

Synthesis, characterization and thermal properties of the nano four arms poly(pentaerythritollactide-*b*-*N,N*-dimethylaminoethyl methacrylate) derivatives

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ABSTRACT

The nano four arms poly(lactide-*b*-*N,N*-dimethylaminoethylmethacrylate) were prepared by pentaerythritol-lactide atom transfer radical polymerization initiators having different repeating units (10, 25, 50 and 100) of L-lactide with the same amount of *N,N*-dimethylaminoethyl methacrylate by atom transfer radical polymerization reaction. The copolymers were characterized FT-IR, ¹H NMR, ¹³C NMR and Gel permeation chromatography. These characterization methods confirmed the structures of prepared copolymers. Scanning electron microscopy, on the other hand, revealed that the presence of a nanostructure in the prepared copolymers attributed to the lactide fibers. Then, the thermal study was carried out on the copolymers the results have proven to increase the thermal stability of the copolymers with the increasing chain length of the lactide.

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1. Introduction

The first report in atom transfer radical polymerization (ATRP), by Kato *et al.* employed RuCl₂(PPh₃) as a catalyst system in the polymerization of methyl methacrylate (MMA) initiated by CCl₄ [1]. The second system reported by Matyjaszewski *et al.* is the polymerization of styrene using CuCl/2,2'-bipyridyl (bpy) as catalyst and 1-phenylethyl chloride as an initiator [2]. Since then, ATRP of styrene, acrylates, methacrylates, and acrylonitrile was carried out using various transition metal complexes, such as nickel, iron, palladium, and rhodium. Compared to other controlled radical polymerization methods, ATRP is very versatile [3-6].

Vivek and Dhamodharan [7] synthesized polystyrene-graft-poly(*N,N*-dimethyl-2-aminoethyl methacrylate) via ambient temperature ATRP from polystyrene macro-initiator with pendant bromo initiating groups. A cationic star polymer, poly(2-dimethylamino)ethyl methacrylate (PDMAEMA), was prepared via ATRP by Zheng *et al.* [8], they are used brominated calix[4]resorcinarene as an initiator. Hydrophobic moieties, methyl methacrylate (MMA) and butyl acrylate (BA), were further incorporated via one-pot method. Well-defined eight-armed star block copolymers bearing hydrophilic blocks

inside and hydrophobic blocks outside were synthesized. ATRP can be carried out in a wide range of polymerization temperatures with controlled molecular weight and narrow (Molecular Weight Distribution, MWD), and it is not very sensitive to the presence of oxygen and other inhibitors [9].

In this work, we reported to the synthesis of nano four arm poly(pentaerythritollactide-*b*-*N,N*-dimethylaminoethylmethacrylate) via ATRP and evaluating some of their thermal properties.

2. Experimental

2.1. Materials

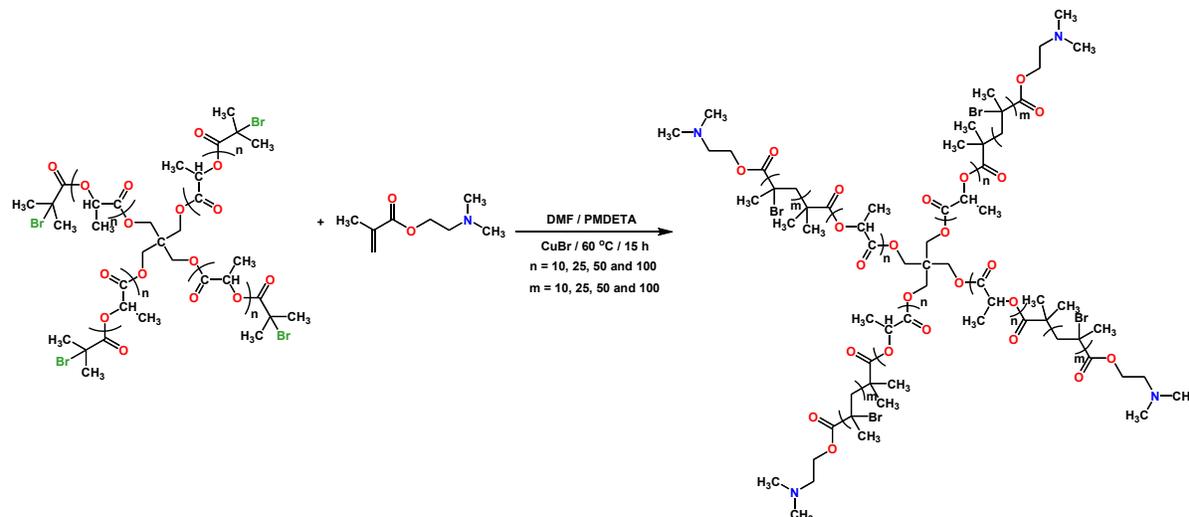
N,N-Dimethylaminoethyl methacrylate, copper(I) bromide, *N,N,N',N',N''*-pentamethyldiethylenetriamine, magnesium sulfate, CDCl₃ and dimethyl sulfoxide-*d*₆ were supplied by Sigma-Aldrich, dichloromethane (DCM) (≥ 99.5%), dimethyl formamide (DMF) (≥ 99.8%) and triethyl amine (≥ 99.5 %) were supplied by MACRON Company, Michigan, USA.

