtained. These results indicate that both of the routes (A1,A2 and B1,B2) are practical ways of obtaining well-defined PSt-PI-PCL. However, the polydispersities of polymers obtained via route B1,B2 were slightly broader than those of the polymers obtained via route A1,A2. Therefore, it can be concluded that ATRP followed by ROP (route A1,A2) is the preferred two-step preparation strategy for PSt-PI-PCL with a low molecular weight distribution. The ¹H-NMR, UV-vis absorption and fluorescence emission spectra of the PSt-PI-PCL diblock copolymers prepared using the two-step strategies were the same as those synthesized by the one-step method.

UV-vis absorption and fluorescence emission measurements (obtained from the one-step process) also evidenced the formation of PSt-PI-PCL with PI at the mid-chain of the copolymer. The UV-vis spectra of PSt-PI-PCL along with its precursor, Br-PI-OH, in CH₂Cl₂

**Figure 6** ¹H-NMR spectra of the macrophotoinitiators PSt-PI-OH (a) and Br-PI-PCL (b).

at room temperature are shown in Figure 7. Each spectrum exhibits the typical absorption band of PI derivatives. The fluorescence emission spectra of PSt-PI-PCL and Br-PI-OH in CH₂Cl₂ (Figure 8) show the vibrational structure of the aryl ketone chromophore

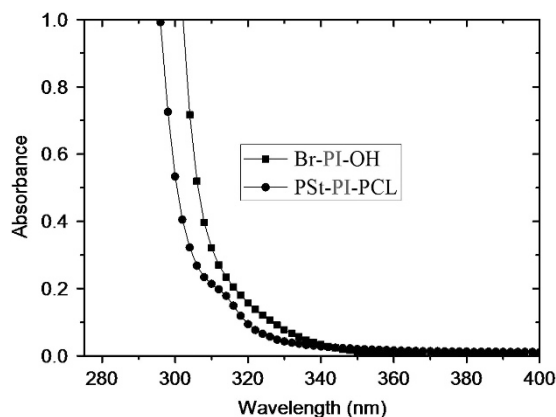


Figure 7 UV-vis absorption spectra of the dual-functional photoinitiator Br-PI-OH ($6.25 \times 10^{-4} \text{ mol l}^{-1}$) and the diblock macrophotoinitiator PSt-PI-PCL ($7.70 \times 10^{-2} \text{ g l}^{-1}$) in CH_2Cl_2 . A full color version of this figure is available at *Polymer Journal* online.

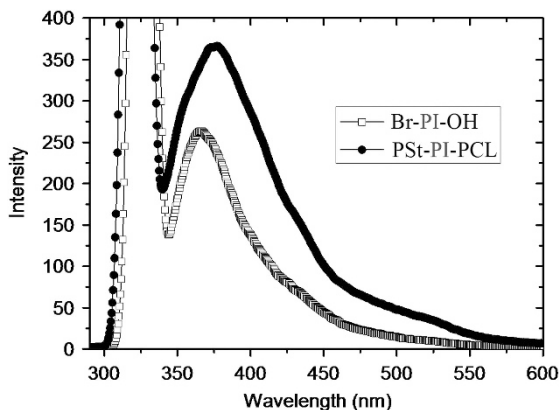
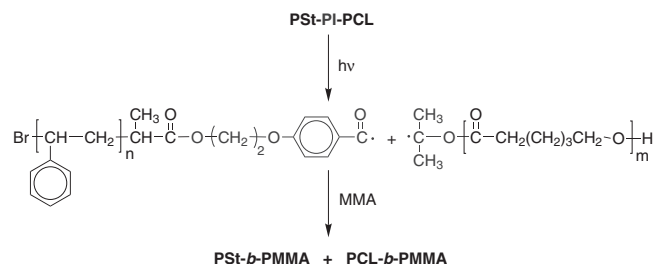


Figure 8 Fluorescence emission spectra of the dual-functional photoinitiator Br-PI-OH ($2.50 \times 10^{-4} \text{ mol l}^{-1}$) and the diblock macrophotoinitiator PSt-PI-PCL ($4.56 \times 10^{-3} \text{ g l}^{-1}$) in CH_2Cl_2 , $\lambda_{\text{exc}} = 325 \text{ nm}$. A full color version of this figure is available at *Polymer Journal* online.

available in the compounds. The spectroscopic results verify that the photochromophoric PI group was conserved during the one-step polymerization reaction.

The availability of the PI group in the middle of the copolymer chain was further shown via photopolymerization studies of the PSt-PI-PCL macrophotoinitiator produced using the one-step polymerization reaction. The photoinitiated free radical polymerization of MMA with the PSt-PI-PCL macrophotoinitiator in bulk at room temperature produced a 22% conversion of MMA after 50 min of irradiation time. A control experiment without the macrophotoinitiator gave only a negligible amount of polymer after the same irradiation time. UV irradiation of the PSt-PI-PCL polymeric photoinitiator caused α -scission and yielded two polymer-bound radicals according to the reaction shown in Scheme 3. Both of these radicals may then initiate the polymerization of MMA. As a result, PSt-PMMA and PCL-PMMA block copolymers were obtained. It should be noted that homopolymers of PSt, PCL and poly(methyl methacrylate) might also be present in the product to some extent because of the uncontrollability of the photopolymerization method used in this



Scheme 3 Photoinitiated free radical polymerization of the diblock macrophotoinitiator PSt-PI-PCL. A full color version of this scheme is available at *Polymer Journal* online.

study. Thus, the product obtained by this method can be used as a compatibilizing agent for PSt and poly(methyl methacrylate).

In conclusion, a new, well-defined mid-chain functional macrophotoinitiator of PSt-PI-PCL was successfully synthesized in a one-step process using a dual-functional photoinitiator able to combine the ATRP of St with the ROP of ϵ -caprolactone. The dual-functional photoinitiator was also used as the initiator in a two-step polymerization by sequentially combining ATRP and ROP to obtain the diblock copolymer (PSt-PI-PCL). The polymers produced in both steps have low molecular weight distributions. The structure of the PSt-PI-PCL and the presence of a photochromophoric group (PI) at its mid-point were shown by spectral analyses. The obtained macrophotoinitiator can be used in the photopolymerization of vinyl monomers, such as MMA.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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