



A Novel Initiator of [5-(benzyloxy)-4-oxo-4H-pyran-2-yl]methyl-2-bromo-2-methylpropanoate in Atom Transfer Radical Polymerization of Styrene and Methyl Methacrylate

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ABSTRACT

A novel nano-initiator containing kojic acid moiety, [5-(benzyloxy)-4-oxo-4H-pyran-2-yl]methyl-2-bromo-2-methylpropanoate was synthesized by the reaction of 5-(benzyloxy)-2-(hydroxymethyl)-4H-pyran-4-one with 2-bromoisobutyryl bromide in triethylamine and used as initiator in the atom transfer radical polymerization (ATRP) of styrene and methyl methacrylate in the presence of Cu(0)/CuCl₂ and *N,N,N',N'',N''*-pentamethyl diethylenetriamine (PMDETA). The characteristics of resulting polymers were verified by proton nuclear magnetic resonance spectroscopy (¹H NMR), thermogravimetric analysis (TGA), and gel permeation chromatography (GPC). ¹H NMR spectra were recorded in deuterated chloroform (CDCl₃) with a Fourier transform (FT)-nuclear magnetic (NMR) spectrometer. To investigate the living nature of polymerization, the obtained polymers were subjected to further chain extension reaction. The chain extension of polystyrene (PS) and poly(methyl methacrylate) (PMMA) macroinitiators demonstrated that the chain ends of the obtained PS-Br and PMMA-Br were enable for further functionalization. After chain extension, the GPC curves shifted to high molecular weight. The values of number average molecular weight (M_n) of PS and PMMA increased from 37853 to 40808 g/mol and from 107640 to 156310 g/mol, respectively. These results demonstrated that the chain extension reaction was successful and exhibited the living features of the chain end. To the best of our knowledge, the synthesis of ATRP initiator containing kojic acid moiety has not been reported. Herein, we report the synthesis and characterization of an ATRP initiator containing kojic acid moiety, and its application for the polymerization of styrene and methyl methacrylate.

Keywords: Kojic acid; initiator; ATRP; polystyrene; poly(methyl methacrylate).

1. Introduction

Atom transfer radical polymerization (ATRP) is one of the most successful polymerization methods in the field of controlled/living radical polymerization that has been successfully applied for the polymerization of various monomers such

as styrene, methyl acrylate, methyl methacrylate, acrylonitrile, meth acrylamide, etc. ATRP usually uses a transition metal complex as the catalyst with an alkyl halide as an initiator (R-X). Various transition metal complexes, e.g., Cu, Fe, Ru, Ni, and Os, have been applied as catalysts for ATRP. In an

ATRP process, the dormant species is activated by the transition metal complex to generate radicals via one electron transfer process. The transition metal is simultaneously oxidized to higher oxidation state. This reversible process rapidly provides an equilibrium which is shifted to the side with low radical concentrations. The number of polymer chains is determined by the number of initiators. Each growing chain has the same probability to propagate with monomers to form living/dormant polymer chains ($R-P_n-X$). In conclusion, polymers with similar molecular weights and narrow molecular weight distributions can be developed [1-3]. Initiator plays an important role in the ATRP process, because it forms an initiating radical species via homolytic cleavage of its labile bond such as carbon-halogen in the presence of a catalyst [4-13]. Selecting a suitable initiator is essential to achieve a well-controlled radical polymerization system. Hence, much attention has been paid to find effective initiators. Various initiators, containing alkyl halides, α -haloesters, α -haloketones, α -halonitriles, benzylic halides and sulfonyl halides have been used successfully to initiate ATRP [14-18]. Alkyl halides having inductive or resonance stabilizing substituents are effective initiators for ATRP. The initiators for ATRP are either commercially available or synthesized.

Kojic acid, 5-hydroxy-2-hydroxymethyl-4H-pyran-4-one, is an organic acid which was produced by several species of fungi or bacteria such as *Aspergillus*, *Acetobacter* and *Penicillium* using a wide range of carbon sources [19-21]. It represents an attractive multifunctional skeleton with several important centers enabling additional reactions [22]. Kojic acid has various applications in several fields. It is widely used in cosmetic, food, agriculture, chemical and medicine industries [23-33]. The kinetic modeling of ligand-metal binding role in controlling the nucleation and growth kinetics [34], the role of capping agents in regulating the size of palladium nanoparticles [35], the preparation of polymer brushes using the materials synthesized via living polymerization methods [36], etc. were also reported in the literature.

