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Synthesis and characterization of star-brush copolymer by RAFT bulk polymerization using "grafting from" method

"Aşılama" yöntemi kullanılarak RAFT kütle polimerizasyonuyla yıldız-fırça kopolimerinin sentezi ve karakterizasyonu

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Abstract

In this study, the star-brush copolymer was prepared by reversible addition/fragmentation chain transfer (RAFT) bulk polymerization in the presence of multifunctional macro-RAFT agent based on poly(ε-caprolactone) (PCL) using the "grafting from" method. For this purpose, multifunctional macro-RAFT agent based on PCL was synthesized from the reaction of the brominated/chlorine-terminated poly(ε-caprolactone) (PCL-Br/Cl) and ethylxanthic acid potassium salt. Then, the poly(ε-caprolactone-g-styrene) [(PCL-g-PSt)] star-brush copolymer was synthesized via RAFT bulk polymerization using multifunctional macro-RAFT agent based on PCL. This polymerization was carried out at 80 °C by changing the polymerization time and, both the polymerization time and the polymerization temperature were investigated on the molecular weight, monomer conversion and dispersity. As a result of this polymerization, very high molecular weight copolymer with low dispersity was obtained. The products were characterized by using multi-instruments such as proton nuclear magnetic resonance spectroscopy, Infrared spectroscopy, gel permeation chromatography, thermo gravimetric analysis and differential scanning calorimetry.

Keywords: Multifunctional RAFT agent; bromine/chlorine-terminated poly(ε-caprolactone); "grafting from" method; RAFT bulk polymerization; styrene.

Öz

Bu çalışmada, poli(ε-kaprolakton) (PCL) bazlı çok fonksiyonlu makro-RAFT ajanı varlığında, "aşılama" yöntemi kullanılarak tersinir katılmalı/ayrışmalı zincir transfer (RAFT) kütle polimerizasyonu ile yıldız-fırça kopolimeri hazırlandı. Bu amaç için, brom/klor uçlu poli(ε-kaprolakton) (PCL-Br/Cl) ve potasyum etil ksantat tuzunun reaksiyonundan PCL bazlı çok fonksiyonlu makro-RAFT ajanı sentezlendi. Daha sonra, PCL bazlı çok fonksiyonlu makro-RAFT ajanı kullanılarak RAFT kütle polimerizasyonu ile poli(ε-kaprolakton-g-stiren) [(PCL-g-PSt)] yıldız-fırça kopolimeri sentezlendi. Bu polimerizasyon, polimerizasyon süresi değiştirilerek 80 °C'de gerçekleştirildi ve hem polimerizasyon süresinin hem de polimerizasyon sıcaklığının molekül ağırlığı, monomer dönüşümü ve dispersite üzerindeki etkileri incelendi. Bu polimerizasyon sonucunda, düşük dispersiteye sahip, çok yüksek molekül ağırlıklı kopolimer elde edildi. Ürünler, proton nükleer manyetik rezonans spektroskopisi, infrared spektroskopisi, jel geçirgenlik kromatografisi, termo gravimetrik analiz ve diferansiyel taramalı kalorimetri gibi cihazlar kullanılarak karakterize edildi.

Anahtar kelimeler: Çok fonksiyonlu RAFT ajanı; brom/klor uçlu poli(ε-kaprolakton); "aşılama" yöntemi; RAFT kütle polimerizasyonu, stiren.

1 Introduction

The Star-brush copolymers have both star and bottlebrush polymers properties. The star-brush copolymers can be designed by grafting another polymer chain or monomer to the active center of the polymer chain and are a important class of the macromolecular structure. These macromolecular structures are using in many areas due to their biocompatibility and biodegradability [1-5]. The three diferent strategies are known to synthesize star-brush copolymers, such as "grafting from", "grafting to" and "grafting through" [6]. Well-known star-brush copolymers could be prepared via either "grafting through" or "grafting from" strategy using the "living"/controlled radical polymerization (CRP) techniques. In recently, the "grafting from" method has been preferred to prepare brush copolymer by the many polymer researchers because this method is easy and inexpensive to design different monomer the same polymer chain for obtaining copolymer structure [7-11]. The "grafting from" method has emerged as a unique method in the field of dispersion or bulk polymerizations, enabling the obtain of well-known brush copolymers with in a one-step or in a separate-step polymerization techniques.