2.2. Instrumentation

Nicolet IR-42, Mid-IR spectrometer was used to record FT-IR spectra. Agilent DDR2 500 MHz NMR spectrometer was used

Table 1. Amount of reactants used in the preparation of PL₂₅Br-D_m, PL₅₀Br-D_m and PL₁₀₀Br-D_m copolymers.

Copolymer Code	Amount of PL _n Br		Weight of DMAEMA		Weight of CuBr (g)	Volume of PMDETA (μL)	Yield (%)	Physical state
	Weight (g)	No. of moles	Weight (g)	No. of moles				
PL ₂₅ BrD _m	0.4	0.00005	0.8	0.005	0.05	20	67	Solid
PL ₅₀ BrD _m	0.4	0.00003	0.8	0.005	0.05	20	71	Solid
PL ₁₀₀ BrD _m	0.4	0.00001	0.8	0.005	0.05	20	69	Solid

**Figure 1.** Synthesis of prepared the copolymers PL₁₀BrD_m, PL₂₅BrD_m, PL₅₀BrD_m and PL₁₀₀BrD_m (m ≈ 10, 25, 50 and 100).

to record ¹H NMR and ¹³C NMR spectra. Copolymers molecular weights and molecular weight distributions (Mw/Mn) were determined using a Waters 1515 Gel Permeation Chromatography (GPC) equipped with a refractive-index detector (Waters 2412), DMF was used as the eluent at a flow rate of 1.0 mL/min and calibrated with poly(methyl methacrylate) standard. The prepared copolymers were examined under Scanning electron microscope type JEOL 7500F supplied by JEOL Company, USA. Computer controlled thermal analysis Instrumentals, TGA-Q500 V20.10 was used to study the thermal stability of the prepared polymers.

2.3. Preparation of pentaerythritol-lactide tetrakis (2-bromoisobutyrate) (Tetrafunctional initiator) (PL_nBr)

Pentaerythritol-lactideisobutyryl bromide ATRP initiators having different repeating units (10, 25, 50 and 100) of L-Lactide have been prepared according to previous works [10] and characterized by FT-IR and NMR spectroscopy.

Copolymer PL₁₀Br: Color: White. Yield: 70%. FT-IR (KBr, ν, cm⁻¹): 2991 (C-H), 1741 (C=O), 1195 (C-O), 649 (C-Br). ¹H NMR (500 MHz, CDCl₃, δ, ppm): 5.3 (O-CH₂), 5.2 (O-CH groups of repeating unit of L-lactide), 1.6 (CH₃ groups of repeating unit of L-lactide), 1.95 (CH₃-C-Br). ¹³C NMR (500 MHz, CDCl₃, δ, ppm): 170 (C=O of repeating unit of L-lactide), 166 (C=O of isobutyryl bromide), 69 (CH₃ group in repeating unit of L-lactide segments), 67 (carbon atom in methine group of pentaerythritol), 55 (C-Br), 41 (center carbon atom of pentaerythritol), 30 (CH₃ of end chains), 17 (O-CH-CH₃ group in repeating unit of L-lactide segments).

Copolymer PL₂₅Br: Color: White. Yield: 73%. FT-IR (KBr, ν, cm⁻¹): 2996 (C-H), 1746 (C=O), 1197 (C-O), 647 (C-Br). ¹H NMR (500 MHz, CDCl₃, δ, ppm): 5.3 (O-CH₂), 5.15 (O-CH groups of repeating unit of L-lactide), 1.97 (CH₃-C-Br), 1.55 (CH₃ groups of repeating unit of L-lactide).