Various initiators were synthesized and used for the polymerization of vinyl monomers such as styrene and methyl methacrylate by the ATRP method [37-40]. To the best of our knowledge, the synthesis of ATRP initiator containing kojic acid moiety has not been reported. Herein, we report the synthesis and characterization of an

ATRP initiator containing kojic acid moiety and its application for the polymerization of styrene and methyl methacrylate.

2. Experimental

2.1. Materials

Reagents were purchased from Merck and Fluka companies and were used without further purification. All solvents were dried and distilled prior to use. The synthesized initiator was purified by preparative layer chromatography (PLC; Merck, silica gel 60 F₂₅₄, CAMAG, Switzerland) using *n*-hexane:acetone (2:1) as eluent.

2.2. Characterization

Melting points were determined on an Electrothermal Barnstead 9200 apparatus (Barnstead, UK). FT-IR spectra were obtained using KBr pellets on a tensor 27-Bruker spectrometer (Shimadzu, Japan). ¹H NMR spectra were recorded in CDCl₃ with a FT-NMR-Bruker spectrometer (Germany) at 400 MHz. The thermogravimetric analysis (TGA) was performed under nitrogen atmosphere at a heating rate of 10 °C min⁻¹ using a Mettler-Toledo thermal analyzer. The glass transition temperature (T_g) was determined by differential scanning calorimeter (DSC) using a TGA/SDTA 851, under nitrogen atmosphere at a heating rate of 10 °C min⁻¹. The number average molecular weight (M_n) and polydispersity index (PDI) of the polymers were determined using an Agilent 1100 series gel permeation chromatography (GPC) instrument (USA) with three columns in PLgel 10 μ m diameter and 300 \times 7.5 mm dimensions with tetrahydrofuran (THF) as eluent with a flow rate of 1 mLmin⁻¹ at 30 °C. Polystyrene was used as calibration standard.

2.3. Synthesis of [5-(benzyloxy)-4-oxo-4H-pyran-2-yl]methyl-2-bromo-2-methylpropanoate 3

Triethylamine (0.36 mL, 2.57 mmol) was added to the solution of 5-benzyloxy-2-(hydroxymethyl)-4H-pyran-4-one 2 (0.1 g, 0.43 mmol) in 25 mL dry tetrahydrofuran (THF) under nitrogen atmosphere and the reaction mixture was cooled to 0 °C using an ice bath. Then, a solution of 2-bromoisobutryl bromide (0.18 mL, 1.45 mmol) in 2 mL THF was added dropwise to above solution. The reaction mixture was stirred at room temperature for 12 h and then at 60 °C for 12 h. After completion of reaction, the product was monitored by thin layer chromatography (TLC). The solvent was removed

under reduced pressure and the crude product was purified by preparative layer chromatography (PLC) on silica gel with *n*-hexane:acetone (2:1) as an eluent. Brown solid, 0.09 g (56%), m.p. 118-120 °C; FT-IR (KBr): ν 3064, 2981, 2869, 1739 (ester C=O), 1650 (pyrone C=O), 1606, 1515, 1454, 1392, 1367, 1269, 1220, 1174, 1018, 966, 842, 736 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 1.48 (s, 6H, $-\text{CH}_3$), 4.96 (s, 2H, $-\text{CH}_2\text{OCO}-$), 5.08 (s, 2H, $-\text{CH}_2\text{O}-$), 6.45 (s, 1H, heterocyclic-H), 7.33-7.39 (m, 5H, Ar-H), 7.54 (s, 1H, heterocyclic-H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 26.1, 61.0, 70.8, 71.2, 113.1, 126.7, 127.5, 127.8, 134.4, 140.2, 146.2, 159.7, 173.2, 175.3 ppm.

