*Karadeniz Fen Bilimleri Dergisi*, 13(3), 882-893, 2023. DOI: 10.31466/kfbd.1260147

KFBD

Karadeniz Fen Bilimleri Dergisi
The Black Sea Journal of Sciences
ISSN (Online): 2564-7377 https://dergipark.org.tr/tr/pub/kfbd

Araştırma Makalesi / Research Article

# Synthesis and Characterization of Poly(β-Propiolactone)-*b*-Poly(methyl methacrylate) Tri-arm Block Copolymer Using Atom Transfer Radical Polymerization

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## Abstract

Terminally dibrominated poly(β-propiolactone) was prepared through sequentially ring-opening polymerization of β-propiolactone and dibromination of the former product. Synthesis of poly(β-propiolactone)-*b*-poly(methyl methacrylate) tri-arm block copolymer was achieved by atom transfer radical polymerization of methyl methacrylate onto the poly(β-propiolactone) with bromide end groups. The characterization of the polymers was carried out using $^1$H-NMR, DSC, TGA, and GPC. GPC analysis of the final product resulted in an unimodal curve corresponding to the weight average molecular weight of 9353 g.mol$^{-1}$. TGA analysis of the tri-arm block copolymer exhibited a two-step decomposition curve corresponding to the β-propiolactone and the methyl methacrylate blocks at 212 ºC and 411 ºC, respectively. DSC analysis of poly(β-propiolactone)-*b*-poly(methyl methacrylate) tri-arm block copolymer showed two glass temperatures corresponding to the β-propiolactone and the methyl methacrylate blocks at -22.02 ºC and 86.55 ºC, respectively. The spectroscopic and thermal analyses proved that the tri-arm block copolymer was successfully synthesized through ring-opening polymerization and atom transfer radical polymerization, respectively.

**Keywords:** Atom Transfer Radical Polymerization, Macro Initiator, Poly(β-Propiolactone), Ring-Opening Polymerization, Tri-Arm Block Copolymer.

# Poli(β-Propiyolakton)-*b*-Poli(Metil Metakrilat) Üç Kollu Blok Kopolimerinin Atom Transfer Radikal Polimerizasyonuyla Sentezi ve Karakterizasyonu

## Öz

Son uçları dibromlanmış poli(β-propiyolakton), sırasıyla β-propiyolaktonun halka açma polimerizasyonu ve poli(β-propiolakton)un dibrominasyonu yoluyla hazırlandı. Poli(β-propiyolakton)-*b*-poli(metil metakrilat) üç kollu blok kopolimer sentezi, metil metakrilatın bromür uç gruplarına sahip poli(β-propiyolakton) üzerine atom transferiyle radikal polimerizasyonuyla elde edildi. Polimerlerin karakterizasyonu, $^1$H-NMR, DSC, TGA ve GPC kullanılarak gerçekleştirildi. Son ürünün GPC analizi, 9353 g.mol$^{-1}$ ortalama molekül ağırlığına karşılık gelen bir tek dağılımlı eğri gösterdi. Üç kollu blok kopolimerin TGA analizi, 212 ºC ve 411 ºC'de sırasıyla β-propiyolakton ve metil metakrilat bloklarına karşılık gelen iki basamaklı bozunma eğrisi sergiledi. Poli(β-propiolakton)-*b*-poli(metil metakrilat) üç kollu blok kopolimerinin DSC analizi, -22.02 ºC ve 86.55 ºC'de sırasıyla β-propiyolakton ve metil metakrilat bloklarına karşılık gelen iki camsı geçiş sıcaklığı gösterdi. Spektroskopik ve termal analizler, üç kollu blok kopolimerin sırasıyla halka açma polimerizasyonu ve atom transfer radikal polimerizasyonu yoluyla başarılı bir şekilde sentezlendiğini kanıtladı.

**Anahtar Kelimeler:** Atom Transfer Radikal Polimerizasyonu, Makro Başlatıcı, Poli(β-propiyolakton), Halka Açılması Polimerizasyonu, Üç Kollu Blok Kopolimer.

