MATERIALE PLASTICE
https://revmaterialeplastice.ro
https://doi.org/10.37358/Mat.Plast.1964

Synthesis and Characterization of Novel Nano Six-arms of (polylactide-dipentaerythritol)-block-N-hydroxyethyl Acrylamide and N,N-dimethylamino Ethyl Methacrylate Biocopolymers by Atom Transfer Radical Polymerization

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***Abstract**: Novel block biocopolymers were made by copolymerizing the prepared polylactide-dipenta-erythritol macromonomer with two different monomers, N-hydroxyethyl acrylamide (HEAA) and N,N-dimethylamino ethyl methacrylate (DMAEMA), with an activator generated by atom transfer radical polymerization (ATRP), to have a different duplicating unit of 10, 25, 50, and 100. ATRP employs a copper(I) bromide (CuBr) catalyst system with N, N, N′, N″, N″-pentamethyl diethylenetriamine (PMDETA). Different spectroscopic and analytical methods used for characterization of the prepared biocopolymers, such as FT-IR, 1H NMR, 13C NMR, and GPC, showed that they had narrow dispersity with controllable molecular weight and were accompanied by nanostructures as examined by SEM technique on all biocopolymers, confirming the correctness of the expected structures of biocopolymers. The shape and size of the produced polymeric nanoparticles were determined using a scanning electron microscope (SEM), and they were developed using the Image-J application.*

***Keywords:** ATRP, dipentaerythritol, N, N-dimethylamino ethyl methacrylate, block biocopolymers, six-arms, N-hydroxyethyl acrylamide*

1.Introduction

ATRP refers to the metal-catalyzed radical addition to alkenes, also known as the Kharasch reaction or the atom transfer radical addition (ATRA) reaction, in chemical synthesis [1]. The application of ATRA in vinyl polymerization was explored using soluble ruthenium and copper halide-based catalysts [2]. A polymer with a narrow molecular weight distribution could be synthesized. In 1995 [3], atom transfer radical polymerization was developed as an extension of transition metal-catalyzed. Catalytic systems for the atom transfer radical addition reaction (ATRA) were used to construct it, and this is an effective method for forming carbon-carbon bonds between organic halides and alkenes [4]. In addition to its ability to produce a wide range of polymers with controlled molecular weight and narrow molecular weight distribution (MWD), the ATRP also excels at a wide range of polymerization temperatures and is impervious to oxygen and other inhibitors [5-10].

Multiple (meth) acrylamides were polymerized utilizing model R-haloamide-based initiators to form well-defined block copolymers [11]. In addition, chloropropionamides were used as an initiator in the polymerization of N-isopropylacrylamide monomers, resulting in a polymer with a low polydispersity index that was used to evaluate the effect of functionalized end groups on the thermal characteristics of the polymer [12].

Polystyrene macroinitiator with pendant Bromo initiating groups was used as a catalyst to carry out ATRP at room temperature [13]. These graft copolymers generate a pseudo-gel in an aqueous solution when the *p*H is acidic, which increases the swelling capacity of the polymer. These graft copolymers generate a pseudo-gel in an aqueous solution when the *p*H is acidic, which increases the swelling capacity of the polymer. This occurs because of the amino group protonation's conformational shift. The *p*H and temperature have an impact on the edema. There is some evidence to suggest that polymers can remove dyes from wastewater because of their ability to absorb various textile hues. Because of their

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capacity to absorb diverse textile colors, there is some evidence that polymers can remove dyes from wastewater.

A novel Y-shaped block copolymer of poly(ethylene glycol) and poly(N-isopropylacrylamide), was successfully synthesized using a difunctional macroinitiator [14].They were prepared by esterification of 2,2-dichloroacetyl chloride with poly (ethylene glycol) monomethyl ether (PEG). The copolymers were produced during the ATRP of N-isopropylacrylamide (NIPAM) at 30 ^{o}C with a CuCl/Me6TREN catalyst system and a DMF/H2O (v/v = 3:1) mixture as a solvent. These block copolymers show controllable molecular weights and narrow molecular weight distributions (PDI < 1.15).

