

Synthesis and Characterization of Poly (lactic acid-b- ϵ -caprolactone) Block Copolymers

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ABSTRACT: In this study, poly (lactic acid-b- ϵ -caprolactone) was synthesized with the ring opening polymerization of ϵ -caprolactone using of the poly lactic acid with the presence of DBTDL catalyst. In order to achieve that, poly lactic acid was synthesized by the condensation from the polymerization of the lactic acid with the SnCl₂ catalyst. Poly (lactic acid-b- ϵ -caprolactone) block copolymer was synthesized from the poly lactic acid (PLA) by changing some polymerization parameters such as polymer and monomer amounts and polymerization time. Block copolymers were characterized by using ¹H-NMR, ¹³C-NMR, FT-IR, DSC and GPC chromatography methods.

Key Words: Condensation polymerization, ring opening polymerization, poly lactic acid, block copolymer

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INTRODUCTION

Poly (lactic acid) (PLA) is a polymer that is incorporated into the group of aliphatic polyesters whose repeating units consist of lactic acid (Jin, Hu, and Park 2019; Basu et al. 2016; Nofar et al. 2019; Saeidlou et al. 2012; Sonchaeng et al. 2018). One of the most important characteristics is that it is a biodegradable (Jin, Hu, and Park 2019; Wu et al. 2019; Nofar et al. 2019) and compostable (Kalita et al. 2019) thermoplastic polymer (Liu et al. 2019) produced from starch rich vegetable sources such as corn, sugarcane and wheat. With the increasing sensitivity of humans to the environment and the discovery of the new properties of the PLA, research on PLA has accelerated and provided more economic synthesis paths for high molecular weight PLA production. Thus, the use of poly (lactic acid) has started to expand and has started to spread to a wide range from packaging industry to general consumer products (Nofar et al. 2019; Gan and Chow 2018).

The lactide monomer forming the polylactic acid can be produced by carbohydrate fermentation or chemical synthesis. The PLA polymer can be synthesized in methods such as azeotropic dehydrative condensation, direct condensation or lactide polymerization. However, the synthesis, which is frequently used in industry, is carried out by ring opening polymerization mechanism. By this method, high molecular weight PLA is obtained. In recent years new synthesis mechanisms have also been found in commercial life (Castro-Aguirre et al. 2016).

ϵ -caprolactone (Moraczewski 2014) can also be copolymerized with a large number of different monomers (ethylene oxide, styrene, methyl methacrylate, vinyl acetate, etc.) (Sisson, Ekinci, and Lendlein 2013; Sinha et al. 2004). In addition, PCL tends to form a mixture compatible with many different polymers (Guindani et al. 2019; Jang et al. 2018;

Wang et al. 2018). Thanks to these properties, PCL can work alone or in combination with other polymers in tissue engineering studies (Dalgic et al. 2019; Pedram Rad, Mokhtari, and Abbasi 2018).

Poly (ϵ)-caprolactone was synthesized by ring-opening polymerization using hydrophobised silylated starch precursor. Poly (ϵ)-caprolactone side chains consist of 40-45 monomer units and are a function of reagent uptake. Poly (ϵ)-caprolactone copolymer was synthesized by (ϵ)-caprolactone ring-opening polymerization in tin octoate medium (Sinha et al. 2004; Wang et al. 2018).

Depending on the chemical components and molecular structures, block copolymers reveal interesting physicochemical properties which cause many applications (Cama et al. 2017). They can be used as stabilizers, emulsifiers, dispersing agents, elastomeric materials and surfactants, as well as in drug release (de Cassan et al. 2018), cosmetics, and many other industrial applications.

Murphy et al. prepared new materials by blending poly (ϵ -caprolactone) (PCL) and poly (lactic acid) (PLA) mixtures (Murphy et al. 2017). In this respect, synthesis with good properties as block copolymers is required.

In this study, poly (lactic acid-b- ϵ -caprolactone) was synthesized by ring opening polymerization of DBTDL catalyzed ϵ -caprolactone using poly lactic acid. Poly (lactic acid-b- ϵ -caprolactone) block copolymer was synthesized by varying various parameters (amount of polymer, amount of monomer and polymerization time)

MATERIALS AND METHODS

Materials

Lactic acid (80% Sigma-Aldrich product), Tin (II) chloride (SnCl_2) (Sigma-Aldrich product), P-toluene sulfonic acid (Sigma-Aldrich product), Diethyl ether (Sigma-Aldrich product),

ϵ - caprolactone (Sigma-Aldrich product), Toluene (Sigma-Aldrich product) and used as received. Silicone oil is a product of Sigma-Aldrich which is used to heat the material to a certain temperature with the heater in the beaker. Methanol (Technical product) was used as received. Chloroform was EMBOY product. Dibutyl tin was used as received dilaurat lens product.