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**Geliş/Received:** 04.03.2023 **Kabul/Accepted:** 01.08.2023

## 1. Introduction

Ring-opening polymerization was greatly used to obtain novel copolymers (Coulembier et al., 2006; Çatiker et al., 2020; Öztürk et al., 2018; Öztürk, Yavuz et al., 2016; Öztürk et al., 2013; Öztürk et al., 2010; Savaş et al., 2021). The polymerization has been carried out many monomers with initiators and catalyst systems (Janata et al., 2003; Göktaş et al., 2014; Kurcok et al., 1992; Arkin et al., 2001; Arslan et al., 1999; Öztürk, and Yörümez, 2019; Öztürk and Türkoğlu, 2022). Polyesters polymerized from lactones have specific characteristics: biocompatibility, excellent mechanical properties, biodegradability, no toxicity, etc. (Chausson et al., 2008; Öztürk and Cavicchi, 2018; Öztürk and Meyvacı, 2017; Savaş et al., 2022). There are a lot of studies in the literature describing the mechanisms of ring-opening polymerization of lactones (Wang et al., 2017; Albertsson and Varma, 2003; Olsén et al., 2016; Lecomte and Jérôme, 2011). Copolymers have significant interest owing to mechanical properties and practices of them (Ruzette and Leibler, 2005; Zhang et al., 2018; Öztürk et al., 2014; Öztürk et al., 2020; Öztürk, Kayğın et al., 2016; Meyvacı and Öztürk, 2022). Block and graft copolymers have applications in industry (Altintas et al., 2011; Altıntas and Tunca, 2011; Çatıker, Meyvacı et al., 2019; Bolton and Rzayev, 2012; Mitra et al., 2018; Hizal et al., 2005; Yigit et al., 2018; Muftuoglu et al., 2009; Dag et al., 2012; Durmaz et al., 2008). Atom transfer radical polymerization as a controlled/living radical polymerization technique has been widely used in copolymer synthesis (Öztürk, Yavuz et al., 2016; Ribelli et al., 2019; Król and Chmielarz, 2014) since first reported in 1995 (Wang and Matyjaszewski, 1995).

This study showed the synthesis of poly(β-propiolactone)-*b*-poly(methyl methacrylate) tri-arm block copolymer by atom transfer radical polymerization of poly(β-propiolactone) with bromide end groups and methyl methacrylate. The polymers were characterized using spectroscopic and thermal methods.

## 2. Experimental

### 2.1. Chemicals

β-propiolactone (Across Organics, 98 %), methyl methacrylate (Sigma-Aldrich, 99 %, a column including aluminum oxide powder was used to remove the inhibitors), sodium tert-butoxide (Sigma-Aldrich, 97%), bromine (Sigma-Aldrich, 98.0-102.0 %), toluene (Sigma-Aldrich, anhydrous ≥ 99.8 %), methanol (Sigma-Aldrich, anhydrous 99.8 %), copper(I) bromide (Sigma-Aldrich, 98 %), and N,N,N′,N′,N″-pentamethyl diethylenetriamine (Sigma-Aldrich, 99 %) were used as purchased.

### 2.2. Synthesis of poly(β-propiolactone) by ring-opening polymerization

Synthesis of poly(β-propiolactone) was carried out according to the literature (Wang et al., 2017). For example: 0.711 g of β-propiolactone and 0.048 g of sodium tert-butoxide were placed in a Schlenk tube equipped with an argon source and magnetic stirrer. After vigorous stirring at ambient temperature mixture solidified in a short time. The solid was treated with a few mL of methanol to remove possible unreacted monomer and the initiator. The white product was filtered and dried using a vacuum pump at ambient temperature.

### 2.3. Synthesis of poly(β-propiolactone) with bromide end groups (ATRP macro initiator, ATRP MI)

Poly(β-propiolactone) with bromide end groups was obtained as the reference (Çatıker, Atakay et al., 2019). For example: 0.200 g of poly(β-propiolactone) was dissolved in 2.0 mL of chloroform. A drop of bromine was added to the solution and the mixture was stirred at room temperature overnight. Then the excess bromine and solvent were evaporated using a vacuum pump. The remaining yellowish solid was regarded as an ATRP macro initiator.

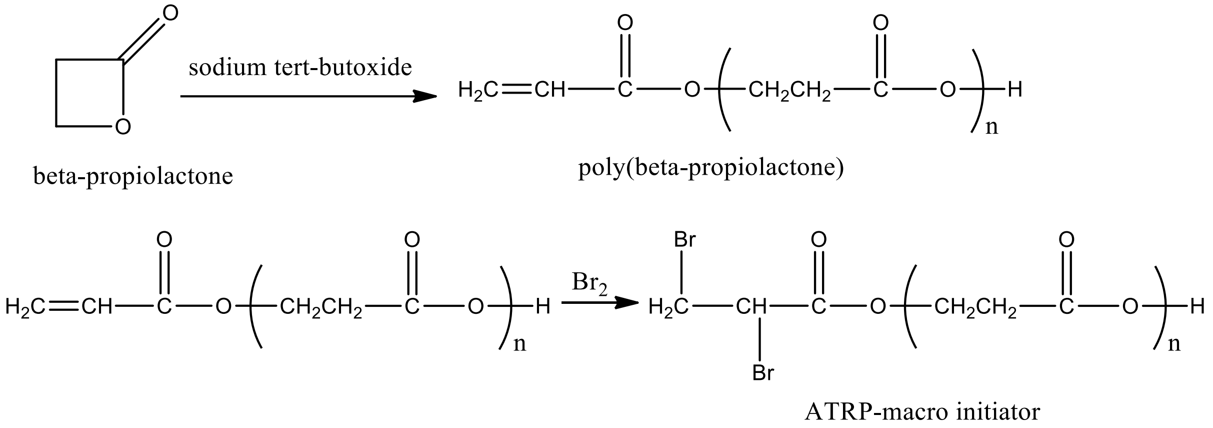
### 2.4. Synthesis of poly(β-propiolactone)-*b*-poly(methyl methacrylate) tri-arm block copolymer