2.4. Polymerization of styrene by ATRP

Polystyrene (PS) was prepared from styrene by the ATRP using 3 as an initiator. The polymerization procedure with the molar ratio of [initiator]/[catalyst]/[ligand]/[monomer]=1/1/2/500 as followed: to a suspension of Cu(0) (0.01 g, 0.16 mmol), CuCl_2 (0.013 g, 0.1 mmol) and PMDETA (0.11 mL, 0.52 mmol) in 9 mL anisole was added a solution of 3 (0.1 g, 0.26 mmol) in 1 mL *N,N*-dimethylformamide (DMF). The styrene (15 mL, 130 mmol) was then added to the reaction mixture and degassed by passing nitrogen gas for 30 min. The reaction mixture was heated at 60 °C for 48 h under a nitrogen atmosphere. PS was precipitated by adding the reaction mixture into methanol. The polymer was filtered, washed with methanol and dried. The obtained polymer was dissolved in CHCl_3 and the solution was passed through a short neutral alumina column to remove the copper catalyst and then was precipitated in methanol and dried.

2.5. Polymerization of methyl methacrylate (MMA) by ATRP

Poly(methyl methacrylate) (PMMA) was prepared from MMA by the ATRP using 3 as an initiator. The polymerization procedure was similar to the synthesis of PS by heating the reaction mixture at 60 °C for 72 h.

2.6. Chain extension reaction with PS as macroinitiator

The obtained PS ($M_{n,\text{GPC}} = 37853 \text{ g/mol}$, $\text{PDI} = M_w/M_n = 1.34$) was successfully used as a macroinitiator for the chain extension polymerization with styrene. The chain extension reaction was conducted with the molar ratio of [initiator]/[catalyst]/[ligand]/[monomer] = 1/20/40/500. The polymerization

procedure as followed: to a suspension of Cu(0) (0.002 g, 0.03 mmol), CuCl_2 (0.003 g, 0.022 mmol) and PMDETA (0.02 mL, 0.104 mmol) in 9 mL anisole was added a solution of obtained PS (0.1 g, 0.0026 mmol) in 7 mL anisole. Subsequently, styrene (0.15 mL, 1.3 mmol) was added to the reaction mixture and degassed by passing nitrogen gas for 30 min. The reaction mixture was heated at 60 °C for 72 h under a nitrogen atmosphere. PS was precipitated by adding the reaction mixture into methanol. The polymer was filtered, washed with methanol and dried. The chain-extended PS was dissolved in CHCl_3 and the solution was passed through a short neutral alumina column to remove the copper catalyst and then was precipitated in methanol and dried.

2.7. Chain extension reaction with PMMA as macroinitiator

The obtained PMMA ($M_{n,\text{GPC}} = 107640 \text{ g/mol}$, $M_w/M_n = 1.18$) was used as the macroinitiator for the chain extension polymerization with MMA. The polymerization procedure of MMA with the molar ratio of [initiator]/[catalyst]/[ligand]/[monomer] = 1/20/40/500 was as above using Cu(0) (0.0032 g, 0.051 mmol), CuCl_2 (0.006 g, 0.041 mmol), PMDETA (0.04 mL, 0.2 mmol) and synthesized PMMA (0.4 g, 0.0048 mmol), followed by addition of fresh MMA (0.25 mL, 2.4 mmol).

3. Results and discussion

In this work, a novel ATRP initiator, [5-(benzyloxy)-4-oxo-4*H*-pyran-2-yl]methyl-2-bromo-2-methylpropanoate 3 was synthesized from commercially available kojic acid 1. First, 5-(benzyloxy)-2-(hydroxymethyl)-4*H*-pyran-4-one 2 was prepared by the reaction of kojic acid 1 with benzyl chloride according to the literature procedure [41], and then it was converted to 3 by subjecting with 2-bromoisobutyryl bromide in triethylamine as a base (Fig. 1). The new initiator was characterized by FT-IR, ^1H NMR, and ^{13}C NMR spectroscopies.