The Reversible addition/fragmentation chain transfer (RAFT) polymerization is one of the CRP techniques which introduced by the Rizzardo and co-worker [12]. This polymerization technique based on the radical closing mechanism and the molecular control of the copolymers which prepared via RAFT is achieved by chain transfer agent (RAFT-agent). With the RAFT polymerization, so many block, graft, star-block, star-brush copolymers have been added to polymer library because of its mild polymerization conditions such as temperature, no-contain metal catalyst system (RAFT agent) and compatibility with most vinyl monomers [12-20].

The poly(ε-caprolactone) is an important polyester that obtained via ring-opening polymerization (ROP) and both homopolymer and copolymer structures are occupied in the synthetic macro material library and they are used as

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biomedical materials because of the advantage of biocompatibility [21,22]. The brush copolymers are synthesized by binding a second monomer to the active sides created on the surface of the poly(ε-caprolactone) by ROP [7]. In our previous study, we synthesized a novel ATRP initiator (PCL-Br/Cl) thanks to the active sides created on the surface of poly(caprolactone) via ROP and the copolymer was obtained by atom transfer radical polymerization (ATRP) in presence of the this ATRP initiator [7]. In this contribution, we designed a novel PCL-based multifunctional macro-RAFT agent from the reaction of the chain transfer agent (CTA) and the PCL-Br/Cl. This PCL-based multifunctional macro-RAFT agent was suitable to synthesis brush copolymer using "grafting from" RAFT method. We tried to prove that the star-brush copolymer could be built on macro monomeric RAFT agents active sides to synthesis macromolecular structures with different block segments via RAFT bulk polymerization with this study.

The Polystyrene (PS) is a important solid thermoplastic with a high melting temperature (~240 °C), is using a commercial polymer in many area both homopolymer and copolymer strucrures. This thermoplastic has occupied with well-known block/graft copolymers structures in the poymer library shelf [23-32].

In here, the poly(ε-caprolactone-*g*-styrene) [(PCL-*g*-PSt)] star-brush copolymer was prepared by a combination of ring-opening polymerization (ROP) and RAFT bulk polymerization in a two-step procedure. For this purpose, the poly(ε-caprolactone)-based RAFT agent (multifunctional macro-RAFT agent) was obtained from reaction of the brominated/chlorine-terminated poly(ε-caprolactone) (PCL-Br/Cl) which synthesized by ROP of the ε-caprolactone using 3-chlor-1,2-propanediol initiator in our previous study [7] and ethylxanthic acid potassium salt. Then, the RAFT polymerization of the styrene was started in presence of the multifunctional macro-RAFT agent based on PCL and thanks to this polymerization of the poly(styrene) block was extended on active sides created on the surface of poly(caprolactone) by RAFT agent and PCL-*g*-PSt star-brush copolymer was synthesized. Our best knowledge, this star-brush copolymer could be added to copolymer library with this study using "grafting from" RAFT method. The star-brush copolymer was characterized by using multi-instruments and characterization results was detailed in manuscript.

2 Experimental Section

2.1 Chemicals

The Styrene was purificated via alumina column then used for the polymerization. The ethylxanthic acid potassium, *2,2'*-azobisisobutyronitrile, tetrahydrofuran and petroleum ether were supplied by Aldrich and used as received. The ε-caprolactone was supplied from Merck.