Methods

Synthesis of Poly (lactic acid) Polymer by Condensation Polymerization

In the study, 50 g of 80% Lactic acid, 1.2 g of SnCl_2 and 1 g of p-toluene sulfonic acid were weighed and placed in a glass flask. When the temperature of a liquid filled beaker was reached to a temperature above 140°C with the heat exchanger, these chemicals were subjected to polymerization with the back cooling and vacuum assembly.

The silicone oil bath was held at 140°C for about 24 hours (the oil filled beaker was surrounded by isocam to prevent temperature loss). The polymer was removed from the flask, added chloroform and stirred for 2 hours with

the aid of a magnet. A portion of the solvent in the flask was evaporated in a rotary evaporator and precipitated with diethyl ether. The polymer was kept in the vacuum oven at 30°C for 1 week. 25.73 g of poly (lactic acid) were obtained in 49.3% yield (Figure 1).

Synthesis of Poly (lactic acid- b- ϵ -caprolactone) Block Copolymers

A quantity of poly (lactic acid) polymer, ϵ -caprolactone monomer, toluene and DBTDL (Dibutyl tin dilaurate) (required catalyst to provide ring opening) was put into a test tube and the tube was sealed. The reaction temperature was adjusted to 95°C and polymerization was carried out. After the polymerization was completed, the polymer was precipitated in methanol and the polymer was withdrawn by precipitation with methanol. To thoroughly remove the methanol, the polymer was allowed to dry well at 30°C in a vacuum oven. The reaction was repeated by changing the test conditions (amount of polymer, amount of monomer and hour)(Figure 2)

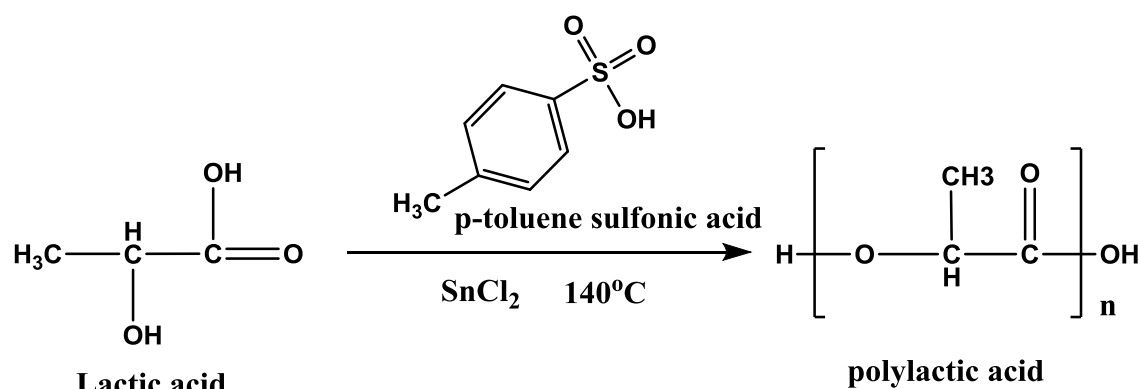


Figure 1. Polymerization of lactic acid

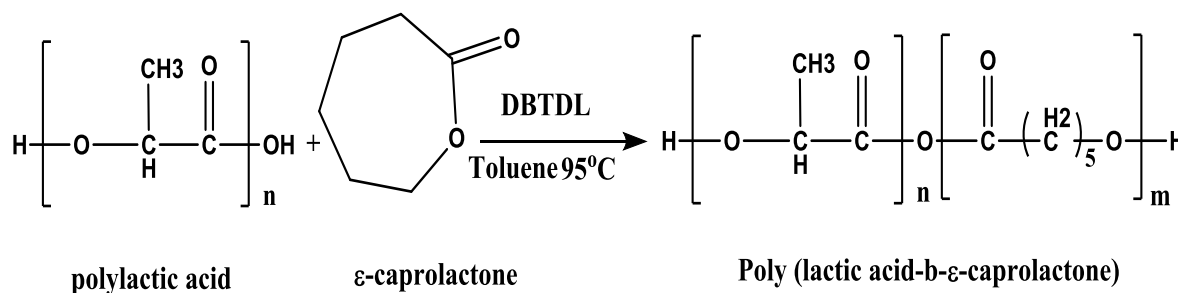


Figure 2. Synthesis reaction of poly (lactic acid-b- ϵ -caprolactone) Block Copolymer

RESULT AND DISCUSSION

Condensation Polymerization of Lactic Acid

Synthesis of Poly (lactic acid) Polymer by Condensation Polymerization

In condensation polymerization, functional monomer groups have proven their success (Mallakpour and Hatami 2017). Polymers with certain molecular weight and low polydispersity indices (PDI) can be given condensation of a wide variety of monomers under mild conditions (Lynd, Meuler, and Hillmyer 2008). In this study, two sets of polymerization of polylactic acid were introduced and the polymerization of ϵ -CL was carried out in two sets. The silicone oil bath was carried out at 140° C as described in the experiment. Synthesis-related reaction conditions and GPC results are given in Table 1.