Copolymer PL₅₀Br: Color: White. Yield: 76%. FT-IR (KBr, ν, cm⁻¹): 2998 (C-H), 1751 (C=O), 1198 (C-O), 641 (C-Br). ¹H NMR (500 MHz, CDCl₃, δ, ppm): 5.3 (O-CH₂), 5.17 (O-CH groups

of repeating unit of L-lactide), 1.96 (CH₃-C-Br), 1.57 (CH₃ groups of repeating unit of L-lactide).

Copolymer PL₁₀₀Br: Color: White. Yield: 78%. FT-IR (KBr, ν, cm⁻¹): 3011 (C-H), 1745 (C=O), 1191 (C-O), 635 (C-Br). ¹H NMR (500 MHz, CDCl₃, δ, ppm): 5.3 (O-CH₂), 5.16 (O-CH groups of repeating unit of L-lactide), 1.96 (CH₃-C-Br), 1.58 (CH₃ groups of repeating unit of L-lactide).

2.4. Synthesis of four arms poly(pentaerythriol-lactide-*b*-*N,N*-dimethylaminoethylmethacrylate) (PL₁₀BrD_m)

Pentaerythritol-lactideisobutyryl bromide (PL₁₀Br) (0.4 g, 0.11 mmol), *N,N*-dimethylaminoethyl methacrylate (DMAEMA) (0.8 g, 5.0 mmol), copper(I) bromide (0.05 g, 0.4 mmol) and *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA) (20 μL) were dissolved in 15 mL dimethyl formamide (DMF) at 60 °C. After stirring for 1 h under nitrogen atmosphere, the reaction was stirred for a further 14 h at 60 °C. Afterwards, the product was added slowly to 500 mL cold diethyl ether to precipitate the copolymer which was then filtered on a Buchner funnel and washed with diethyl ether and then the filtrate was dissolved in DMF (15 mL). The copolymer was recovered through the column chromatography filled with silica gel. The solvent DMF was removed by rotary evaporator and the copolymer was dried in vacuum oven at 25 °C for 24 hours, (Solid, yield: 65%).

The same procedure was repeated to prepare the copolymers PL₂₅BrD_m, PL₅₀BrD_m and PL₁₀₀BrD_m. Table 1 shows the quantities of reactants used in the preparation of these copolymers and Figure 1 exhibits the chemical equations of the preparation method.

Copolymer PL₁₀BrD_m: Color: Light green. Yield: 65%. FT-IR (KBr, ν, cm⁻¹): 1741 (C=O), 1133 (N-C). ¹H NMR (500 MHz, DMSO-*d*₆, δ, ppm): 5.19 (O-CH groups in branched part of DMAEMA), 4.2 (O-CH₂), 4.1 (O-CH₂), 3.4 (N-CH₂ groups in branched part of DMAEMA), 2.9 (N-CH₃ groups in branched part of DMAEMA), 2.7 (CH₂ groups of repeating unit of DMAEMA), 2.3 (CH₃ groups of repeating unit of DMAEMA), 1.45 (O-CH-CH₃), 1.4 (CH₃).

Table 2. GPC results for prepared copolymers.

No	Copolymer	Value of m	M _n (Daltons)	M _w (Daltons)	Polydispersity index (PDI)
1	PL ₁₀ BrD _m	13	11725	12651	1.08
2	PL ₂₅ BrD _m	28	25475	27339	1.07
3	PL ₅₀ BrD _m	57	50947	58105	1.14
4	PL ₁₀₀ BrD _m	115	101795	110018	1.08

Table 3. TGA data for prepared copolymers PL₁₀BrD_m, PL₂₅BrD_m, PL₅₀BrD_m and PL₁₀₀BrD_m.