2.2 Instruments

The functional groups in the polymer were identified by Infrared spectroscopy (FT-IR) using the Perkin Elmer Spectrum 100 Model spectrometer in transmit mode with a scanning speed of 4000 to 550 cm^{-1} and the data analysis was interpreted via Origin software. The chemical shift of the polymers were recorded via the proton nuclear magnetic resonance spectroscopy (^{1}H-NMR) analysis using the Bruker Ultra Shield Plus 400 MHz NMR spectrometer with chloroform (CDCl3) as a solvent and the data analysis was interpreted via Mestrevova software. The molecular weight of the polymers were identified via gel permeation chromatography (GPC) analysis using the High Performance Liquid Chromatography HPLC-Shimadzu and LC-20AD gel permeation chromatography with THF solvent and data analysis was interpreted via Origin software. The thermal analysis of the products were conducted by Lab SYS EVO TGA/DSC thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC) device under Argon gas with a heating rate of 10 °C/min. TGA temperature range was from 25 °C to 600 °C while the DSC was performing by the temperature between 25 °C and 200 °C.

2.3 Synthesis of multifunctional macro-RAFT agent based on poly(ε-caprolactone)

To a large 250 mL degassed flask equipped with a stirrer bar, PCL-Cl/Br was used the same synthesized in our previous study [7] (2.10 g, 1.09 mmol), ethylxanthic acid potassium salt (KXa: 4.00 g, 25.00 mmol), and THF (60 mL) were added stirred at room temperature for 72 hours. then, the KCl/KBr that emerged from and unreactive excess KXa salts were separated via filtration. The THF was removed using a rotary in the final product and was poured into cold diethyl ether to precipitate the multifunctional macro-RAFT agent based on PCL. The yield was 1.25 g that calculated from dried product which under vacuum overnight.

2.4 Synthesis of poly(ε-caprolactone-g-styrene) star-brush copolymer

For this bulk polymerization, to a Schlenk tube equipped with a stirrer bar, macro RAFT agent, Styrene (St), AIBN were added. The RAFT agent (mol)/AIBN (mol) ratio was took 10/1(mol/mol) for the RAFT bulk polymerization as in literature. These procedures were performed under nitrogen gas. All the chemicals amount was showed in the Tables 1 for this copolymerization. The Schlenk tube was placed into oil baht at 80 °C and stirred for specific time. At the end of these periods, the tubes content was poured into excess petroleum ether to precipitate the P(CL-*g*-St) star-brush copolymer

3 Result and discussion

3.1 Synthesis of multifunctional macro-RAFT agent

In this contribution: firstly, the multifunctional macro-RAFT agent based on poly(ε-caprolactone) (PCL) was prepared by replacing the active chlorine/bromine centers formed on poly(ε-caprolactone) which synthesized in our previous study [7] with ethylxanthic acid potassium. The poly(ε-caprolactone) based multifunctional macro RAFT agent was obtained with 76% conversion which calculated from the^{1}H-NMR by comparing O**C**$\mathbf{H}_2$ (4.3-4.6 ppm) and C$\mathbf{H}_3$ (0.8 ppm) of the ethylxanthic acid. To the best of our knowledge, this multifunctional macro RAFT agent based on PCL could be added to polymer library with the this study. This step chemical reaction was showed in Figure 1. The FT-IR spectra of the multifunctional macro RAFT agent based on PCL showed in Figure 2 and the bands confirmed that at 1600 cm^{-1} of the C=S group, 1720 cm^{-1} of the C=O group and 2864-2943 cm^{-1} of the aliphatic CH group. The ^{1}H-NMR peaks of the multifunctional macro RAFT agent was showed in Figure 3 and the signals atributed to δ: 0.8 ppm of the ethylxanthic acid C$\mathbf{H}_3$, δ: 1.2,1.3,1.6 and 2.2 ppm of the PCL C$\mathbf{H}_2$, δ: 3.1-3.6 ppm of the 3-chloro-1.2-propanediol C$\mathbf{H}_2$ and C**H**, δ: 4.0 ppm of the PCL OC$\mathbf{H}_2$, δ: 4.3-4.6 ppm of the ethylxanthic acid OC$\mathbf{H}_2$. The molecular weight of the poly(ε-caprolactone) based multifunctional macro RAFT agent (M_{nGPC} = 1910 g/mol and DPI = 1.3) was determined by GPC. The GPC curves of the macro RAFT agent

was showed in Figure 6. The thermal properties of the RAFT agent was determined by the TGA and DSC analyses. TGA analysis was performed from 25 °C to 600 °C and the decomposition temperature (T_d) observed aroun the 280 °C in Figure 7. Both the glass transition temperature (T_g= 28 °C) and the melting point temperature (T_m= 52 °C) were observed of the RAFT agent via DSC analysis in Figure 8.