The amount of PLA and ϵ -CL were fixed and the polymerization time was changed. When the amount of polymer (PLA) is increased and the amount of monomer (ϵ -CL) is kept constant, the amount of polymer (PLA) is kept constant and the amount of monomer (ϵ -CL) is increased or the amount of polymer (PLA) and monomer (ϵ -CL) are kept constant. It was. The heterogeneity index of the obtained block copolymers was found to be between 1.55-3.42. The synthesized PLA was found to be 2.27. The molecular weight of PLA was 1448.9 g / mol and the block copolymer of 1728.9-7471.0 g / mol. The fact that the molecular weight of the obtained block copolymers is higher than the PLA used as initiators indicates the synthesis of block copolymers.

Table 1. Reaction conditions and GPC results of synthesis of polylactic acid

80% Lactic acid (g)	SnCl ₂ (g)	p-toluene sulfonic acid (g)	Yield (%)	\overline{M}_n (g mol ⁻¹)	$\overline{M}_w/\overline{M}_n$
50	1.2	1	49.3	1448.8	2.27

FT-IR (KBr): 3647.05-3511.33 cm⁻¹ OH strain vibration, 2998.79-2879.55 cm⁻¹ Aliphatic C-H strain vibration, 1760.99 cm⁻¹ C = O tensile

vibration, 1292.30-1212.58 cm⁻¹ COO strain vibration peaks are observed. PLA FT-IR graph is given in figure 3.

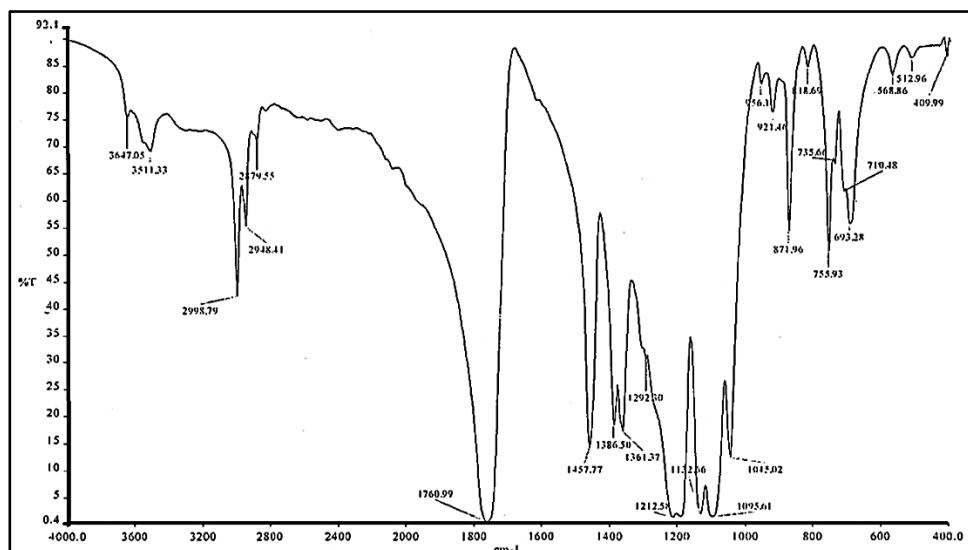


Figure 3. FT-IR spectrum of poly lactic acid (PLA)

$^1\text{H-NMR}$ (CDCl_3): The protons of the $-\text{CH}_3$ group at 1.5 ppm, the protons of the proton groups at 4.3-4.4 ppm, and the proton of the CH

group at 5.1-5.3 ppm are seen. PLA $^1\text{H-NMR}$ graph is given in figure 4.