0.1411 g of poly(β-propiolactone) with bromide end groups (ATRP macro initiator, ATRP MI) as the macro initiator, 0.4725 g of methyl methacrylate as the monomer, 0.07 mL of N,N,N′,N′,N″-pentamethyl diethylenetriamine as the ligand and 5 mL of toluene as the solvent were placed in a glass tube. After dissolution, 0.0188 g of copper(I) bromide as the catalyst was poured into the tube, followed by $N_2$ gas injection for 3 minutes. The tube was set in an oil bath on a hot plate with a stirrer for 18 hours at 90 °C. At the end of the block copolymerization, the content of the tube was precipitated using excess methanol. After decantation, poly(β-propiolactone)-*b*-poly(methyl methacrylate) tri-arm block copolymer was dried in a vacuum at ambient temperature.

## 3. Results and Discussion

### 3.1. Syntheses of poly(β-propiolactone) and ATRP macro initiator (ATRP MI)

The synthesis outline of poly(β-propiolactone) was shown in Scheme 1 (line 1). Reaction yield was quantitatively determined as 98.2 % wt. Scheme 1 (line 2) showed the synthesis pathway of ATRP macro initiator. Reaction yield was nearly 100 % wt. The $^1$H-NMR spectrum (Bruker UltraShield Plus 400 MHz) of poly(β-propiolactone) in Figure 1 showed signals at; (δ, ppm): 7.2 ($CDCl_3$), 5.8-6.5 ($-CH=CH_2$), 4.4 ($-C\underline{H}_2O$), and 2.7 ($-C\underline{H}_2C=O$). The peaks of the vinyl group at 5.8-6.5 ppm in the NMR spectrum (Jedliński et al., 1991) proved the synthesis of poly(β-propiolactone) with the vinyl end group.



**Scheme 1.** Reaction outlines in the syntheses of poly(β-propiolactone) and poly(β-propiolactone) with bromide end groups (ATRP macro initiator, ATRP MI).