In FT-IR spectrum of the initiator 3, the peaks at 1739 and 1650 cm^{-1} were assigned to the ester C=O and kojic acid C=O stretching vibrations, respectively. Fig. 2 shows ^1H NMR spectrum of the initiator. In ^1H NMR spectrum of the initiator, a signal at 1.48 ppm was assigned to methyl protons. The signals at 4.96 and 5.08 ppm were correlated with $-\text{CH}_2\text{OCO}-$ and $-\text{CH}_2\text{O}-$ protons, respectively. The signals at 7.33-7.39 ppm were attributed to the

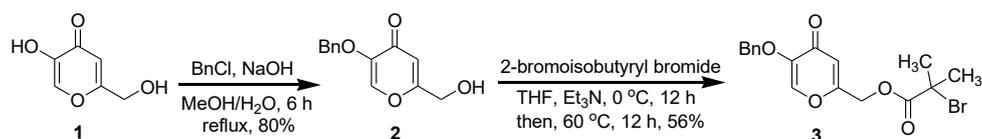


Fig. 1- Synthesis of the new initiator 3 for ATRP.

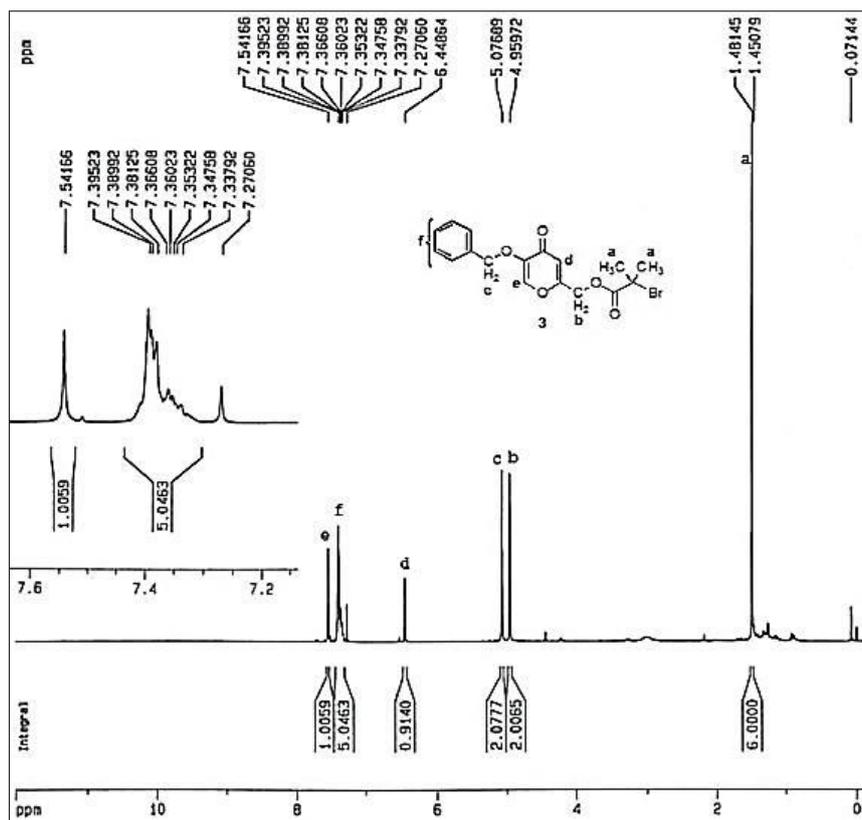


Fig. 2- ^1H NMR spectrum of initiator 3 in CDCl_3 .

protons of aromatic ring. The signals at 6.45 and 7.54 ppm stood for the protons of heterocyclic ring. These results confirmed the successful synthesis of initiator 3.

The ATRP reactions of styrene and MMA with the mole ratio of $[\text{initiator}]/[\text{catalyst}]/[\text{ligand}]/[\text{monomer}] = 1/1/2/500$ were carried out by employing 3 as an initiator, $\text{Cu}(0)/\text{CuCl}_2$ as catalyst, and PMDETA as the ligand (Fig. 3). The resulting PS and PMMA were characterized by FT-IR, ^1H NMR, GPC, DSC and TGA analysis.

In ^1H NMR spectrum of PS (Fig. 4), the signals at 1.35 and 1.77 ppm were assigned to the protons

(b, c, and e in Fig. 4) of methylene and methine in main chain of polystyrene, respectively. The methyl protons from initiator (d) should be observed at 1.48 ppm. However, these protons were merged with protons of PS at 1.35-1.77 ppm. The signal at 4.94 ppm was attributed to the proton in the α position (a in Fig. 4) to the bromine chain end, that it was merged with protons of $-\text{CH}_2\text{OCO}-$ (f in Fig. 4) from the initiator. The signal at 5.16 ppm was for the protons of $-\text{CH}_2\text{O}-$ (j in Fig. 4) from the initiator. The signals in the range of 6.31-7.28 ppm were correlated with the protons of aromatic and heterocyclic rings.

