

Synthesis and Characterization of Poly(ϵ -caprolactone-b-Styrene) Block Copolymer by Ring-Opening Polymerization and Reversible Addition-Fragmentation Chain Transfer Polymerization

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ABSTRACT: The synthesis of the block copolymer was carried out using the RAFT polymerization technique and the ring-opening polymerization (ROP) technique using a novel two functional initiator (RAFT-ROP agent). For this purpose, RAFT-ROP agent was obtained using 5-bromo-2-hydroxybenzaldehyde and potassium salt of ethyl xanthogenate. RAFT-macro agent was synthesized by ROP of ϵ -caprolactone (CL) with RAFT-ROP agent. Then, poly(ϵ -caprolactone-b-styrene) block copolymer was synthesized using RAFT polymerization in the presence of RAFT-macro agent using styrene. The products were characterized using GPC, FT-IR and ¹H-NMR analyses. Decomposition temperatures of the block copolymer were monitored by TGA method. Spectroscopic and thermal analyses revealed that the reactions were successfully carried out.

Keywords: Novel Two Functional Initiator; RAFT-Macro Agent; Block Copolymer; RAFT Polymerization; Ring-Opening Polymerization (ROP).

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INTRODUCTION

Recently, complex-structured macromolecules, in which the polymer chain end functionality and the block and graft chain fragment are arranged, are highly synthesized starting from controlled polymerization processes (Nomura and Abdellatif 2010; Cai, Li et al., 2012; Chang and Dong 2013). Multipurpose polymer chains are combined in the desired polymer architecture. Block copolymers have attracted great attention in many areas. These areas are surfactants, adhesive, thermoplastic elastomers, dispersants, etc. (Matzner, Noshay et al., 1977; Price and Goodman 1982). RAFT polymerization technique is the latest development of the controlled free-radical polymerization method. And this method is a powerful technique for macromolecular synthesis (Chiefari, Chong et al., 1998; Patton, Mullings, et al., 2005; Yang, Chai et al., 2011; Öztürk, Atalar et al., 2013; Robin, Wilson et al., 2013; Schmidt and Barner-Kowollik, 2013; Bağlan et al., 2018). The usefulness of the method has been demonstrated by its compatibility with many various monomers and reaction conditions (Xie, Dang et al., 2008). Reversible chain transfer contains homolytic replacement, addition breakup, or another transfer techniques (Kartal et al., 2014). Graft and block copolymers are used in both theoretical research and technological applications (Ruzette and Leibler 2005; Ozturk, Yilmaz et al., 2008; Öztürk, Göktaş et al., 2010; Noshay and McGrath 2013; Göktaş, Öztürk et al., 2014; Öztürk, Göktaş et al., 2014; Çakmak et al., 2017). Lactones show special properties such as biocompatibility, good mechanical properties, biodegradability, and no toxicity. Therefore, ring-opening polymerization (ROP) of lactones is of great interest (Gross, Kumar et al., 2001; Kobayashi, Uyama et al., 2001; Cretu, Gattin et al., 2004; Öztürk et al., 2019).

This study shows the synthesis of poly(ϵ -caprolactone-*b*-styrene) [poly(CL-*b*-St)] block copolymer by using ROP and RAFT polymerization. For this purpose, a novel two functional initiator (RAFT-ROP agent) was obtained using 5-bromo-2-hydroxybenzaldehyde and potassium salt of ethyl xanthogenate. Then, RAFT-macro agent was synthesized by ROP of ϵ -caprolactone (CL) with RAFT-ROP agent. RAFT-macro agent and styrene (St) were used to obtain poly(CL-*b*-St) block copolymer by RAFT polymerization. Characterization of block copolymer was done in detail.

MATERIALS AND METHODS

Materials

5-bromo-2-hydroxybenzaldehyde, 2,2'-azobis(2-methylpropionitrile) (AIBN), potassium ethyl xanthogenate, St, and CL were supplied by Merck. Methanol, N,N-dimethylformamide (DMF), tetrahydrofuran (THF), toluene and stannous octoate [Sn(Oct)₂] were received from Sigma-Aldrich. Sn(Oct)₂ was used as a catalyst for ROP. The alumina column was used to send away inhibitors from St. The other chemicals were used without further purifications.