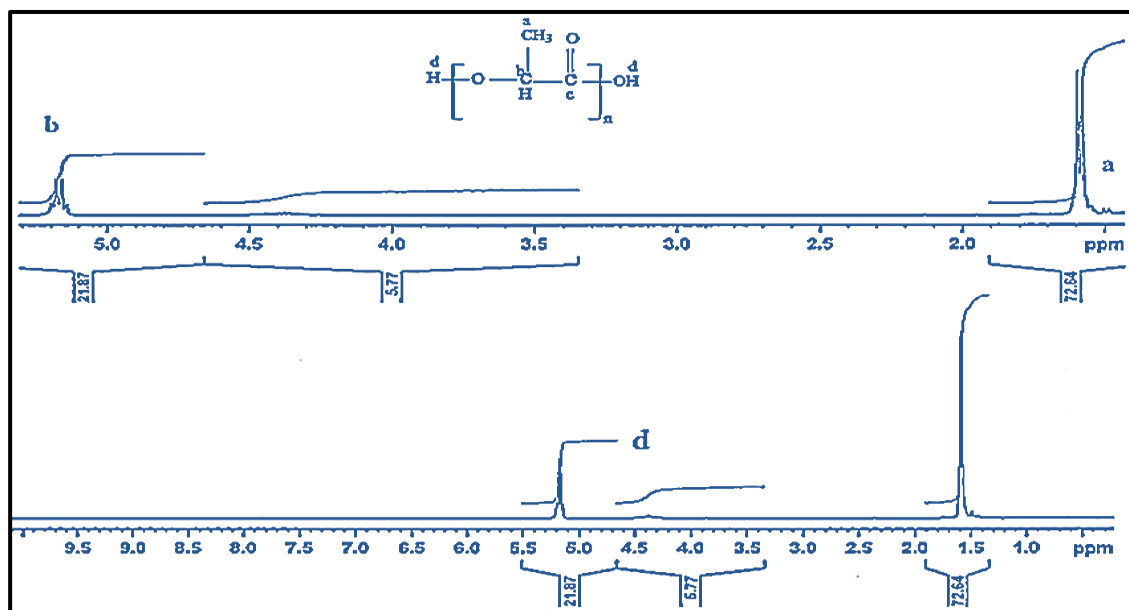


Figure 4. $^1\text{H-NMR}$ spectrum of poly lactic acid (PLA)

$^{13}\text{C-NMR}$ (CDCl_3): At 16.62-16.66 ppm, the carbon atom of the $-\text{CH}_3$ group, the carbon atom of the "CH" group at 69.01 ppm, the peaks

of the carbon atom of the "C = O" group at 169.60 ppm. PLA $^{13}\text{C-NMR}$ graph is given in figure 5.

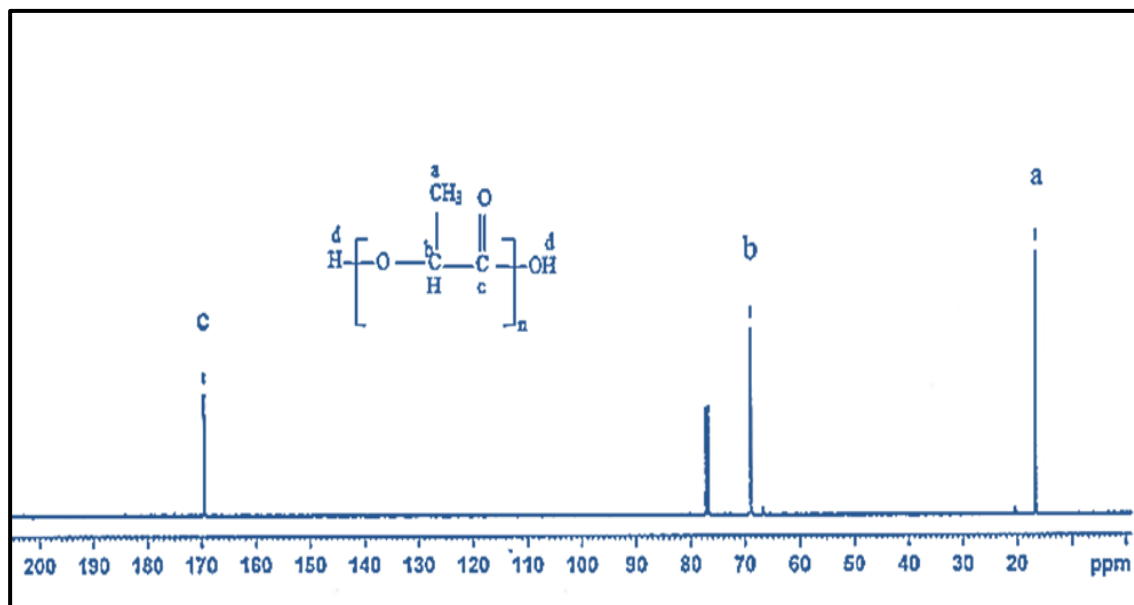


Figure 5. ^{13}C -NMR spectrum of poly lactic acid (PLA)

The reaction conditions and GPC results of the synthesis of poly (lactic acid- b- ϵ -caprolactone) block copolymers are given in

Table 2. Poly (lactic acid-b- ϵ -caprolactone) Graphical drawings were drawn with the OriginPro 9 program.