Copolymer	First decomposition step			Activation energy	Weight loss (%)
	T _i (°C)	T _f (°C)	Rate of decomposition		
PL ₁₀ BrD _m	145.82	216.80	0.38	0.015	27.77
PL ₂₅ BrD _m	158.33	241.70	0.37	0.020	24.95
PL ₅₀ BrD _m	173.92	246.26	0.32	0.023	32.71
PL ₁₀₀ BrD _m	190.03	253.74	0.31	0.044	20.97
Copolymer	Second decomposition step			Residue (%)	T ₅₀ (°C)
	T _i (°C)	T _f (°C)	Rate of decomposition		
PL ₁₀ BrD _m	289.74	356.11	0.67	0.016	18.39
PL ₂₅ BrD _m	295.37	375.75	0.65	0.018	17.21
PL ₅₀ BrD _m	291.71	388.38	0.63	0.021	19.09
PL ₁₀₀ BrD _m	306.03	384.04	0.51	0.033	14.86

¹³C NMR (500 MHz, DMSO-*d*₆, δ, ppm): 178 (C=O), 174 (C=O), 170 (C=O), 69 (CH-O), 63 (CH₂-O), 59 (CH₂-O), 56 (C-quat.), 50 (CH₂), 47 (CH₃-N), 44 (C-quat.), 32 (CH₃), 20 (CH₃), 17 (CH₃).

Copolymer PL₂₅BrD_m: Color: Light green. Yield: 67%. FT-IR (KBr, ν, cm⁻¹): 1746 (C=O), 1134 (N-C). ¹H NMR (500 MHz, DMSO-*d*₆, δ, ppm): 5.2 (O-CH groups in branched part of DMAEMA), 4.2 (O-CH₂), 4 (O-CH₂), 3.35 (N-CH₂ groups in branched part of DMAEMA), 2.88 (N-CH₃ groups in branched part of DMAEMA), 2.71 (CH₂ groups of repeating unit of DMAEMA), 2.25 (CH₃ groups of repeating unit of DMAEMA), 1.45 (O-CH-CH₃), 1.41 (CH₃). ¹³C NMR (500 MHz, DMSO-*d*₆, δ, ppm): 177 (C=O), 174 (C=O), 170 (C=O), 70 (CH-O), 62 (CH₂-O), 60 (CH₂-O), 58 (C-quat.), 50 (CH₂), 48 (CH₃-N), 44 (C-quat.), 30 (CH₃), 22 (CH₃), 17 (CH₃).

Copolymer PL₅₀BrD_m: Color: Light green. Yield: 71%. FT-IR (KBr, ν, cm⁻¹): 1751 (C=O), 1136 (N-C). ¹H NMR (500 MHz, DMSO-*d*₆, δ, ppm): 5.2 (O-CH groups in branched part of DMAEMA), 4.19 (O-CH₂), 4.0 (O-CH₂), 3.36 (N-CH₂ groups in branched part of DMAEMA), 2.86 (N-CH₃ groups in branched part of DMAEMA), 2.71 (CH₂ groups of repeating unit of DMAEMA), 2.24 (CH₃ groups of repeating unit of DMAEMA), 1.44 (O-CH-CH₃), 1.41 (CH₃). ¹³C NMR (500 MHz, DMSO-*d*₆, δ, ppm): 176 (C=O), 174 (C=O), 170 (C=O), 69 (CH-O), 64 (CH₂-O), 62 (CH₂-O), 58 (C-quat.), 54 (CH₂), 50 (CH₃-N), 44 (C-quat.), 32 (CH₃), 20 (CH₃), 16 (CH₃).

Copolymer PL₁₀₀BrD_m: Color: Light green. Yield: 69%. FT-IR (KBr, ν, cm⁻¹): 1745 (C=O), 1133 (N-C). ¹H NMR (500 MHz, DMSO-*d*₆, δ, ppm): 5.19 (O-CH groups in branched part of DMAEMA), 4.19 (O-CH₂), 4.1 (O-CH₂), 3.34 (N-CH₂ groups in branched part of DMAEMA), 2.86 (N-CH₃ groups in branched part of DMAEMA), 2.72 (CH₂ groups of repeating unit of DMAEMA), 2.26 (CH₃ groups of repeating unit of DMAEMA), 1.45 (O-CH-CH₃), 1.41 (CH₃). ¹³C NMR (500 MHz, DMSO-*d*₆, δ, ppm): 175 (C=O), 174 (C=O), 169 (C=O), 69 (CH-O), 64 (CH₂-O), 62 (CH₂-O), 59 (C-quat.), 51 (CH₂), 48 (CH₃-N), 44 (C-quat.), 31 (CH₃), 20 (CH₃), 17 (CH₃).