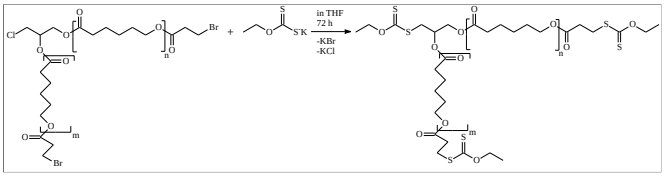

Figure 1. The chemical obtain pathway of PCL-based multifunctional RAFT agent.

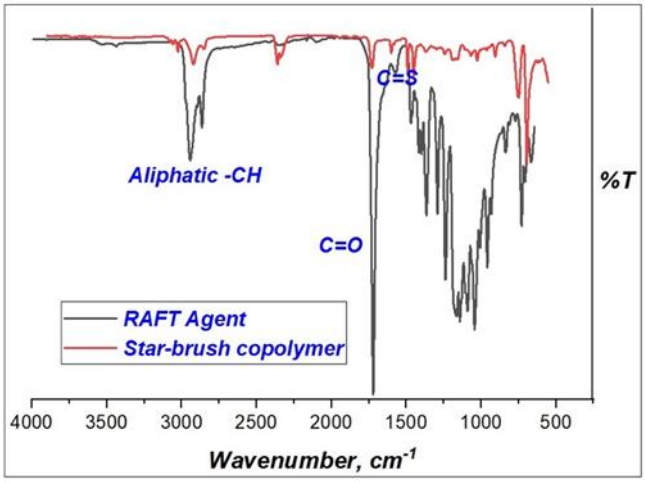

Figure 2. The FT-IR spectra of the multifunctional macro RAFT agent based on PCL and P(CL-g-St) star-brush copolymer.

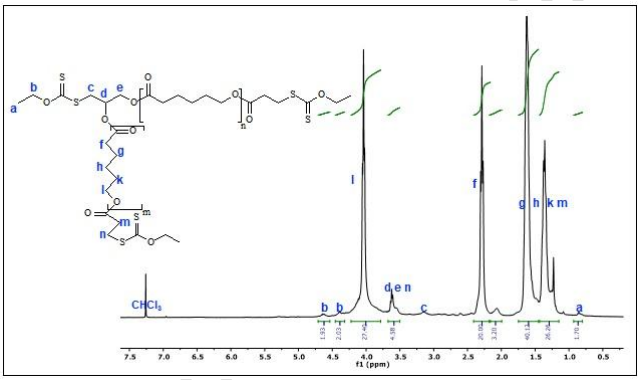

Figure 3. The ^{1}H-NMR spectrum of the multifunctional macro RAFT agent based on PCL in $CHCl_3$.

3.2 Synthesis of the star-brush copolymer by RAFT bulk polymerization using "grafting from" method

Secondly, the RAFT bulk polymerization of the styrene was carried out in presence of the poly(ε-caprolactone) based multifunctional macro RAFT agent by changing the polymerization time at 80 °C. In this bulk RAFT polymerization, the poly(CL-*g*-St) star-brush copolymer was synthesized at high molecular weights using "grafting from" method. The polymerization conditions and results of the star-brush copolymer are given in Tables 1. The Figure 4 shows the synthesis mechanizm of the copolymer. The star-brush copolymer was characterized using FT-IR, ^{1}H-NMR, GPC, TGA, DSC. The FT-IR image of the poly(CL-*g*-St) star-brush copolymer was observed that the signals attributed to the bands: 1720 cm^{-1} of the C=O group and 2864-2943 cm^{-1} of the aliphatic CH group in Figure 2. The proton signals of the poly(CL-*g*-St) star-brush copolymer was taken via ^{1}H-NMR. The ^{1}H-NMR spectrum said that the peaks could be corresponded; δ: 1.4-2.3 ppm of the PCL and PSt blocks C**H**$_2$, C**H**, δ: 4.0 ppm of the PCL block OC**H**$_2$, and δ: 6.3-7.2 ppm of the PSt block phenyl protons in Figure 5.