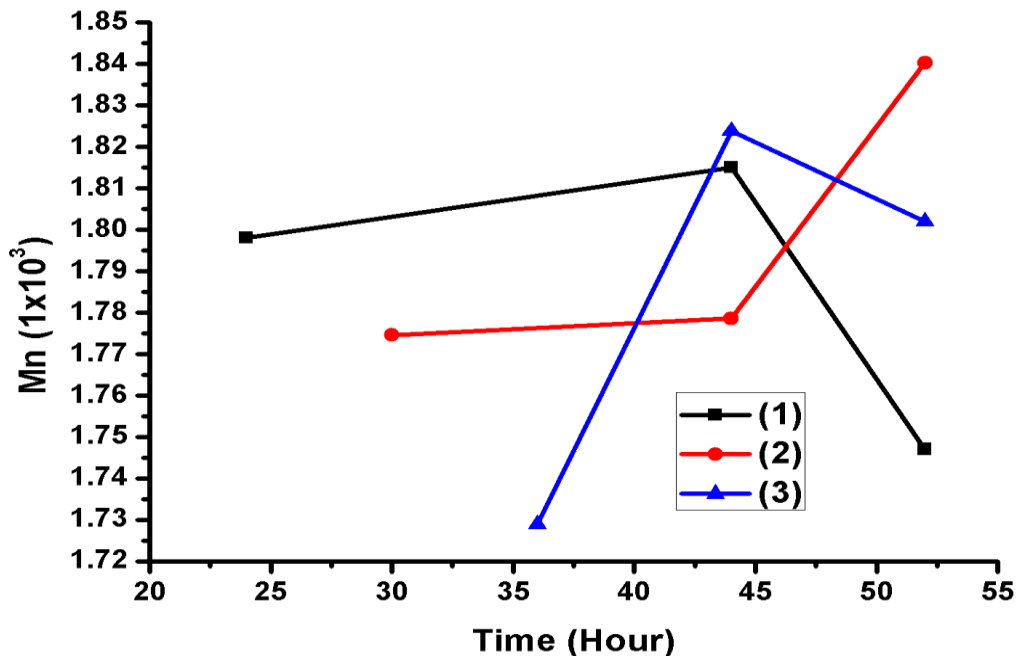
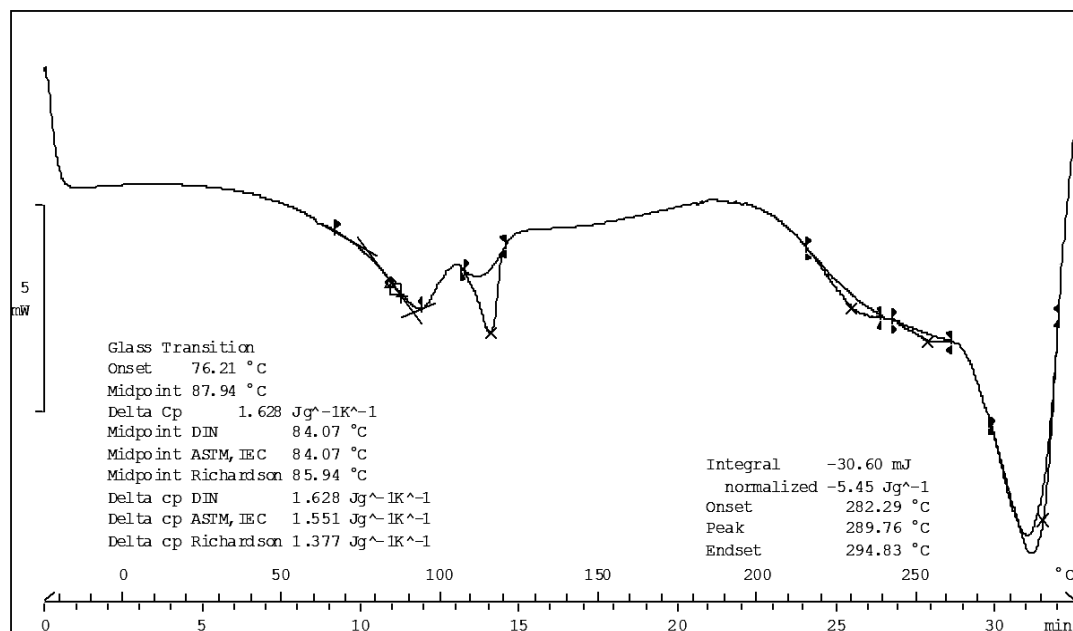


Figure 6. Molecular weight graph of poly (lactic acid-b- ϵ -caprolactone) reaction against time

Table 2. Poly (lactic acid-b- ϵ -caprolactone) Reaction conditions and GPC results of Block Copolymer synthesis

Exp. No.	Exp. Code	PLA (g)	E-CL (g)	Test time (h)	\overline{M}_n (g mol ⁻¹)	M_w/\overline{M}_n	Yield (%)
1	A ₁	0.3038	1.0150	44	1815.7	1.67	52
2	B ₁	0.5018	1.0066	52	7471.0	2.38	54
3	C ₁	0.2540	1.0235	24	1798.4	1.99	67
4	A ₂	0.5006	1.2000	44	1774.6	1.94	56
5	B ₂	0.5025	1.2875	52	1840.3	1.88	61
6	C ₂	0.2505	1.0326	30	1774.6	1.72	73
7	A ₃	0.6023	1.0000	44	1823.9	3.42	59
8	B ₃	0.5014	1.5300	52	1802.0	1.92	70
9	C ₃	0.2502	1.0841	36	1728.9	1.70	76
10	B ₄	0.5021	2.7686	52	1753.1	1.55	45