Instrumentation

The number of molecular weight (M_n), molecular weight (M_w) and dispersity values were evaluated with the GPC-Shimadzu (RID-10A GPC) / HPLC device with THF mobile phase of 40 °C. ¹H-NMR peaks were found on Bruker UltraShield Plus instrument using NMR 400 spectrometer. FT-IR spectra were recorded by (IR 6600 FT-IR) / Jasco FT brand device. TGA values were obtained by (Exstar 6000) Seiko II model device. The product was heated from 30 °C to 800 °C under N₂, changing at 10 °C per minute.

Synthesis of novel two functional initiator (RAFT-ROP agent)

A 250 mL flask was mixed with 30 mL of THF, 1.004 g of 5-bromo-2-hydroxybenzaldehyde, 1.612 g of potassium ethyl xanthogenate, respectively. The flask containing the mixture was placed on a magnetic stirrer in an oil bath at 30 °C. After 72 hours, the content was filtered to remove the unreacted salts. The solvent partially removed. The residue was precipitated in cold diethyl ether and petroleum ether [1(v)/1(v)]. The mixture was kept in a refrigerator overnight. After decantation, RAFT-ROP agent was dried in a vacuum oven at room temperature for 48 hours. RAFT-ROP agent yield was determined gravimetrically.

Synthesis of RAFT-macro agent by ROP

0.192 g of Sn(Oct)₂, 0.320 g of RAFT-ROP agent, 15.093 g of CL, and 10 mL of DMF were placed in a 250 mL glass flask, respectively. Argon gas was passed through for 5 minutes to obtain inert medium. After the glass vial was capped, the flask was stirred in an oil bath for 72 hours at 110 °C. The mixture was cooled to room temperature and then poured into excess methanol. After decantation, RAFT-macro agent was dried in a vacuum oven at room temperature for 24 hours. The product yield was defined gravimetrically.

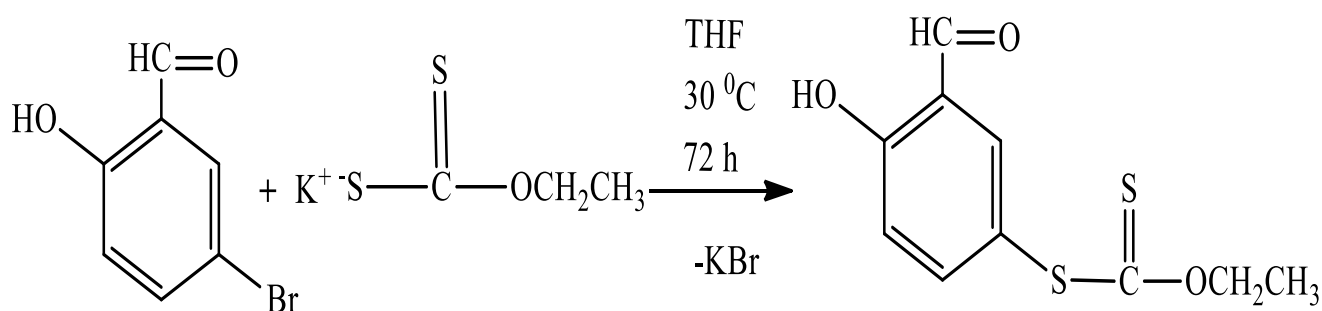
Synthesis of poly(CL-*b*-St) block copolymer by RAFT polymerization

0.109 g of RAFT-macro agent, 2.010 g of St, 0.001 g of AIBN, and 2 mL of toluene were placed in a 250 mL glass flask, respectively. Argon gas was passed through for 5 minutes to obtain inert medium. The flask was placed on a magnetic stirrer in an oil bath at 90 °C. After 24 hours, poly (CL-*b*-St) block copolymer was poured into excess methanol. The precipitated copolymer was dried in a vacuum oven at room temperature for 48 hours. The copolymer yield was defined gravimetrically.