The ATRP copolymerization process of methyl methacrylate (MMA) was also investigated to produce a series of well-controlled copolymers of 6-hydroxyhexanoic acid 2-(2-methacryloyloxy) ethyl ester, also known as caprolactone-2-(methacryloyloxy) ethyl ester (CLMA) [15]. The results showed that polymers with low polydispersity indexes (Mw/Mn = 1.34, 1.36, 1.43, and 1.41 for 25%, 50%, 75, and 100% mol percent CLMA, respectively) could be formed when the reaction was carried out with a higher initial monomer-to-initiator ratio (800:1).

In our previous work [16,17], nano four arms, poly(Lactide-b-N-hydroxyethyl acrylamide), were prepared by having different repeating units (10, 25, 50, and 100) from L-lactide with N-hydroxy ethyl acrylamide and N,N-Dimethylamino ethyl methacrylate. The prepared copolymers were found to have a nanostructure due to the lactide fibers as examined by a scanning electron microscope (SEM).

In 2020 [18], we reported on the synthesis of nanostar polymers of L-lactide with dipentaerythritol (D-PLn) having six arms of varied poly(L-lactide), (n = 10, 25, 50, and 100). The SEM micrographs revealed that the polymer nanoparticles are less than 100 nm in diameter. The simplicity of the reaction conditions, the ready availability of the catalyst, and the exquisite control over the polymerization were demonstrated, and in turn, this encouraged us to continue this work by copolymerizing this macro-monomer with N-hydroxyethyl acrylamide (HEAA) and N,N-dimethylamino ethyl methacrylate (DMAEMA).

2.Materials and methods

Materials

As previously mentioned in our recent work [18], dipentaerythritol-lactide biopolymers (D-PLLAn) were synthesized. Sigma-Aldrich Co. provided us with dimethylformamide (DMF, Assay 99.8 %), triethylamine (TEA, Assay 99.9 %), and dichloromethane (DCM) (Assay 99.5 %), 2-bromoisobutyryl bromide (BIBB, Assay 98%) and N-hydroxyethyl acrylamide (HEAA, Assay 97 %), and N,N-dimethyl-amino ethyl methacrylate (DMAEMA, Assay 97 %).

Instruments

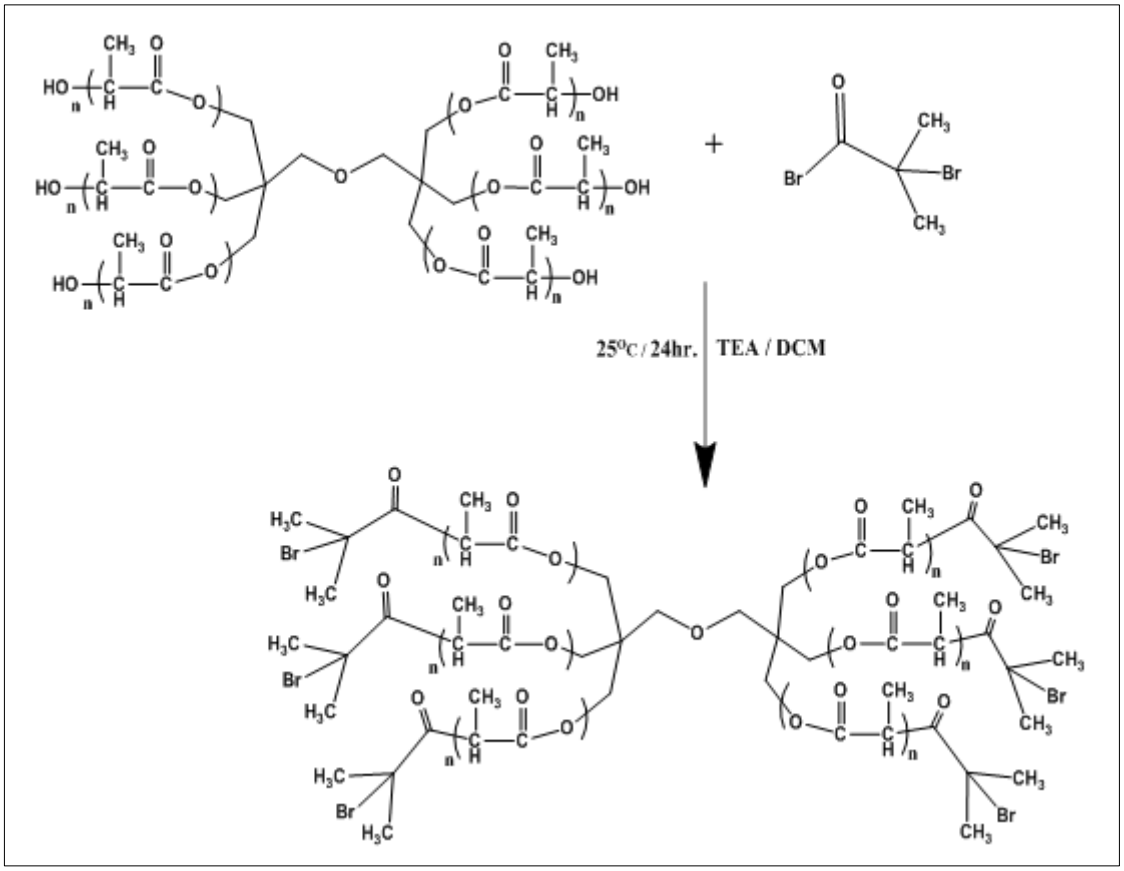
1H-NMR and 13C-NMR spectra were obtained using spectrometers from 500MHz Agilent and Nicolet nuclear magnetic spectroscopy. The microstructure of the produced polymers was investigated using a Scanning Electron Microscope (SEM) from the JEOL Company in the United States.