Temperature = 95°C; Toluene = 2 ml; DBTDL; 1 drop; * precipitator (methanol, ml)

**Figure 7.** DSC diagram of poly lactic acid (PLA)

Differential scanning calorimetry based techniques are important when characterizing polymers (Drzeżdżon et al. 2019; Fitzharris, Rosen, and Shofner 2019). In the DSC spectrum of poly (lactic acid), T_g (glass transition temperature) at 76.21°C and T_d (melting temperature) at 115.65°C were seen in Figure 7.

The DSC spectrum of poly (lactic acid-b- ϵ -caprolactone) showed T_g (glass transition temperature) at 29.04°C and T_d (melting temperature) at 52.16°C in Figure 8. Differential scanning calorimetry (DSC) and glass transition

temperature (T_g) and melting temperature (T_m) of the obtained polymers were determined. The addition of poly (lactic acid) g e ϵ -CL reduced the T_g and T_d values of the block copolymer of poly (lactic acid). The ratio of the glass transition temperature (T_g) and melting temperature (T_m) of the obtained block copolymer to a value between the glass transition temperature (T_g) and the melting temperature (T_m) of the poly (lactic acid) and ϵ -CL were determined. it is confirmed.

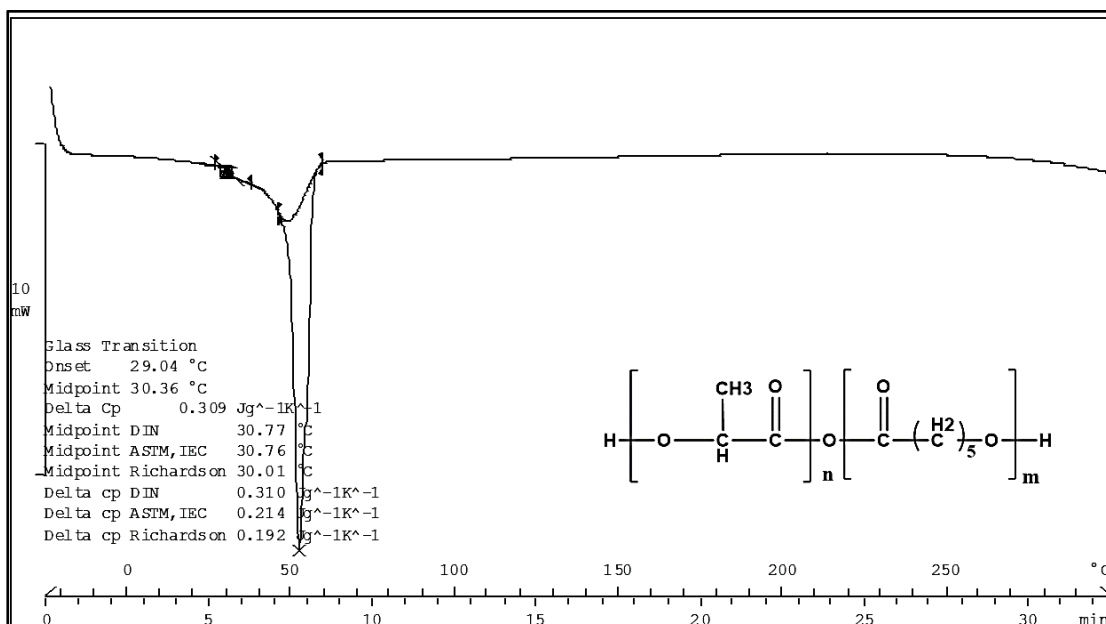


Figure 8. DSC spectrum of poly (lactic acid- b- ϵ -caprolactone) block copolymer

FT-IR (KBr): 3630.25 - 3551.82 cm^{-1} OH tensile vibration, 2946.97 - 2867.02 cm^{-1} Aliphatic C-H tensile vibration, 1725.52 cm^{-1} C = O stress vibration, 1243.62 - 1295.77 cm^{-1} COO stress vibration peaks are observed.

3439.03 cm^{-1} C = O overtone band (2x1725.52). The FT-IR graph of the poly (lactic acid-b- ϵ -caprolactone) block copolymer is given in figure 9.