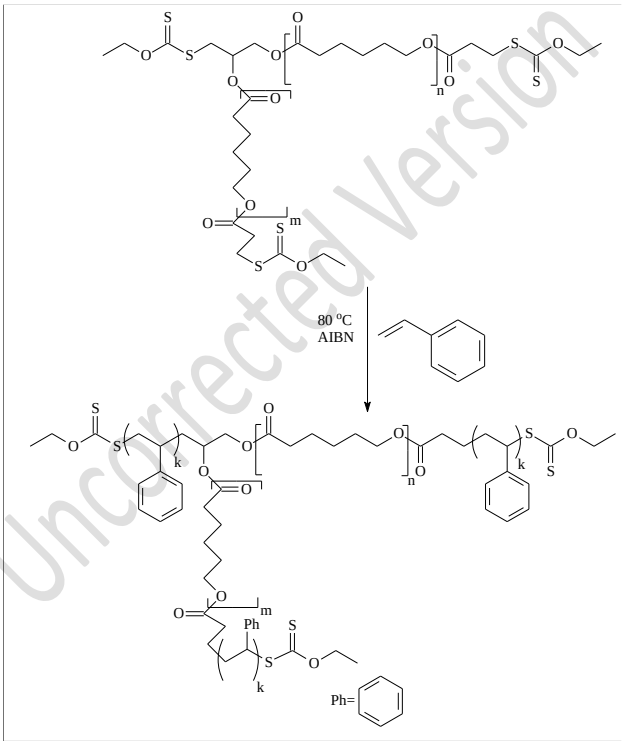

Figure 4. The synthesis mechanizm of the poly(CL-g-St) star-brush copolymer.

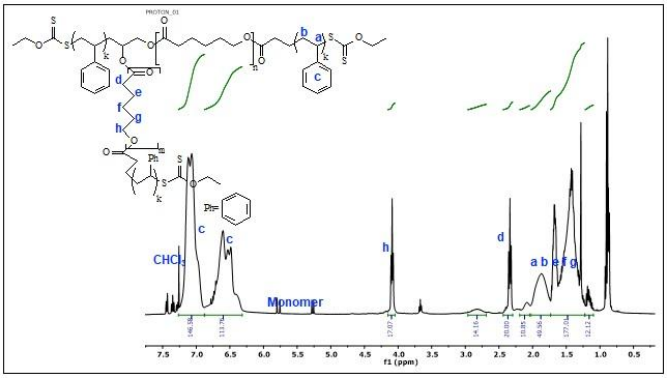

Figure 5. The ^{1}H-NMR spectrum of the poly(CL-g-St) star-brush copolymer in $CHCl_3$.

The number molar mass of the star-brush copolymer was clarified via gel permeation chromatography (GPC). The GPC curves of star-brush copolymer was showed in Figure 6. By changing the polymerization time, the copolymer molecular weight relatively increased, but decreased after the fourth hour of polymerization (in Table 1). It could be said that these fluctuations in molecular weight determined by GPC are compatible with CRP techniques that occur according to first-order reaction kinetics. Because, according to this kinetics, as the polymerization time increases, the molecular weight first