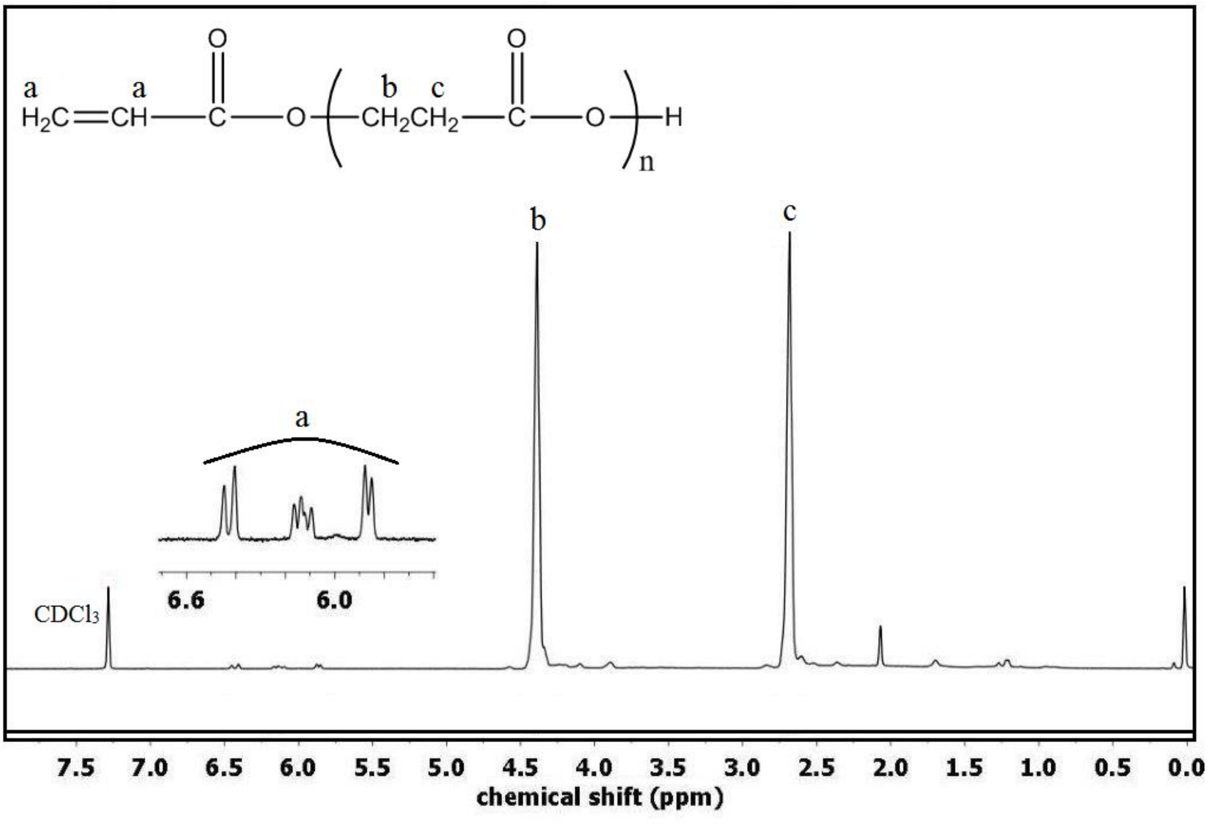
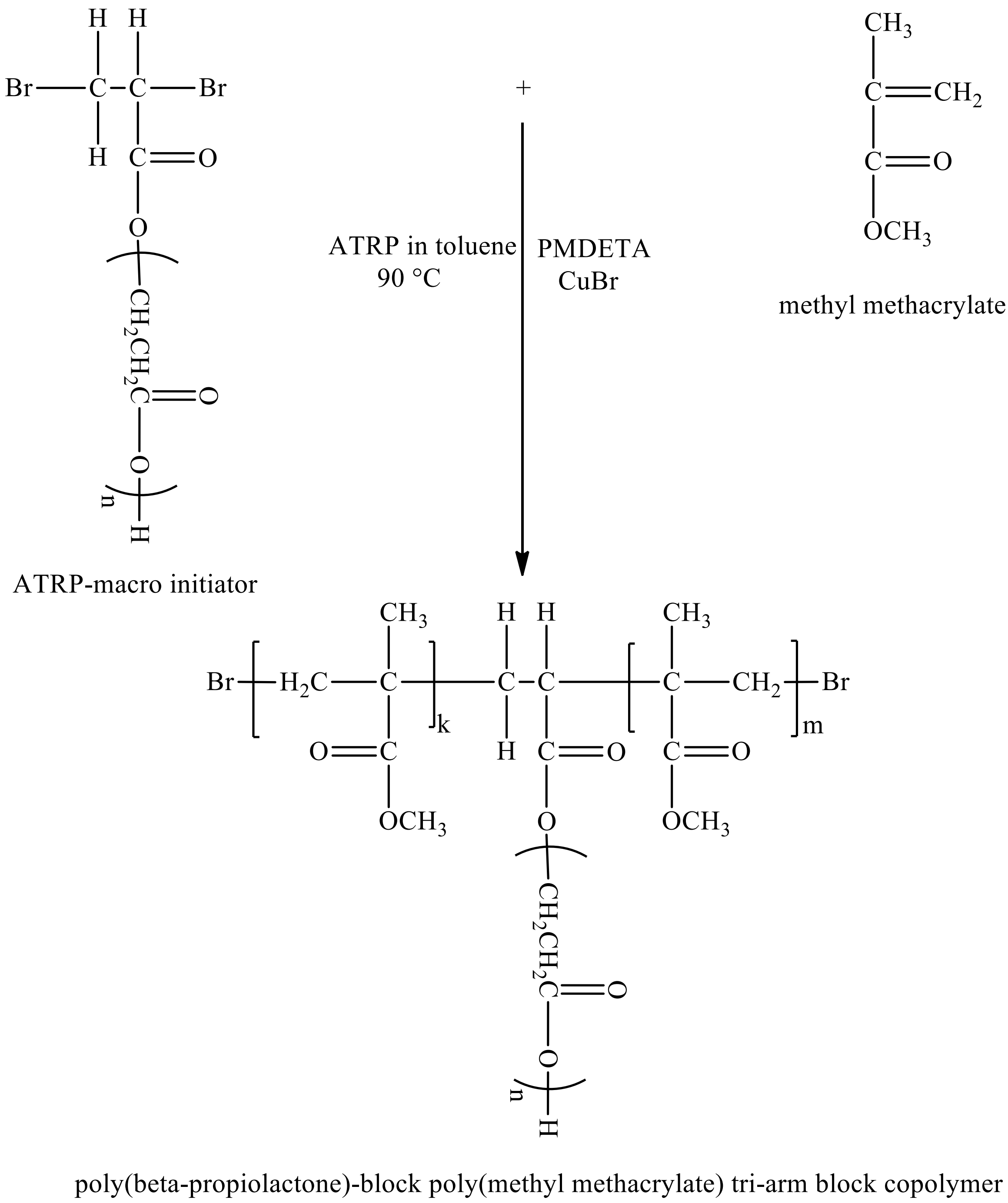