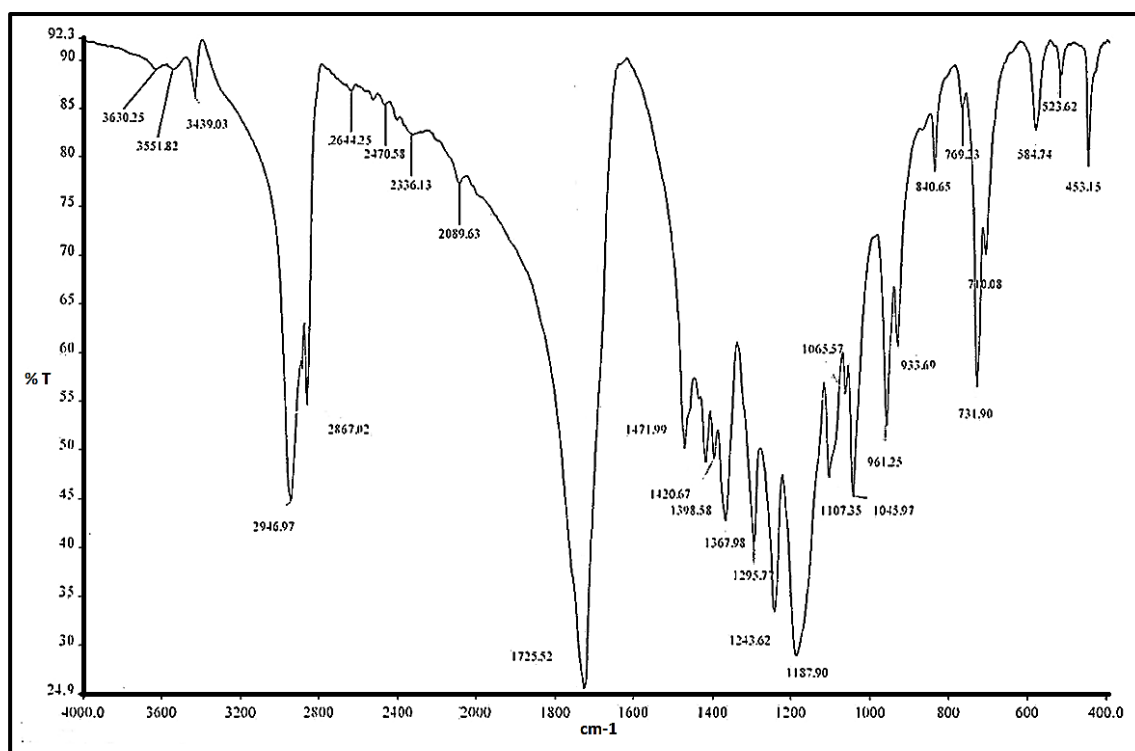


Figure 9. FT-IR spectrum of poly (lactic acid- b- ϵ -caprolactone) block copolymer (B4)

$^1\text{H-NMR}$ (CDCl_3): protons of (a) at 5.1446-5.1619 ppm, protons of (b) at 4.0357-4.0655 ppm, protons of (i) at 2.2774-2.3139 ppm, 1.5588-1.6323 ppm The protons of (k) show

protons of (c) at 1.3590-1.4090 ppm. The $^1\text{H-NMR}$ graph of the poly (lactic acid-b- ϵ -caprolactone) block copolymer is given in figure 10.