RESULTS AND DISCUSSION

Synthesis of RAFT-ROP agent

RAFT-ROP agent was obtained by reaction of 5-bromo-2-hydroxybenzaldehyde and potassium ethyl xanthogenate. The yield was obtained with a 42.99 wt %. The chemical synthesis mechanism of RAFT-ROP agent was shown in Scheme 1.

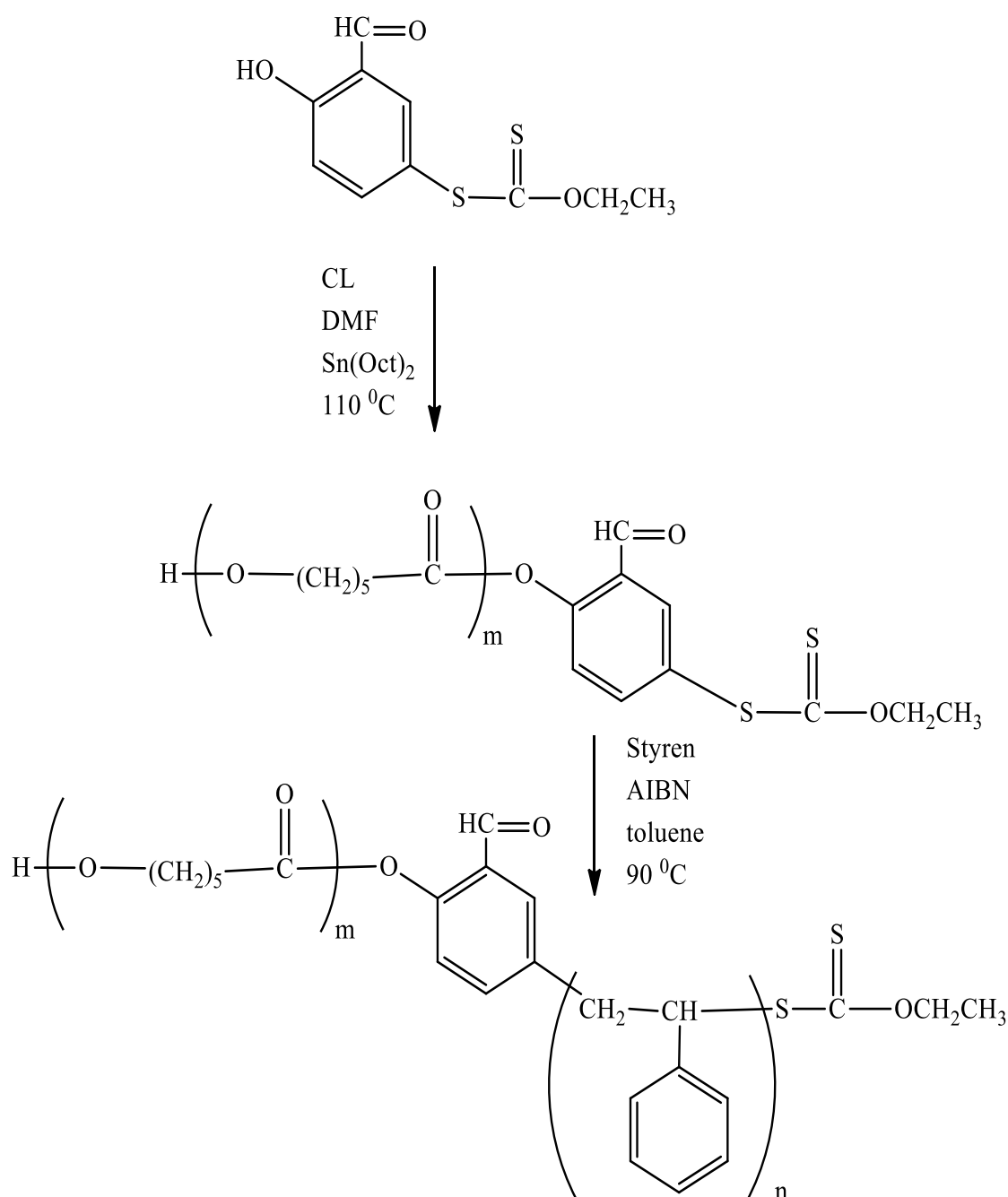


Scheme 1. The mechanism of RAFT-ROP agent.