increases and then begins to decrease. In addition, the theoretical molecular weight ($M_{n,theo}$) and the GPC molecular weight ($M_{n(GPC)}$) changed harmonically in this polymerization kinetics in Table 1. It was observed that the highest copolymer molecular weight was reached at the third hour in RAFT bulk polymerization. In this polymerization, the high molecular weight copolymer was obtained. This situation can be explained by the fact that RAFT bulk polymerization occurs on more active sides on the multifunctional macro RAFT agent. The dispersity (M_w/M_n) value of the copolymers was found high than expected. The reason for this can be explained by the synthesis of high molecular weight polymers by performing RAFT bulk polymerization on more active center. We also observed in our previous studies that the Mw/Mn value was high than expected [5]. The theoretical molar mass ($M_{n,theo}$) of the poly(CL-*g*-St) star-brush copolymer was calculated using *Equation 1* [5]; where $[M]_o$ and $[RAFT\text{-}agent]_o$ are the beginning molarity of styrene and multifunctional macro RAFT agent based on PCL, $(Mmon)_o$ shows the molecular weight of the styrene, and 1910 the molecular weight of the multifunctional macro RAFT agent based on PCL. The theoretical molar mass ($M_{n,theo}$) of the poly (CL-*g*-St) star-brush copolymer which calculated using *Equation 1* was demonstrated in Table 1.

$$M_{n,theo} = 1910 + \{([M]_o/[RAFT\ agent]_o)\} \text{x conversion x Mmon} \quad (1)$$

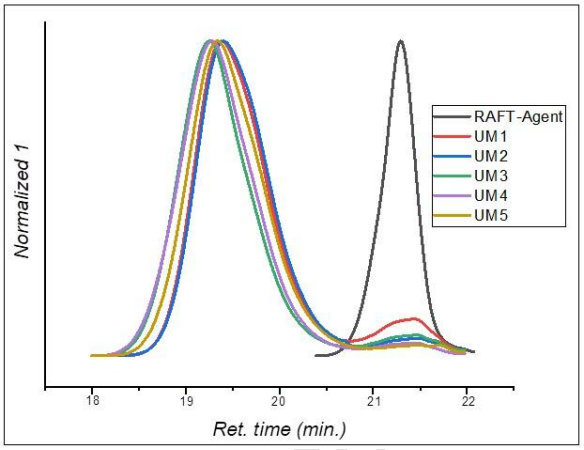

Figure 6. The GPC curves of the multifunctional macro RAFT agent and the P(CL-g-St) star-brush copolymer.

3.3 The thermal behavior of star-brush copolymer

The thermal behavior of polymers is important parameter that determine the usage areas of the polymer. The glass transition temperature and thermal decomposition temperature of polymers can provide information about the durability of polymers used as materials. In our study, the thermal properties of the P(CL-*g*-St) star-brush copolymer was investigated by DSC and TGA. The TGA analysis observed that the block-brush copolymer had two decomposition temperature when the copolymer heated from 25 °C to 600 °C. These decomposition temperature could be attributed to for PCL and PSt at 280 °C and 410 °C, respectively in Figure 7. The glass transition temperature (T_g) was observed about 35 °C for the P(CL-*g*-St) star-brush copolymer with no indication of a melting endotherm in Figure 8. This DSC result said that the star-brush copolymer was both amorphous with limited to no crystallinity and was showed harmonic behavior between of the two block of the star-brush copolymer. Furthermore, this T_g could be proved by decreasing of amount homopolymer formation and the increasing of star-brush copolymer.

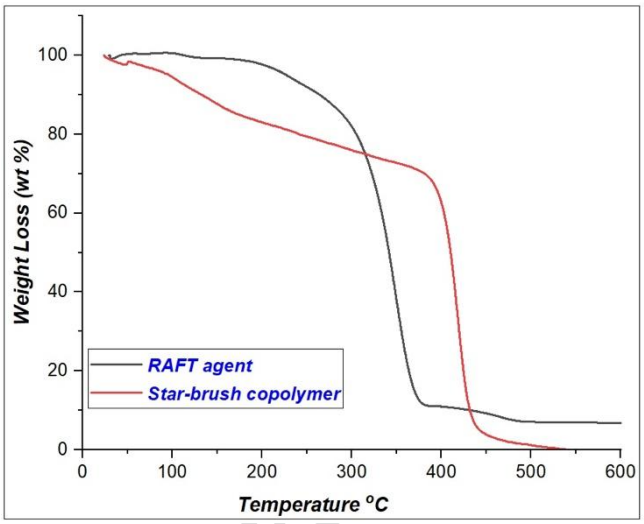

Figure 7. The TGA weight loss of the RAFT agent and, and P(CL-g-St) star-brush copolymer.