**Figure 1.** $^1$H-NMR of poly(β-propiolactone) synthesized by ring-opening polymerization.

### 3.2. Synthesis of poly(β-propiolactone)-*b*-poly(methyl methacrylate) block copolymer

Synthesized poly(β-propiolactone)-*b*-poly(methyl methacrylate) tri-arm block copolymer was weighed as 0.1950 g. The block copolymerization outline was shown in Scheme 2. The $^1$H-NMR spectrum of tri-arm block copolymer in Figure 2 monitored signals at; (δ, ppm): 4.4 ($-C\underline{H}_2O$ of poly(β-propiolactone) unit), 3.6 ($-C\underline{H}_3$ of poly(methyl methacrylate) unit), 2.7 ($-C\underline{H}_2C{=}O$ of poly(β-propiolactone) unit), 1.8 ($-C\underline{H}_2$ of poly(methyl methacrylate) unit), and 0.9 ($-C\underline{H}_3$ of poly(methyl methacrylate) unit). GPC analysis (HPLC/GPC-Shimadzu, LC-20AD with tetrahydrofuran at rate of 1 ml.min$^{-1}$. Poly(methyl methacrylate) standards: 2950, 5100, 12000, 35300, 73000 and 123000 g.mol$^{-1}$) of poly(β-propiolactone)-*b*-poly(methyl methacrylate) tri-arm block copolymer (Figure 3) resulted in a unimodal curve corresponding to the weight average molecular weight of 9353 g.mol$^{-1}$. The dispersity of the tri-arm block copolymer was 2.42. TGA analysis (Seiko II Exstar 6000, 10 °C.min$^{-1}$ under $N_2$) of the tri-arm block copolymer (Figure 4) exhibited a two-step decomposition curve corresponding to the β-propiolactone and the methyl methacrylate blocks at 212 $^oC$ and 411 $^oC$, respectively. Furthermore, DSC analysis (TA, DSC Q 2000, 20 °C.min$^{-1}$ under $N_2$) of poly(β-propiolactone)-*b*-poly(methyl methacrylate) tri-arm block copolymer (Figure 5) showed two glass temperatures corresponding to the β-propiolactone and the methyl methacrylate blocks at -22.02 $^oC$ and 86.55 $^oC$, respectively.



**Scheme 2.** Reaction pathway in the synthesis of poly(β-propiolactone)-*b*-poly(methyl methacrylate) tri-arm block copolymer.