Synthesis of RAFT-macro agent

RAFT-macro agent was synthesized by reaction of RAFT-ROP agent and CL via ROP. Scheme 2 (first line and second line) shows the synthesis route for the RAFT-macro agent. The yield of RAFT-macro agent was 41.90 wt %. M_n ,GPC value of RAFT-macro agent was 7.507 g.mol⁻¹. Dispersity value

of RAFT-macro agent was 1.20. The $^1\text{H-NMR}$ spectrum of RAFT-macro agent in Figure 1(a) displayed peaks at 1.2 ppm for $-\text{CH}_3$ of ethyl xanthogenate unit, 1.6 ppm for $-\text{CH}_2$ of PCL unit, 2.3 ppm for $-\text{CH}_2$ linked carbonyl group of PCL unit, 3.4 ppm $-\text{OH}$ of PCL unit, 3.6 ppm for $-\text{OCH}_2$ of ethyl xanthogenate unit, 4.0 ppm for $-\text{OCH}_2$ of PCL unit, 7.8 ppm and 7.9 ppm for aromatic $-\text{CH}$, 8.2 ppm for $-\text{HC}=\text{O}$. The FT-IR spectrum of RAFT-macro agent in Figure 2(a) indicated signals at 2944 and 2900 cm^{-1} for aliphatic $-\text{CH}_3$ and $-\text{CH}_2$, 1720 cm^{-1} for $\text{C}=\text{O}$, 1174 cm^{-1} for $-\text{OC}$, 1107 cm^{-1} for $-\text{SC}$.



Scheme 2. Reaction outlines for syntheses of RAFT-macro agent and poly(CL-*b*-St) block copolymer.