The molecular weights and molecular weight distributions (Mw/Mn) of the biocopolymer were determined using Waters 1515 gel permeation chromatography (GPC) and a refractive index detector (Waters 2412). This experiment used DMF as the eluent, and the poly(methyl methacrylate) standard was obtained from the Department of Chemistry at Michigan State University.

Preparation of ATRP initiator (D-PLLA$_{10}$Br)

Dipentaerythritol-lactide polymer (D-PLLA$_{10}$) (4.558 g, 1 mmol) [18] and trimethylamine (TEA) (0.84 mL, 6 mmol) were dissolved in 25 mL dichloromethane (DCM) at 0°C. After stirring for 15 min in a nitrogen atmosphere, 0.74 mL of 2-bromoisobutyryl bromide (BIBB) (0.74 mL, 6 mmol (dissolved in 5 mL of DCM) was added dropwise to the initial mixed solution, Scheme 1. The stirring reaction was maintained under nitrogen in an ice bath for 1 h. After that, the reaction was left stirring at room temperature for another 24 h. This was followed by three rounds of washing with 1 M HCl, saturated

sodium bicarbonate, and distilled water, respectively. Then, the product was dried on anhydrous magnesium sulfate. The yield of the final product was 72%. The same approach was used to prepare the polymers (D-PLLA$_{25}$Br), (D-PLLA$_{50}$Br), and (D-PLLA$_{100}$Br), using the chemicals and their amounts listed in Table 1 of those ATRP initiators.



Scheme 1. The chemical equation of preparation D-PLLA$_n$Br ATRP initiators

Table 1. The amount of reactants used in the synthesis of D-PLLA$_{25}$Br, D-PLLA$_{50}$Br, and D-PLLA$_{100}$Br ATRP initiators

Polymer Code	Amount of D-PLLA$_n$		Amount of TEA		Amount of BIBB		Yield %
	Weight (g)	No. of mmol	Volume (mL)	No. of mmol	Volume (mL)	No. of mmol	
D-PLLA$_{25}$Br	5.519	0. 5	0.28	2	0.25	2	74
D-PLLA$_{50}$Br	5.459	0. 25	0.14	1	0.13	1	77
D-PLLA$_{100}$Br	4.343	0. 1	0.06	0.4	0.05	0.4	77