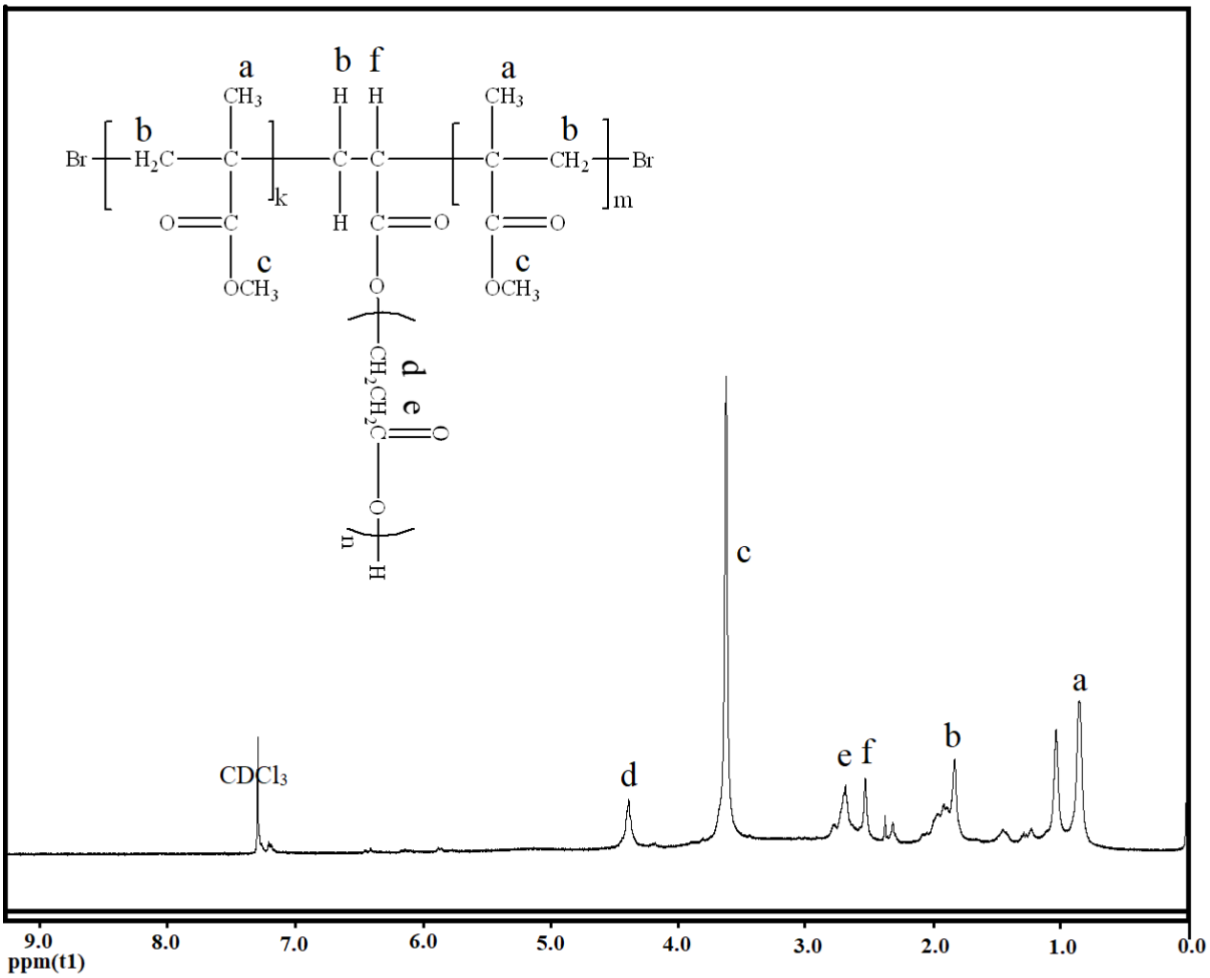


**Figure 2**. $^1$H-NMR of poly(β-propiolactone)-*b*-poly(methyl methacrylate) tri-arm block copolymer.

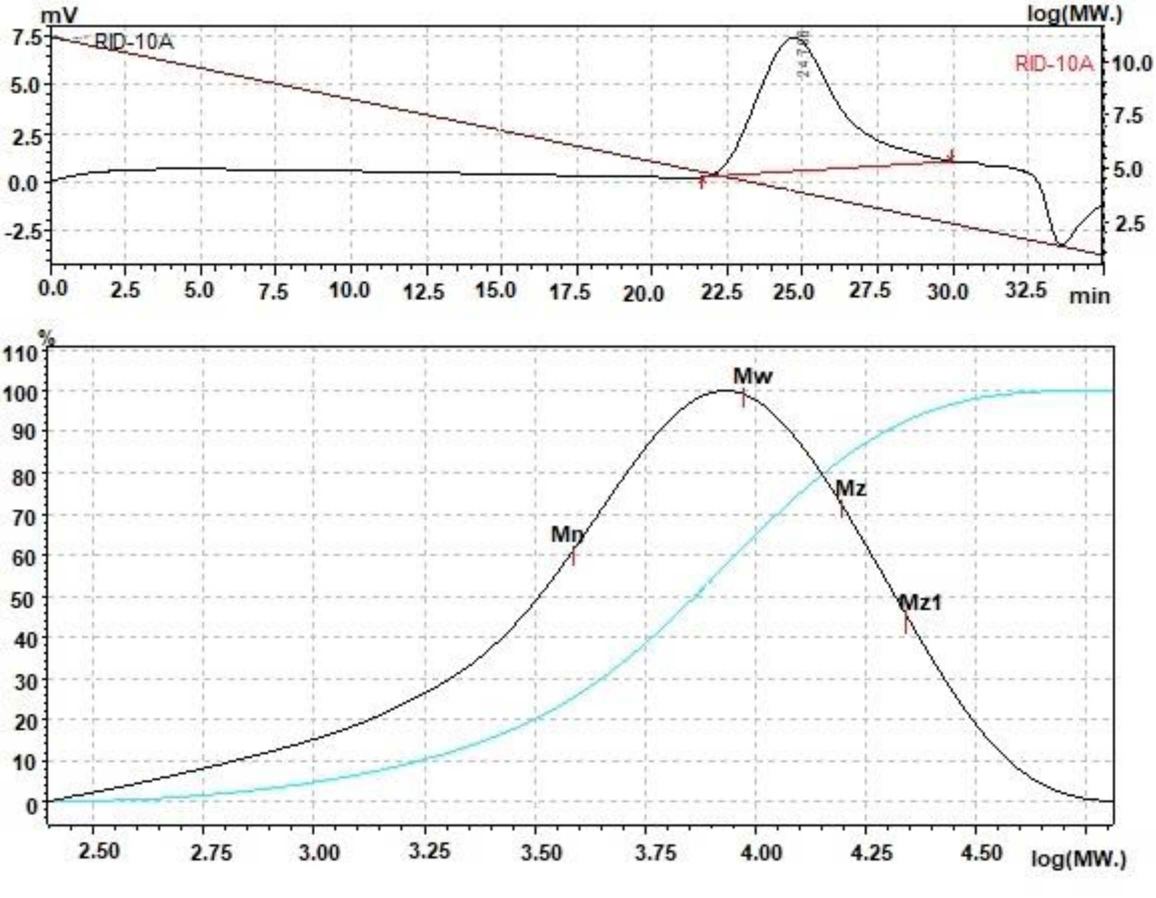


**Figure 3.** GPC curves of poly(β-propiolactone)-*b*-poly(methyl methacrylate) tri-arm block copolymer.

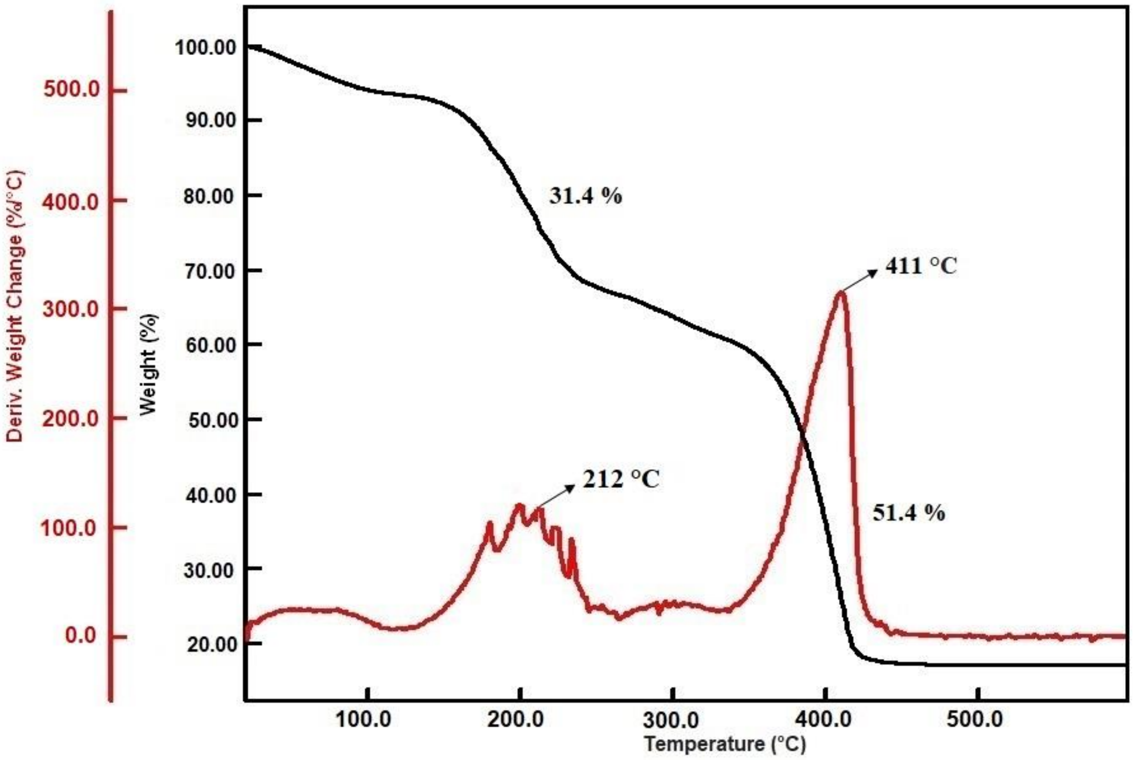


**Figure 4.** TGA curve of poly(β-propiolactone)-*b*-poly(methyl methacrylate) tri-arm block copolymer.

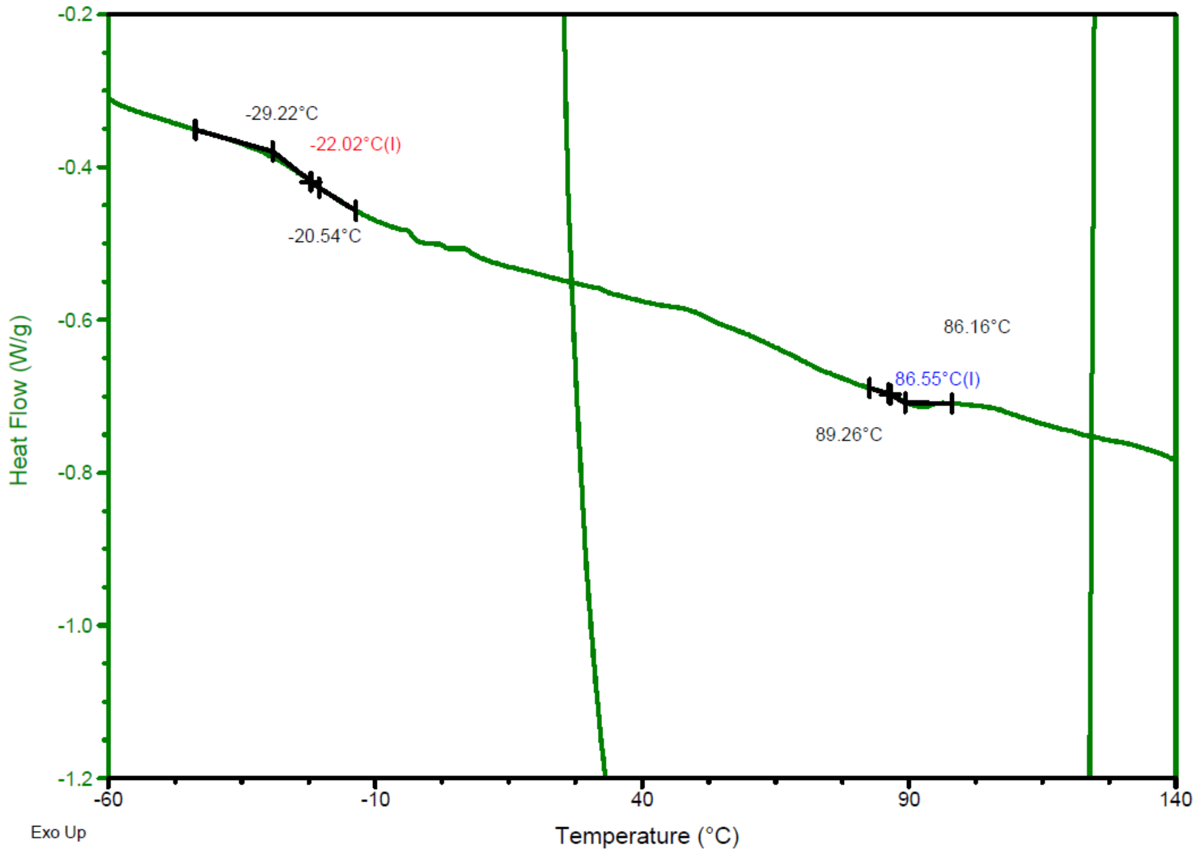


**Figure 5.** DSC curve of poly(β-propiolactone)-*b*-poly(methyl methacrylate) tri-arm block copolymer.

## 4. Conclusion

Poly(β-propiolactone)-*b*-poly(methyl methacrylate) tri-arm block copolymer was synthesized successfully via atom transfer radical polymerization using poly(β-propiolactone) with bromide end groups and methyl methacrylate. $^1$H-NMR, DSC, GPC, and TGA were carried out for the polymer characterization. These characterization techniques revealed that the tri-arm block copolymer was obtained. The weight average molecular weight of poly(β-propiolactone)-*b*-poly(methyl methacrylate) tri-arm block copolymer obtained was 9353 g.mol$^{-1}$. By varying the input ratios, the tri-arm block copolymer synthesis with desired mechanical properties can be achieved. This work is a good example of tri-arm block copolymer synthesis using ring-opening polymerization and atom transfer radical polymerization techniques.

## Authors' Contributions

All authors contributed equally to the study.

## Statement of Conflicts of Interest

There is no conflict of interest between the authors.

## Statement of Research and Publication Ethics

The author declares that this study complies with Research and Publication Ethics.

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