3. Results and discussion

3.1. Characterization of new copolymers by FT-IR

The prepared solid copolymers were characterized as KBr discs. The FT-IR spectra of copolymers PL₁₀BrD_m, PL₂₅BrD_m, PL₅₀BrD_m and PL₁₀₀BrD_m showed characteristic intense absorption bands due to the ν(N-C) groups at 1133, 1134, 1136 and 1133 cm⁻¹, respectively, and the ν(C=O) groups at 1741, 1746, 1751 and 1745 cm⁻¹, respectively.

3.2. Characterization of new copolymer by NMR

¹H NMR and ¹³C NMR of PL₁₀BrD_m, PL₂₅BrD_m, PL₅₀BrD_m and PL₁₀₀BrD_m copolymers was recorded by using dimethyl

sulfoxide-*d*₆ as solvent. The signals belong to the O-CH-CO, O-CH₂, O-CH-CH₃ and CH₃ groups in repeating unit of L-lactide segments of the synthesized all copolymers were observed approximately at δ 5.2, 4.0 1.5 and 1.4 ppm in the ¹H NMR spectra, respectively. Also, the signals belong to the CH₂ and CH₃ groups in repeating unit of DMAEMA and O-CH₂, N-CH₂ N-CH₃ groups in branched part of DMAEMA were showed around at δ 2.7, 2.3, 4.1, 3.4 and 2.9 ppm, respectively. In the ¹³C NMR spectra, the signals belong to the C=O group of DMAEMA segments of the synthesized all copolymers were observed approximately at δ 175 ppm. Also, the signals belong to the CH₂ and CH₃ groups in repeating unit of DMAEMA and O-CH₂, N-CH₂ N-CH₃ groups in branched part of DMAEMA were showed around at δ 50, 59, 62, 62 and 46 ppm, respectively.

3.3. Copolymers molecular weight and polydispersity index

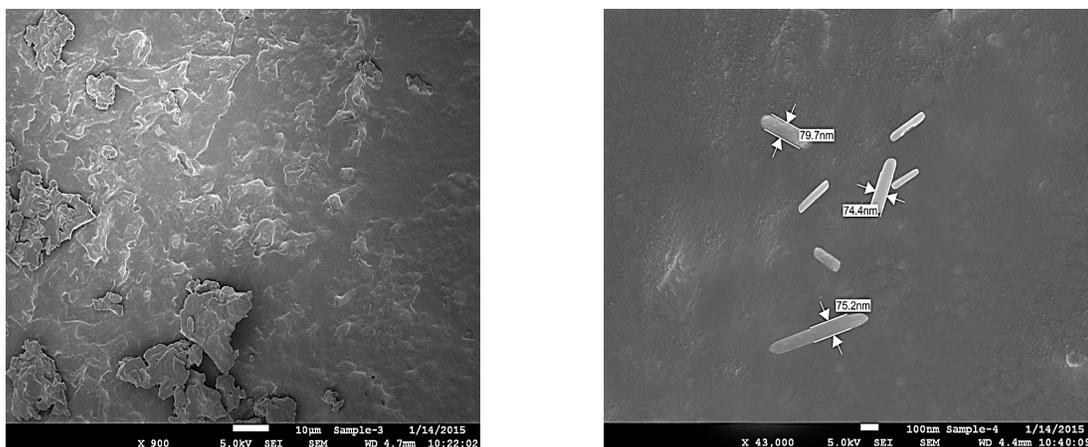
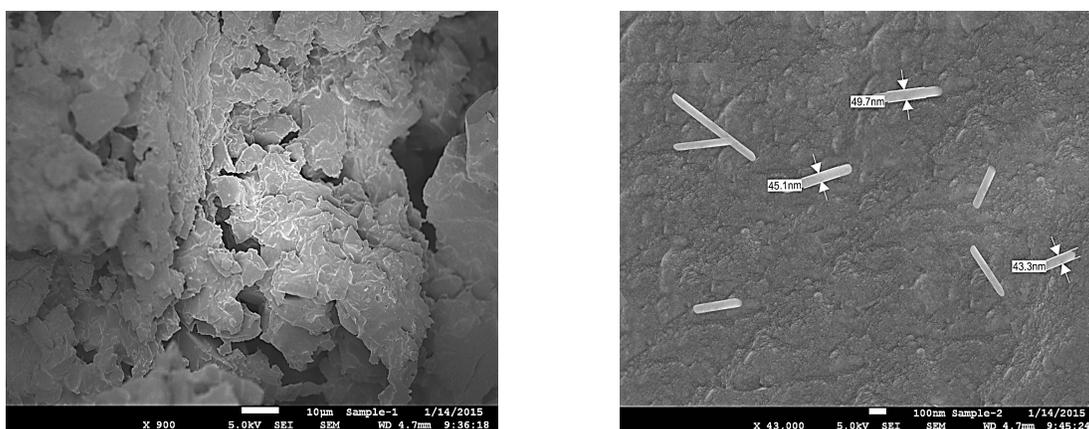
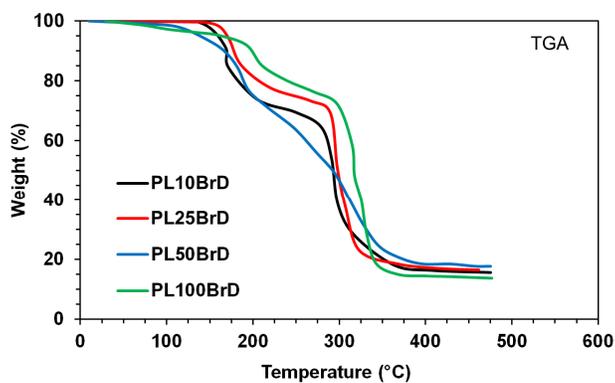
The molecular weight and the polydispersity index (M_w/M_n) were determined by GPC for all prepared copolymers and Table 2 shows the results. The results of GPC showed that the prepared copolymers had a polydispersity index (PDI) close to unity. This implies that the correctness of the suggested structure for the prepared copolymers.