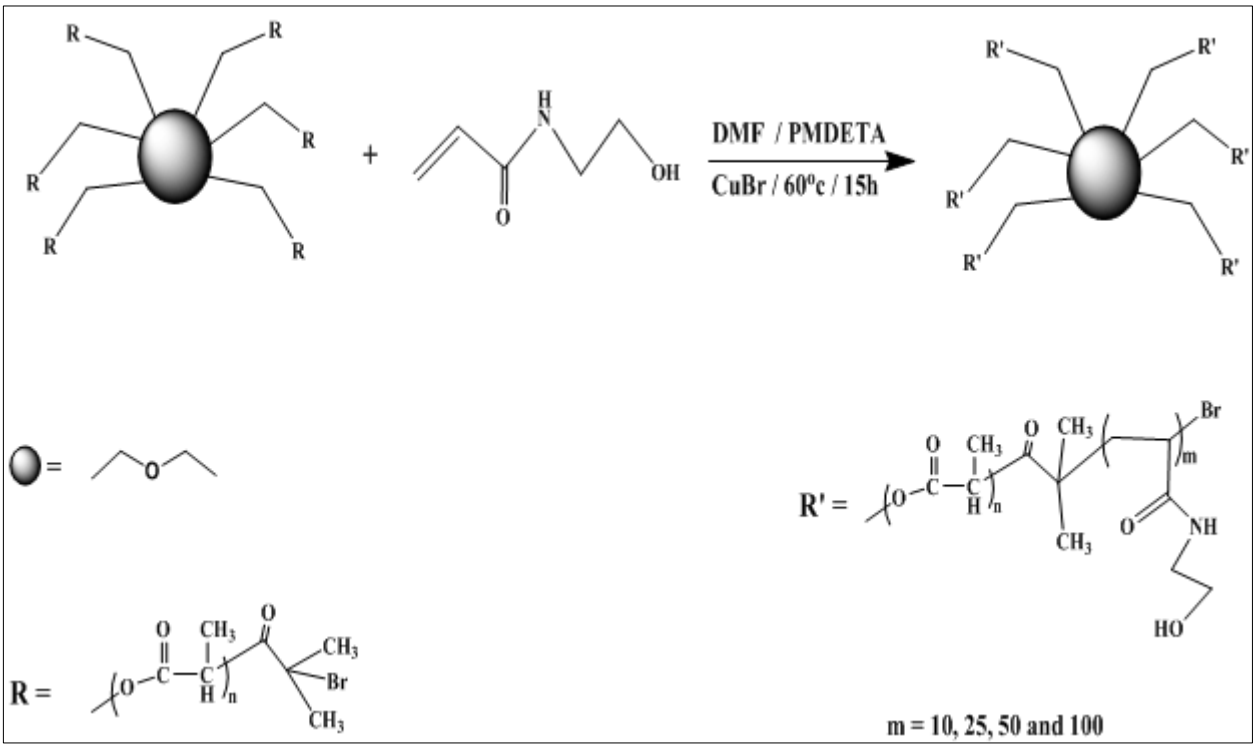
Synthesis of six-arms poly(dipentaerythritol-lactide-b-N-hydroxyethyl acrylamide) (D-PLLA$_{10}$BrNm)

D-PLLA$_{10}$Br (0.535 g, 0.1 mmol), N-hydroxy ethyl acrylamide (HEAA) (0. 685 g, 7 mmol), copper(I) bromide (0.05 g) and PMDETA N,N,N′,N″,N″-pentamethyldiethylenetriamine (20 μL) in (25 mL) dimethylformamide (DMF) were mixed and heated at 60°C and stirred for one hour under a nitrogen atmosphere. The reaction was stirred for additional 14 h, and then the mixture was slowly added to 500 mL of cold diethyl ether to precipitate the product. The copolymer was filtered-washed with diethyl ether, and then dissolved in 25 mL of DMF. The copolymer was recovered through column chromatography filled with silica gel (200-400 mesh). The DMF was removed using a rotary evaporator, and the copolymer was dried in a vacuum oven at 25°C for 24 h (yield: 71%).