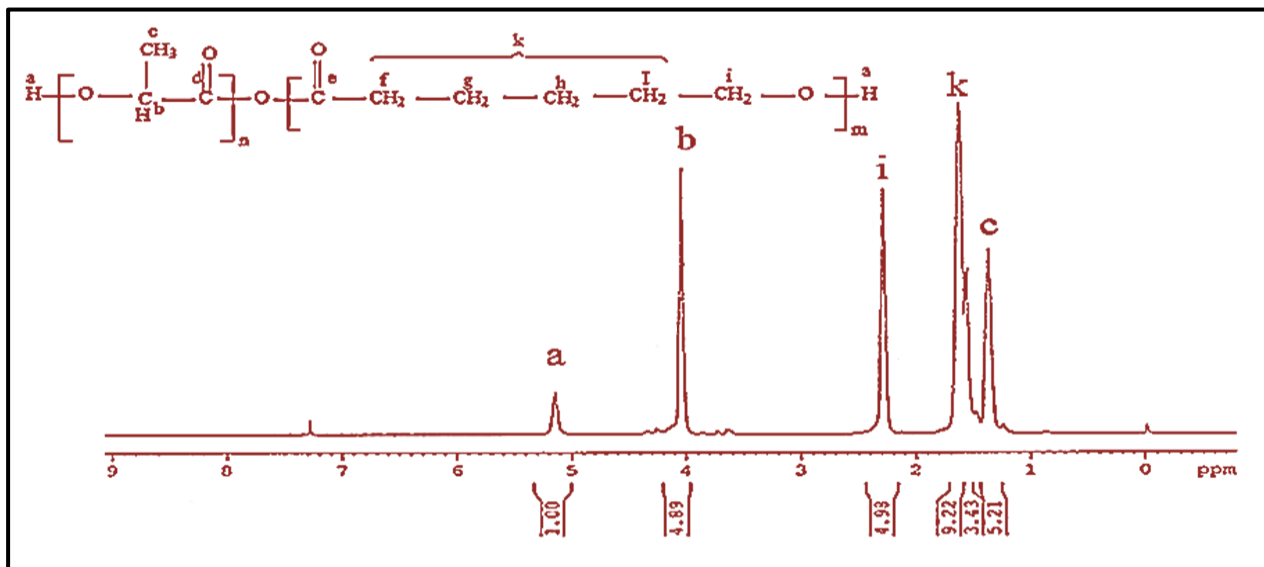


Figure 10. $^1\text{H-NMR}$ spectrum of poly (lactic acid-b- ϵ -caprolactone) block copolymer

$^{13}\text{C-NMR}$ (CDCl_3 , δ , ppm): 173.52 (carbon of e'), 169.56 (carbon of d), 68.98 (carbon of b), 64.11 (carbon of i), 34.09 (carbon of f), 28.32 (carbon of g), 25.50 (carbon of I), 24.55 (carbon

of h), 16.61 (carbon of c). The $^{13}\text{C-NMR}$ graph of the poly (lactic acid-b- ϵ -caprolactone) block copolymer is given in figure 11.

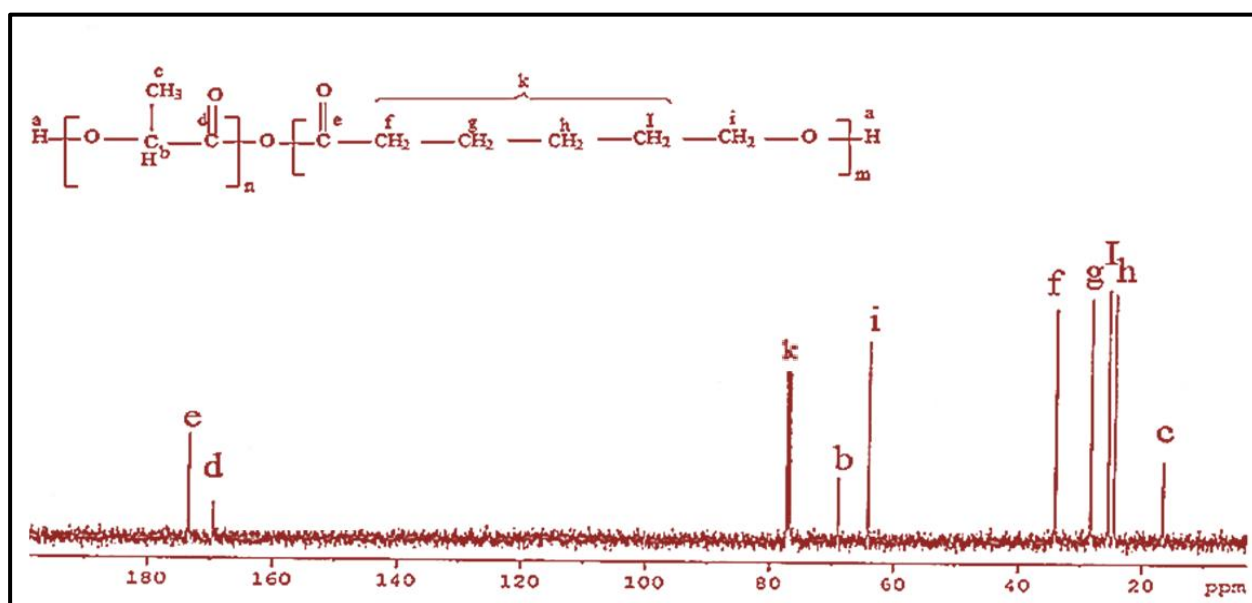


Figure 11. $^{13}\text{C-NMR}$ spectrum of poly (lactic acid- b- ϵ -caprolactone) block copolymer

CONCLUSION

In this study, the synthesis of poly (lactic acid-b- ϵ -caprolactone) block copolymers was carried out by ring opening polymerization of ϵ -caprolactone of poly lactic acid. Poly lactic acid (PLA) was synthesized by condensation polymerization of lactic acid. Poly (lactic acid-b- ϵ -caprolactone) block copolymer was synthesized by changing various parameters (amount of polymer, amount of monomer and polymerization time).

The use of biomaterials of bio-origin, biocompatible, and biocompatible, plays an active role in many areas of the world of technology. Particularly, poly (lactic acid) (PLA), which is in the part of biopolymers, has different degradation processes and it increases the usage areas of this polymer, block copolymers and composites. With the new block properties of poly (lactic acid- b- ϵ -caprolactone) block copolymers, medical, environmental, packaging and textiles will increase their importance in many areas.

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