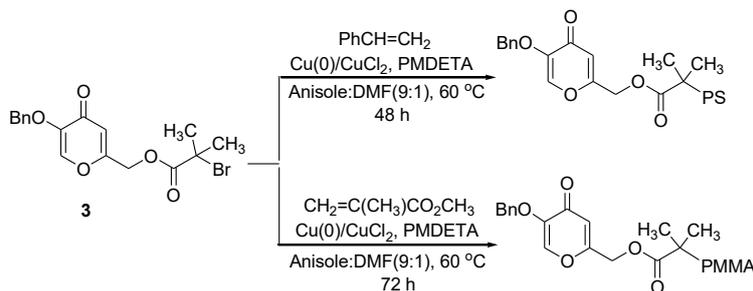


Fig. 3- General procedure for the synthesis of PS and PMMA.

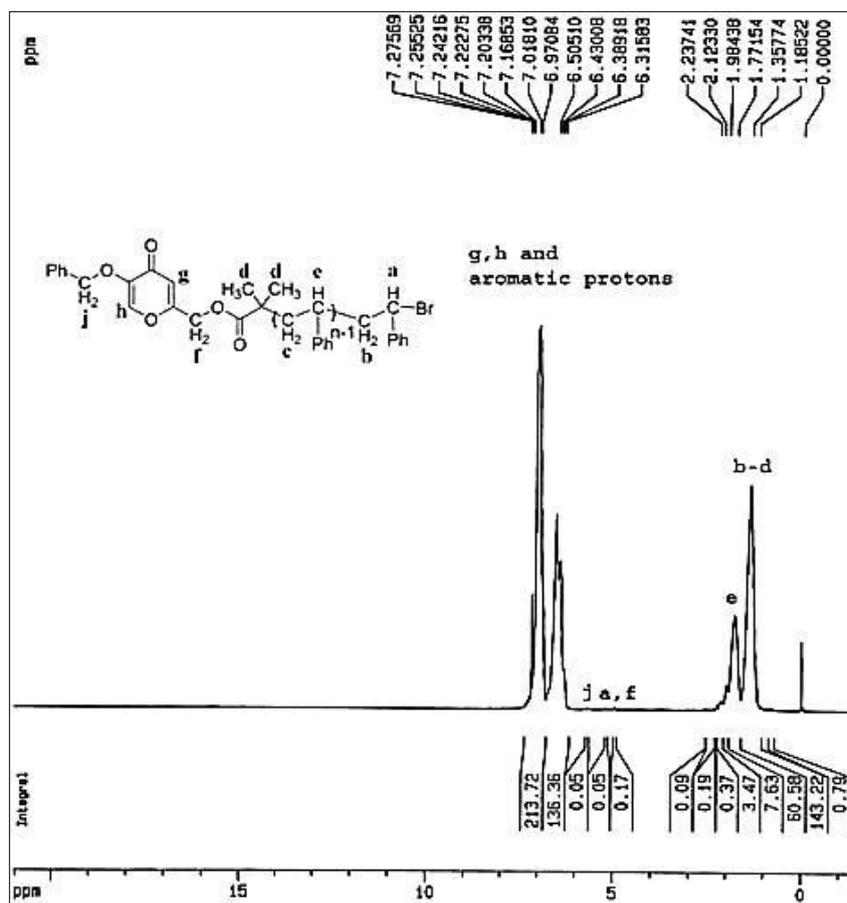


Fig. 4- ^1H NMR spectrum of PS ($M_{n,\text{GPC}} = 37853$ g/mol, $M_w/M_n = 1.34$) in CDCl_3 .