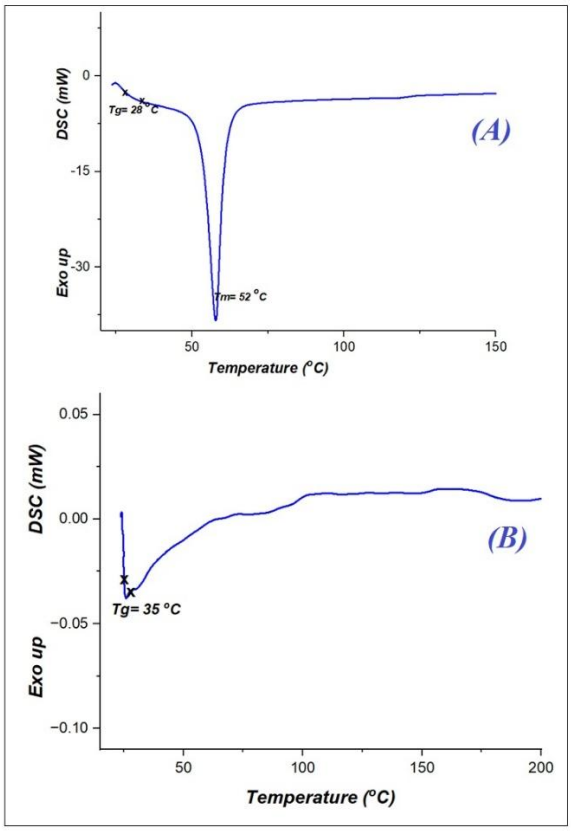

Figure 8. The DSC curve of the RAFT agent ***(A)***, and P(CL-g-St) star-brush copolymer ***(B).***

Table 1. The synthesis conditions and results of the star-brush copolymer.

Code	Time (min.)	Yield (gr)	$M_{n(GPC)}$ (g/mol)	M_w/M_n	Conv. (%)	$M_{n,theo}$ (g/mol)
UM-1	60	0.3855	68980	1.70	72	57400
UM-2	120	0.7091	69640	1.61	75	59710
UM-3	180	0.7275	90280	1.83	88	69730
UM-4	240	1.0736	87440	1.88	85	67420
UM-5	300	1.1237	64370	1.74	68	54320

Polym temp. = 80 °C; RAFT agent = 0.05 mmol; Styrene = 38.40 mmol; AIBN= 0.005 mmol.

4 Conclusion

In this study, the poly(ε-caprolactone-*g*-styrene) star-brush copolymer with different PCL and PSt block lengths were successfully synthesized by RAFT bulk polymerization using "grafting from" method as proved by using multi-instruments such as FT-IR, ^{1}H-NMR, GPC, TGA and DSC analysis. In general, with the study the high molecular weights copolymer was obtained when produced at 80 °C. By changing the polymerization time, the copolymer molecular weight relatively increased, but decreased after the fourth hour of polymerization. The glass transition temperature (T_g) (about 35 °C) found for the star-brush copolymer. The TGA analysis could be confirmed the formation of star-brush copolymer with two different degradation temperatures.

5 Author contributions

1: Supervision, Conceptualization, Methodology, Project administration, Writing–original draft, and Writing–review and editing. **2:** All experimental works, Methodology, and conceptualization. **3:** partially experimental works, conceptualization.

6 Ethics committee approval and conflict of interest statement

"There is no need for ethics committee approval for the prepared article".

"The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper".

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