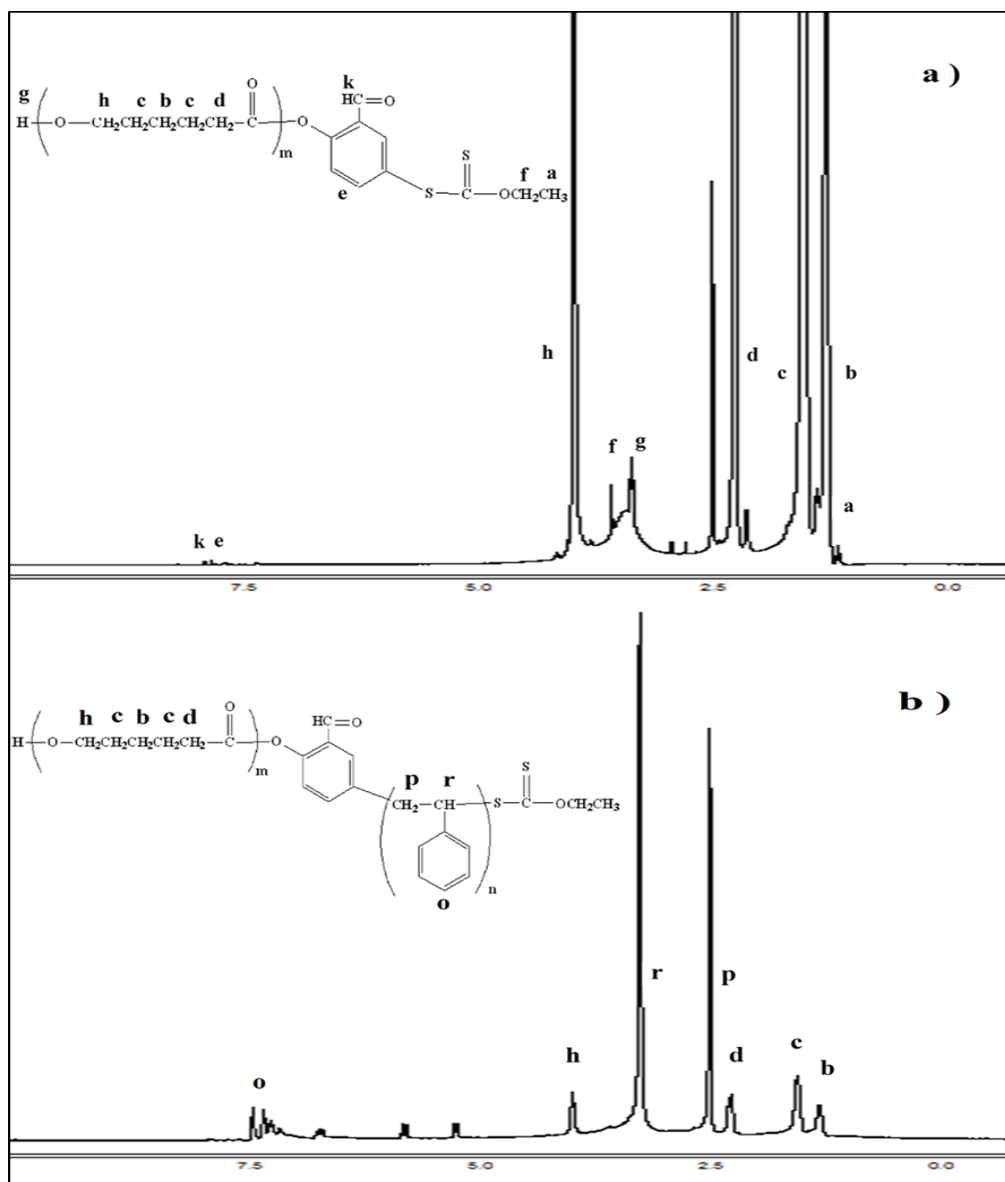


Figure 1. ¹H-NMR spectra of (a) RAFT-macro agent; (b) poly(CL-*b*-St) block copolymer.

Synthesis of poly(CL-*b*-St) block copolymer

Poly(CL-*b*-St) block copolymer was synthesized by RAFT polymerization of RAFT-macro agent and St at 90 °C. Scheme 2 (second line and third line) indicates the synthesis route for the block copolymer. The block copolymer yield was 52 wt %. M_n ,GPC of poly(CL-*b*-St) block copolymer was 66,683 g.mol⁻¹. Dispersity value of the block copolymer was 2.70. Increases in the molecular weight of poly(CL-*b*-St) block copolymer as compared with the molecular weight of RAFT-macro agent was proved the production of the block copolymer. The ¹H-NMR spectrum of the copolymer in Figure 1(b) displayed peaks at 1.6 ppm for -CH₂ of PCL unit, 2.3 ppm for -CH₂ linked carbonyl group of PCL unit, 2.5 ppm for -CH₂ of PS unit, 3.3 ppm for -CH of PS unit, 4.0 ppm for -OCH₂ of PCL unit, 7.3 ppm and 7.5 ppm for aromatic -CH of PS unit. The FT-IR spectrum of the copolymer in Figure 2(b) indicated signals at 3025 cm⁻¹ for aromatic -CH, 2920 and 2860 cm⁻¹ for aliphatic -CH₃, -CH₂ and -CH, 1720 cm⁻¹ for C=O, 1490 cm⁻¹ for aromatic -C=C, 1190 cm⁻¹ for -OC, 1070 cm⁻¹ for -SC.