In ^1H NMR spectrum of PMMA (Fig. 5), the signal at 3.64 ppm (d in Fig. 5) was attributed to the protons of methoxy group next to the halogen chain end, which deviated from the signal 3.53 ppm (c in Fig. 5) of other methoxy groups in PMMA because of the electron attracting function of ω -Br atom in PMMA chain end. The signals at 0.78, 0.95 and 1.18 ppm (a in Fig. 5) were corresponded to syndiotactic

(rr), atactic (mr) and isotactic (mm) PMMA, respectively. The assigned signals explained that the polymer had predominantly syndiotactic structure [42]. According to ^1H NMR spectral data, rr, mr and mm percents of PMMA were 58%, 11.30% and 31%, respectively. The signals at 1.65-1.98 ppm (b, e and f in Fig. 5) were attributed to the protons of methylene in main chain of PMMA and

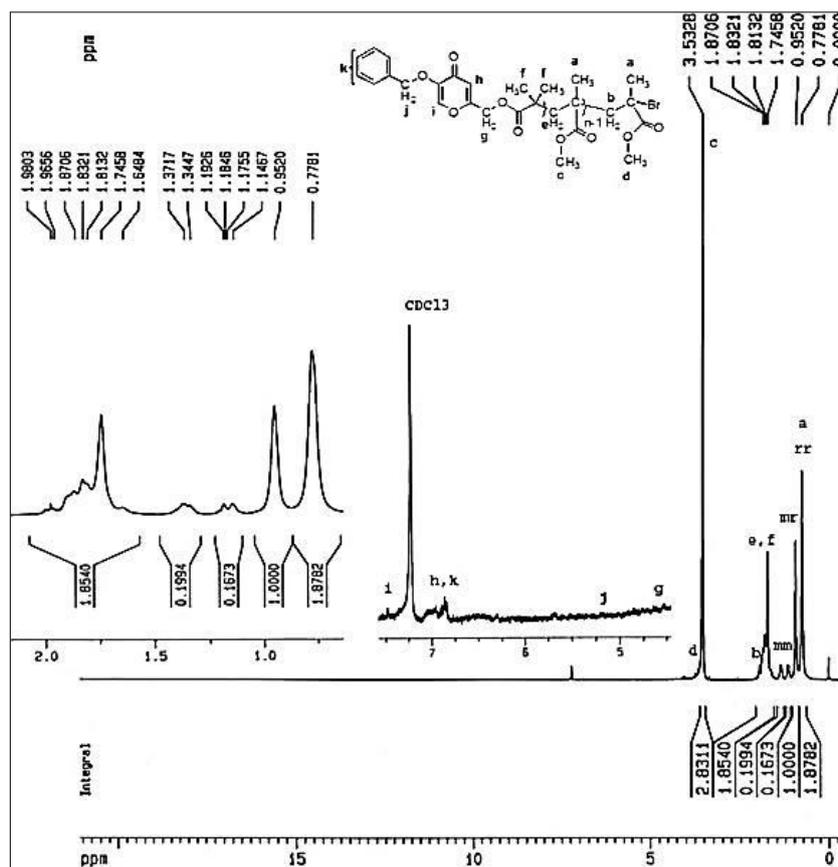


Fig. 5 ¹H NMR spectrum of PMMA ($M_{n,GPC} = 107640$ g/mol, $M_w/M_n = 1.18$) in CDCl₃.

methyl from the initiator. The signals at 6.83-7.04 ppm were related to the protons of aromatic and heterocyclic rings.

To determine the living nature of the polymerization, the obtained PS ($M_{n,GPC} = 37853$ g/mol, $M_w/M_n = 1.34$) and PMMA ($M_{n,GPC} = 107640$ g/mol, $M_w/M_n = 1.18$) were used as the macroinitiator for chain extension reaction. The GPC curves of PS and PMMA before and after chain extension are displayed in Figs. 6 and 7. After chain extension, the GPC curves shifted to higher molecular weight. The values of M_n of PS and PMMA increased from 37853 to 40808 g/mol and from 107640 to 156310 g/mol, respectively. These results demonstrated that the chain extension reactions were successful and exhibited the living features of the chain ends. In addition, the GPC traces of PS samples prepared within 24 h ($M_n = 37850$ g/mol, $M_w/M_n = 1.35$), 48 h ($M_n = 39150$ g/mol, $M_w/M_n = 1.35$), and 72 h ($M_n = 40800$ g/mol, $M_w/M_n = 1.36$) are represented in Fig. 6(b). The M_n evolution of PS versus reaction time is also displayed in Fig. 6(c). Likewise, the GPC traces of PMMA samples prepared within 24 h (M_n

= 107640 g/mol, $M_w/M_n = 1.15$), 48 h ($M_n = 133440$ g/mol, $M_w/M_n = 1.13$), and 72 h ($M_n = 156310$ g/mol, $M_w/M_n = 1.14$) are represented in Fig. 7(b). The M_n evolution of PMMA versus reaction time is also exhibited in Fig. 7(c).