The copolymers (D-PLLA$_{25}$BrNm), (D-PLLA$_{50}$BrNm), and (D-PLLA$_{100}$BrNm) were also prepared using the same procedure. Table 2 indicates the reactant quantities utilized in the preparation, and Scheme 2 gives the chemical equations for the obtained copolymers.

Table 2. The amount of reactants used in the synthesis of (D-PLLA$_{25}$BrN$_m$), (D-PLLA$_{50}$BrN$_m$), and (D-PLLA$_{100}$BrN$_m$) copolymers

Copolymer Code	D-PLLA$_n$Br		HEAA		CuBr (g)	PMDETA (µL)	Yield (%)
	Weight (g)	No. of mmol	Weight (g)	No. of mmol			
D-PLLA$_{25}$BrN$_m$	0.591	0.05	0.456	4	0.05	20	76
D-PLLA$_{50}$BrN$_m$	0.679	0.03	0.228	2	0.05	20	76
D-PLLA$_{100}$BrN$_m$	0.442	0.01	0. 685	7	0.05	20	74



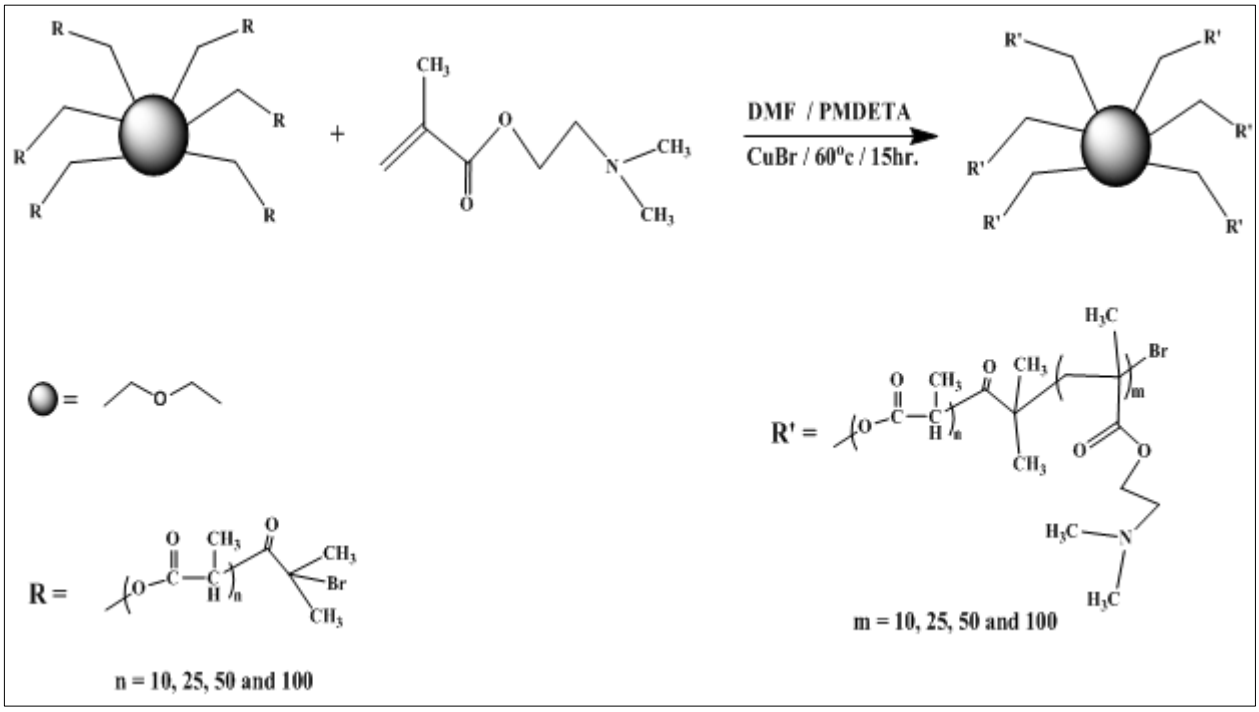
Scheme 2. The chemical equation of preparation of (D-PLnBrNm) copolymers