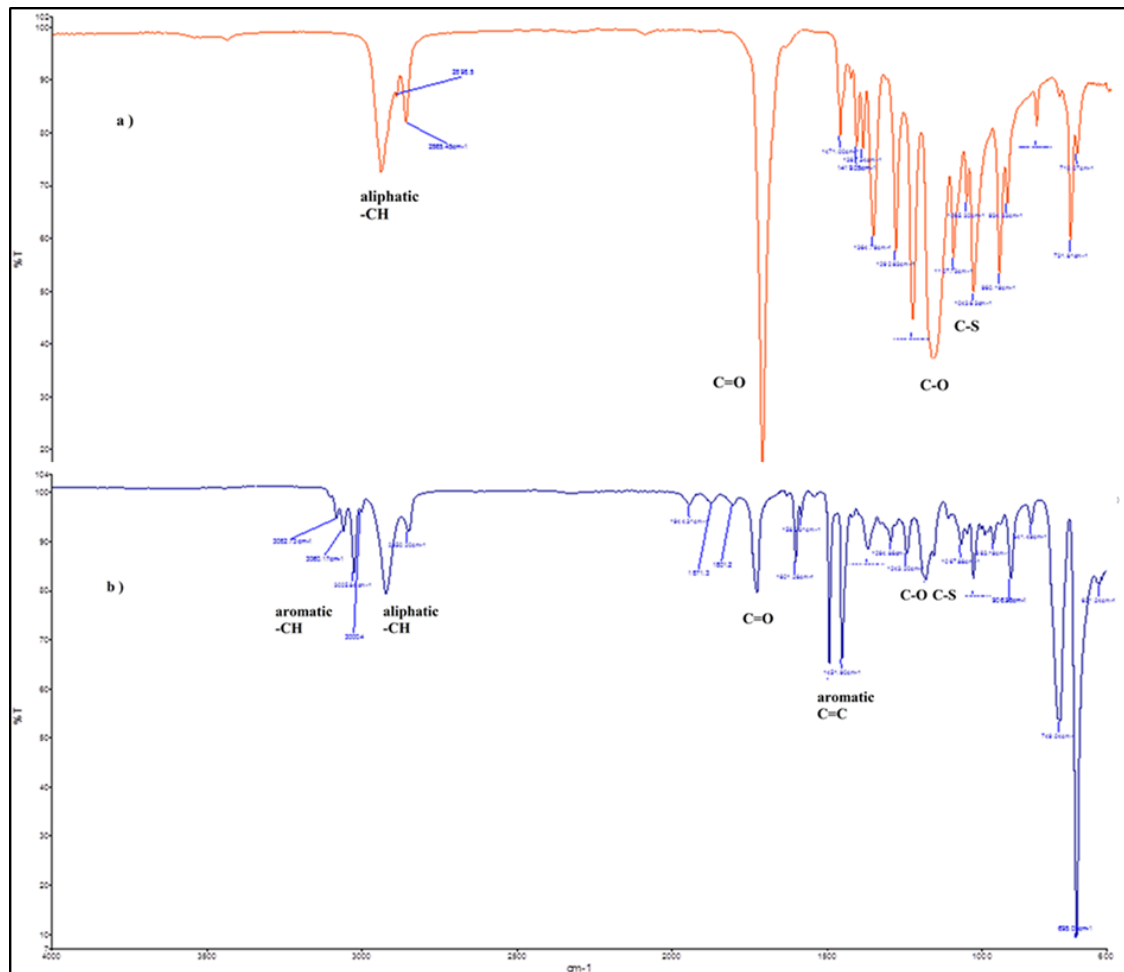


Figure 2. FT-IR spectra of (a) RAFT-macro agent; (b) poly(CL-*b*-St) block copolymer.

Thermal properties of poly(CL-*b*-St) block copolymer were shown by TGA method. When the TGA curves of the poly (CL-*b*-St) block copolymer are examined, it is seen that the degradation starts from 300 °C to 450 °C and the maximum degradation is at 418 °C as shown Figure 4. In the poly(CL-*b*-St) block copolymer, the PCL and PS units do not have separate decomposition temperature (T_d) values. A single T_d value of the block copolymer can show a high level of compatibility of the block copolymer in the amorphous regions of the PCL and PS.