The efficiency of the synthesized initiator was evaluated on the basis of molecular weight and polydispersity of polymers. The above-mentioned results indicated that PS and PMMA with the higher molecular weight ($M_{n,GPC} = 37853$ and 107640 g/mol) can be synthesized using 5-(benzyloxy)-4-oxo-4H-pyran-2-yl]methyl-2-bromo-2-methylpropanoate as a novel ATRP initiator. Narrow molecular weight distribution of PS and PMMA ($M_w/M_n = 1.34$ and 1.18) indicated living/controlled polymerization.

Thermal behavior of the obtained polymers was investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA curves of the PS and PMMA are shown in Figs. 8 and 9. In the TGA curve of the PS, there were two steps for the degradation. The first step at 137-150 °C may be due to absorbed solvent. The second step

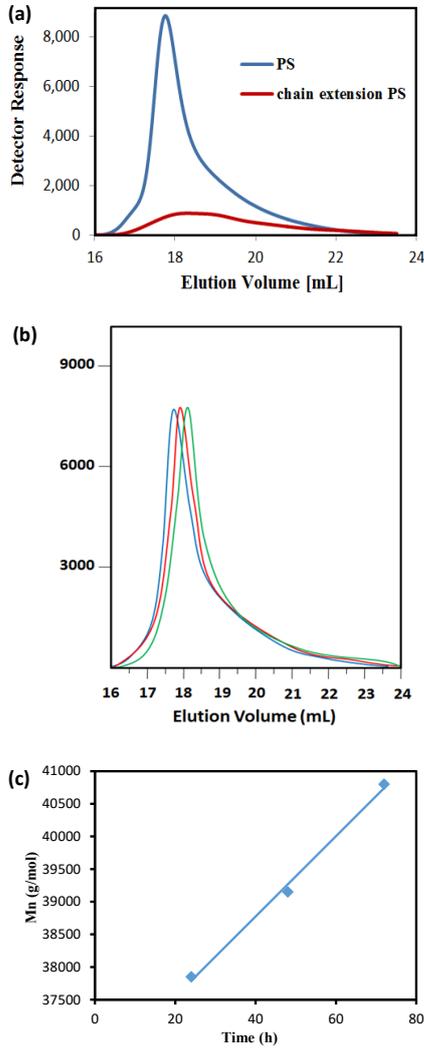


Fig. 6- GPC traces of the PS before and after chain extension (a); PS within 72 h (blue trace, left), 48 h (red trace, middle), and 24 h (green trace, right) (b); M_n versus reaction time (c).

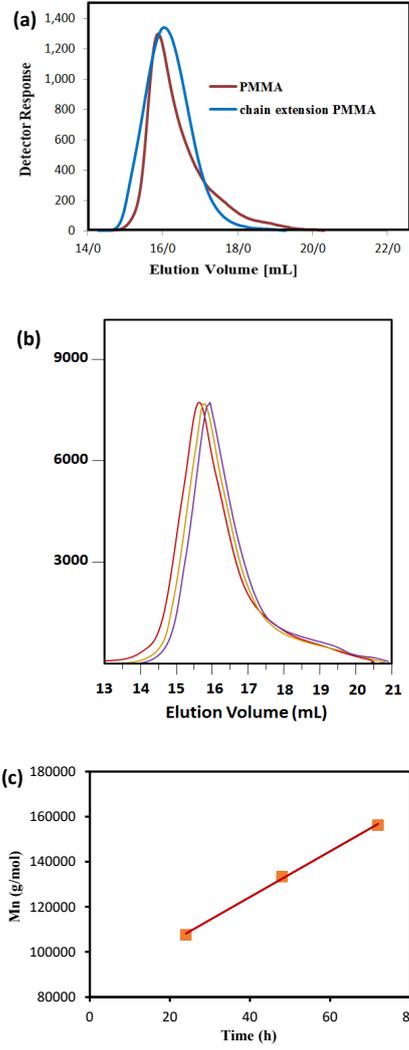


Fig. 7- GPC traces of the PMMA before and after chain extension (a); PMMA within 72 h (red trace, left), 48 h (orange trace, middle), and 24 h (violet trace, right) (b); M_n versus reaction time (c).