Synthesis of six-arms poly(dipentaerythritol-lactide-b-N,N-dimethylamino ethyl methacrylate)(D-PLLA$_{10}$BrDm)

D-PLLA$_{10}$Br (0.535 g, 0.1 mmol), N-hydroxy ethyl acrylamide (HEAA) (0.685 g, 7 mmol), copper (I) bromide (0.05 g), and N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA) were used with (25 mL) dimethylformamide (DMF). The reaction was agitated for 1 h at 60°C, and then left to stir for 14 h under a nitrogen atmosphere, before being slowly added to 500 mL of cold diethyl ether to precipitate the copolymer, and then it was dissolved in DMF (25mL). The copolymer was recovered through column chromatography filled with silica gel (200-400 mesh). The rotary evaporator removed the solvent DMF and the copolymer was dried in a vacuum oven at 25°C for 24 h (yield: 71%). The copolymers (D-PLLA$_{25}$BrNm), (D-PLLA$_{50}$BrNm), and (D-PLLA$_{100}$BrNm) were prepared using the same process. Table 3 shows the reactant quantities utilized in the preparation, and Scheme 3 gives the chemical equation routs for the prepared copolymers.

Table 3. The quantities of reactants used in the preparation of (D-PLLA$_{25}$BrD$_m$), (D-PLLA$_{50}$BrD$_m$), and (D-PLLA$_{100}$BrD$_m$) copolymers

Copolymer Code	Amount of D-PLLA$_n$Br		Amount of DMAEMA		Wt. of CuBr (g)	Volume of PMDETA (µL)	Yield %
	Weight (g)	No. of mmol	Weight (g)	No. of mmol			
D-PLLA$_{25}$BrD$_m$	0.591	0.05	0.64	4	0.05	20	73
D-PLLA$_{50}$BrD$_m$	0.679	0.03	0.32	2	0.05	20	75
D-PLLA$_{100}$BrD$_m$	0.442	0.01	1. 12	7	0.05	20	78



Scheme 3. Chemical equation of the preparation of (D-PL$_n$BrD$_m$) copolymers

3. Results and discussions

Characterization of ATRP initiators and copolymers by FT-IR

All prepared polymers and copolymers were characterized as KBr discs. The spectra of ATRP initiators (D-PLLA$_{10}$Br, D-PLLA$_{25}$Br, D-PLLA$_{50}$Br, and D-PLAL$_{100}$Br) polymers revealed strong new distinctive bands at (655, 645, 654, and 644) cm^{-1}, respectively, attributed to the formation of the new C-Br bonds, and this was accompanied by the removal of dipentaerythritol-lactide hydroxyl group polymers utilized to make ATRP [17]. The copolymers (D-PLLA$_{10}$BrNm, D-PLLA$_{25}$BrNm, D-PLLA$_{50}$BrNm, and D-PLLA$_{100}$BrNm) produced by ATRP copolymerization of D-PLLAnBr with N-hydroxyethyl acrylamide having different L-lactide chain lengths show intense bands at 3390, 3380, 3410, and 3415 cm^{-1}, respectively, due to the attached hydroxyl groups.

DMAEMA-produced D-PLLA$_{10}$BrDm, D-PLLA$_{25}$BrDm, D-PLLA$_{50}$BrDm, and D-PLLA$_{100}$BrDm copolymers exhibit additional distinct absorption bands owing to (C-N) stretching at 1140, 1143, 1144, and 1144 cm^{-1}, respectively, as well as bands at (3120, 3090, 3088, and 3091) cm^{-1}.

Characterization of ATRP initiators and copolymers by NMR

The structure of all produced polymers and copolymers is also confirmed using ^{1}H and ^{13}C NMR methods, as shown in Figures 1-6 for these synthesized copolymers, respectively.