3.4. Scanning electron microscopy (SEM)

All the spectroscopic examinations of the prepared copolymers, FT-IR, ¹H NMR and ¹³C NMR proved the suggested structure for the prepared copolymers and promoted this matter with greater accuracy results of GPC as they are shown a significant matching to the molecular weight calculated theoretically and result the awesome polydispersity index (PDI) is close to one. The examination of the morphology and the nanoparticles geometry of the prepared copolymers was performed by using SEM at different amplifications (10 μm and 100 nm). Figures 2 and 3 are show the SEM micrographs of examined PL₂₅BrD_m and PL₁₀₀BrD_m copolymers. The images obtained from Scanning electronic microscopy revealed the existence of nano-structures in the prepared copolymers due to the presence of the lactide array to give nanofiber within the final compositions.

3.5. Thermogravimetric analysis (TGA)

Thermal stability of the prepared copolymers was studied and Figure 4 shows the resulted thermograms. Table 3 shows some thermal functions resulted from the thermal analysis, namely initiation and final decomposition temperatures T_i and T_f, rate of decomposition, the activation energy of the decomposition, temperature of 50% weight loss (T₅₀), and char content for first and second decomposition step.

Figure 2. SEM image of PL₂₅BrD_m.Figure 3. SEM image of PL₁₀₀BrD_m.Figure 4. Thermogram of PL₁₀BrD_m, PL₂₅BrD_m, PL₅₀BrD_m and PL₁₀₀BrD_m copolymers.

Thermal gravimetric results indicates that the initial decomposition temperature (T_i) ranging between 145 and 190 °C for first decomposition and between 289-306 °C for second decomposition. Table 3 indicates that the initial decomposition temperature for prepared polymers were increased with increasing of repeating units of lactide and the rate of decomposition were decreased with increasing of repeating units, this is an expected result because with increasing molecular weight of the copolymers will increase the thermal stability.

4. Conclusions

A series of block copolymers are obtained by reaction of pentaerythritol-lactide and dimethylamino ethyl methacrylate by atom transfer radical polymerization. Spectroscopic examination of the preparedness copolymers by FT-IR, ¹H NMR and ¹³C NMR proved the suggested structure for the prepared copolymers, also GPC results revealed that all the preparations copolymers are of nearly monodispers polymer with very narrow distributions accompanied by nano

structures were obtained as shown by SEM micrographs due to the presence of lactide polymer chains. The thermal gravimetric results showed that the initial and final decomposition temperatures for preparing polymers were increased with the increasing of repeating units of lactide whereas the rate of decompositions decreased with the increasing of repeating units.

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