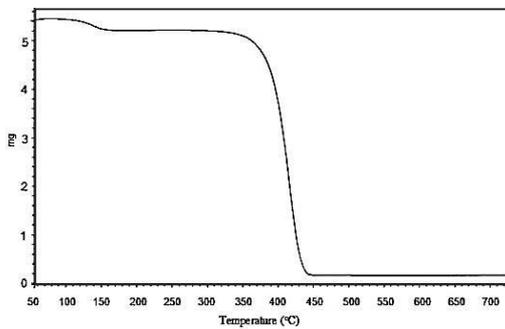


Fig. 8- TGA curve of PS.

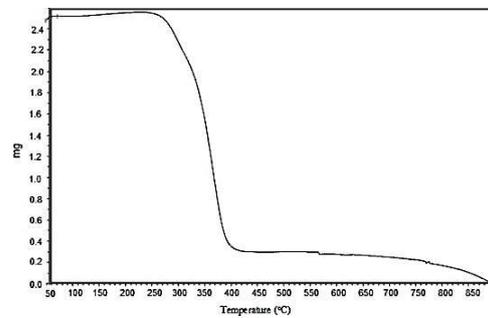


Fig. 9- TGA curve of PMMA.

of PS degradation at 350-440 °C was attributed to the main chain decomposition. Likewise, in TGA curve of the PMMA, there were two steps in the degradation. The first step at 50-243 °C may be due to absorbed solvent. The second step of PMMA degradation at 300-400 °C was related to the main chain decomposition. The DSC curves of PS and PMMA are displayed in Figs. 10 and 11, respectively. The transitions at 124.90 and 136.15 °C could be assigned to the glass transition temperatures of the PS and PMMA, respectively.

4. Conclusions

In the present work, we have synthesized a novel ATRP initiator containing kojic acid moiety, [5-(benzyloxy)-4-oxo-4*H*-pyran-2-yl)methyl-2-bromo-2-methylpropanoate, by the reaction of 5-(benzyloxy)-2-(hydroxymethyl)-4*H*-pyran-4-one with 2-bromoisobutryl bromide. The ATRP of styrene and methyl methacrylate was successfully carried out using the mentioned in-initiator at 60 °C. The obtained PS and PMMA samples were subsequently used as macroinitiators for chain extension polymerizations. The chain extension of PS and PMMA macroinitiators demonstrated that the chain ends of the obtained PS-Br and PMMA-Br were enable for further functionalization.

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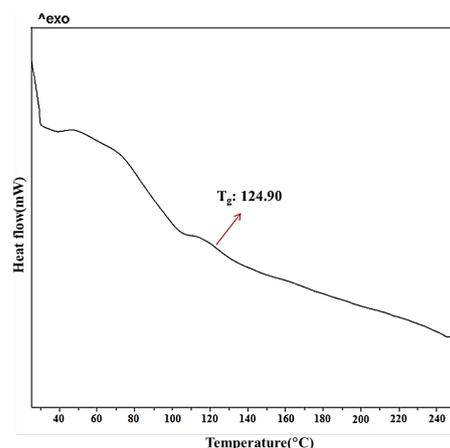


Fig. 10- DSC curve of PS.

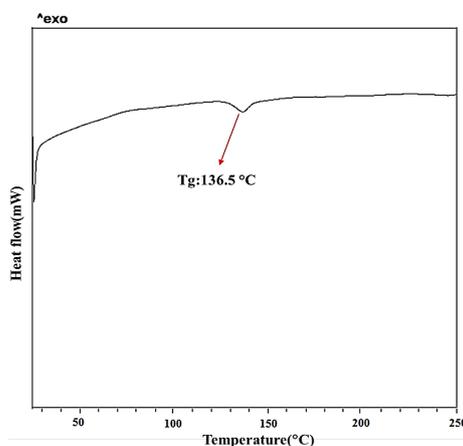


Fig. 11- DSC curve of PMMA.

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