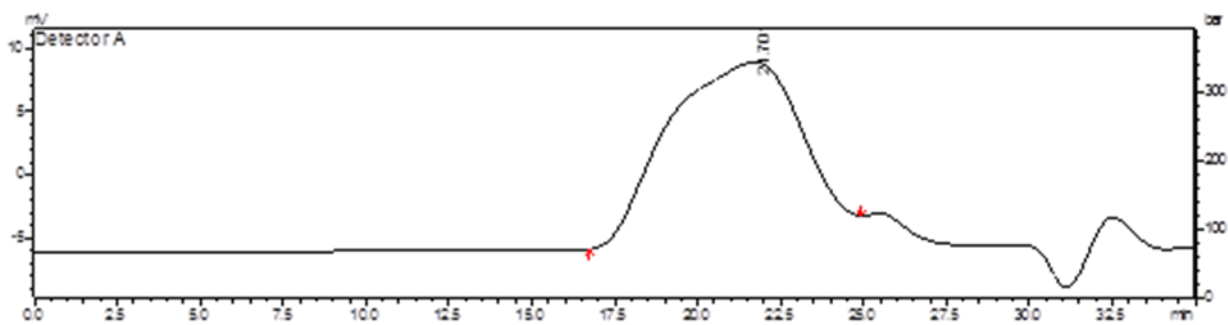


Figure 3. GPC curve of poly(CL-*b*-St) block copolymer.

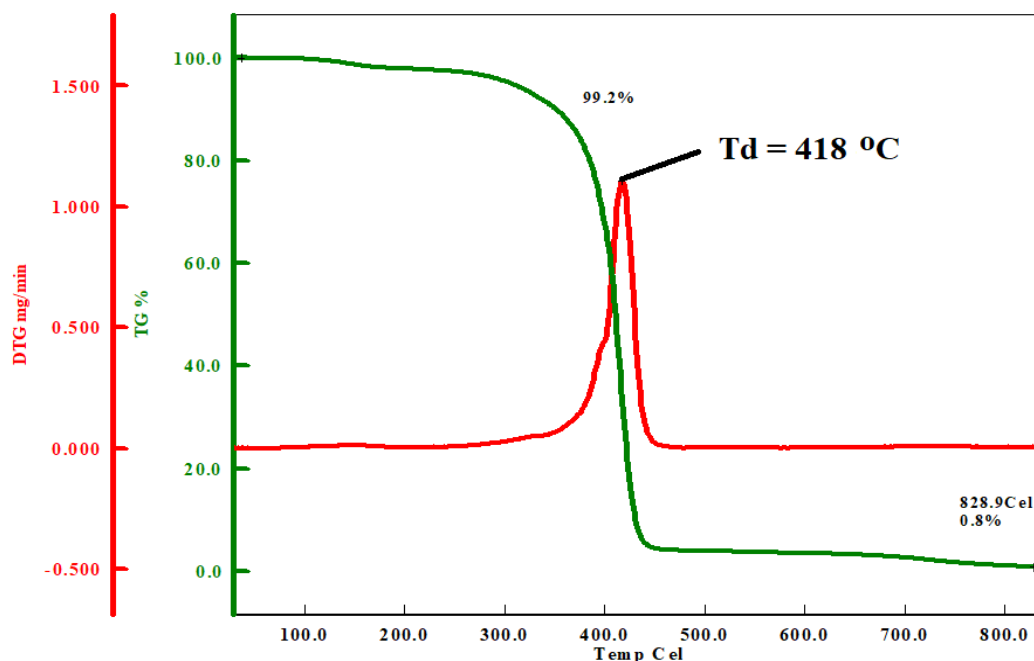


Figure 4. TGA curve of poly(CL-*b*-St) block copolymer.

CONCLUSIONS

Synthesis of poly(CL-*b*-St) block copolymer was performed with RAFT and ROP. The block copolymer was obtained with relatively high molecular weight. The method is simple and effective for synthesis of block copolymer. This study showed that the materials obtained with the synergistic combination of PCL and PS can be used in areas with wide technological application potential.

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