Figure 1 shows the 1HNMR spectrum of the ATRP initiators. A signal (a) at 4.2 ppm was found, which is attributed to the two protons in the (CH) group of dipentaerythritol. The (CH) protons of the L-lactide repeating unit segments are represented by signal (c) at 5.2 ppm, while the (CH_3) protons of the repeated unit are represented by signal (d) at about 1.5 ppm. The strongest signal is found at 2 ppm (e), which is owed to the new methyl protons of the same two (CH_3) end chain groups of bromoisobutyryl, showing that dipentaerythritol-lactide Bromide ATRP initiators were prepared from dipentaerythritol-lactide. This was confirmed by the removal of signals at 2.9 ppm attributed to hydroxyl groups at polymer end chains.

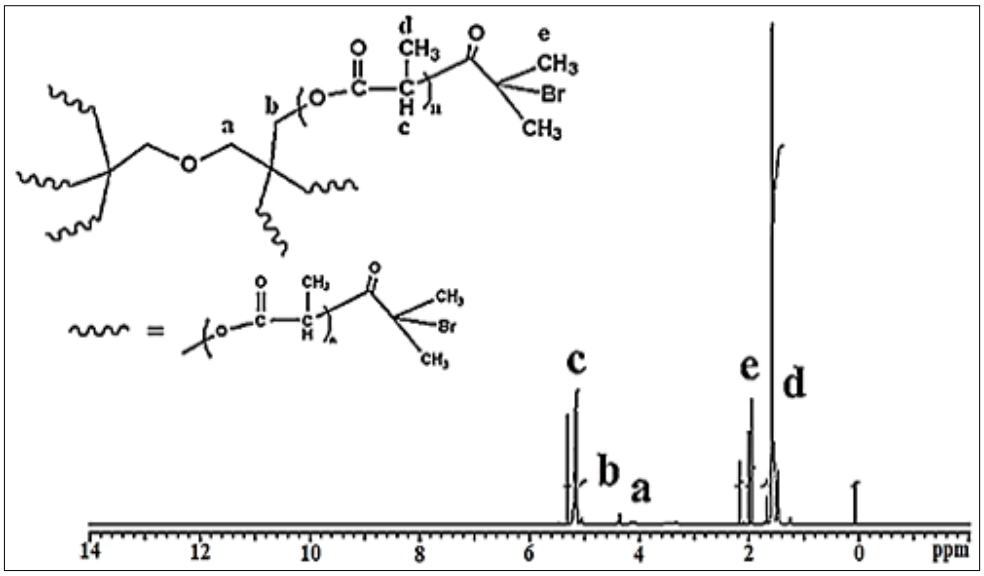


Figure 1. ^{1}H NMR spectrum of the ATRP initiators (D-PLLAnBr)

The ATRP copolymerization of D-PLLAnBr with N-hydroxyethyl acrylamide (HEAA) revealed a signal at 8 ppm (h) for the NH group, signals at 2.7 ppm and 2.8 ppm (i & j) for the (CH_2) protons of hydroxyethyl acrylamide, and a signal at 5.6 ppm (k) for the terminal hydroxyl proton groups. The protons of the (CH_2) and (CH) groups belonging to N-hydroxyethyl acrylamide-repeated unit are shown in Figure 2 at about 1.6 (f) and 3.4 ppm (g), respectively.

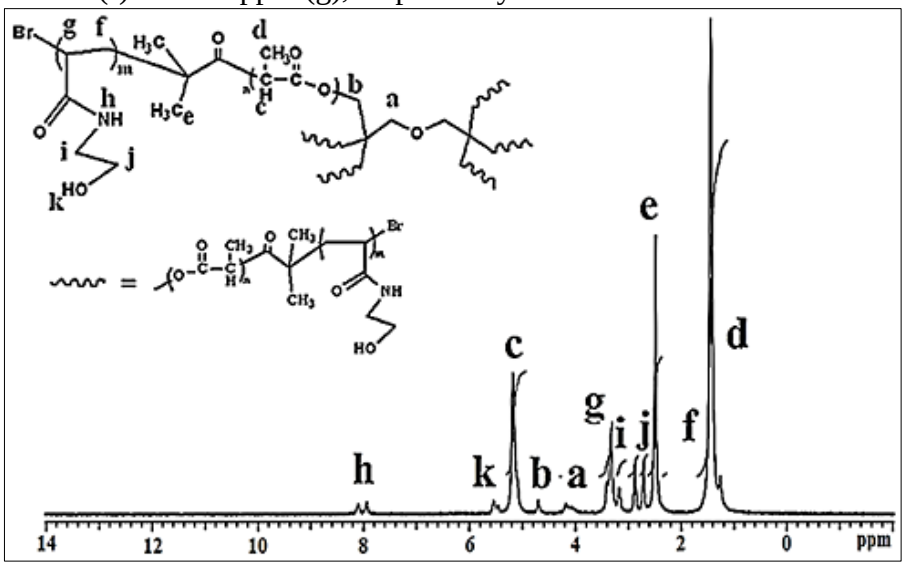


Figure 2. ^{1}H NMR spectrum of the prepared copolymers (D-PLLAnBrNm)

Signals belonging to the CH_2 and CH_3 groups in the repeated unit of DMAEMA (f and g) were around 1.6 and 2.5 ppm, respectively, while OCH_2, NCH_2, and NCH_3 sets in the side chain of DMAEMA (h, I, and j) were at 5.7, 2.9, and 2.8 ppm, respectively, in D-PLLAnDBr copolymers (Figure 3).

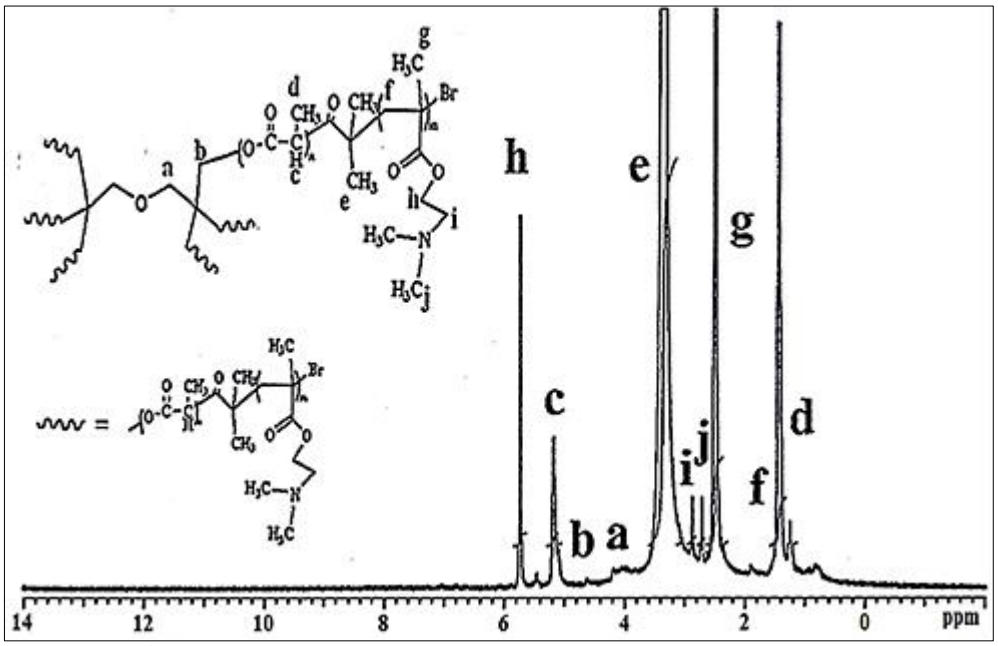


Figure 3. ^{1}H NMR spectrum of the prepared copolymers (D-PLLAnBrDm)

The structures of all of the newly produced polymers and copolymers were confirmed using 13C NMR. The 13C NMR spectrum of the ATRP initiator polymer is shown in Figure 4. As a result, when isobutyryl bromide is present, two separate signals emerge one at 176 ppm (g) for the carbon atom of the last carbonyl group, and another at 55 ppm (h) for the carbon atom of the bromine atom, which is tertiary bound to it. The final dimethyl group is represented by the carbon atom at 20 ppm (i) at the end of the chain. Because the other signals were formed from dipentaerythritol-lactide, they appear in their normal quantities before their interaction with isobutyryl bromide [17].

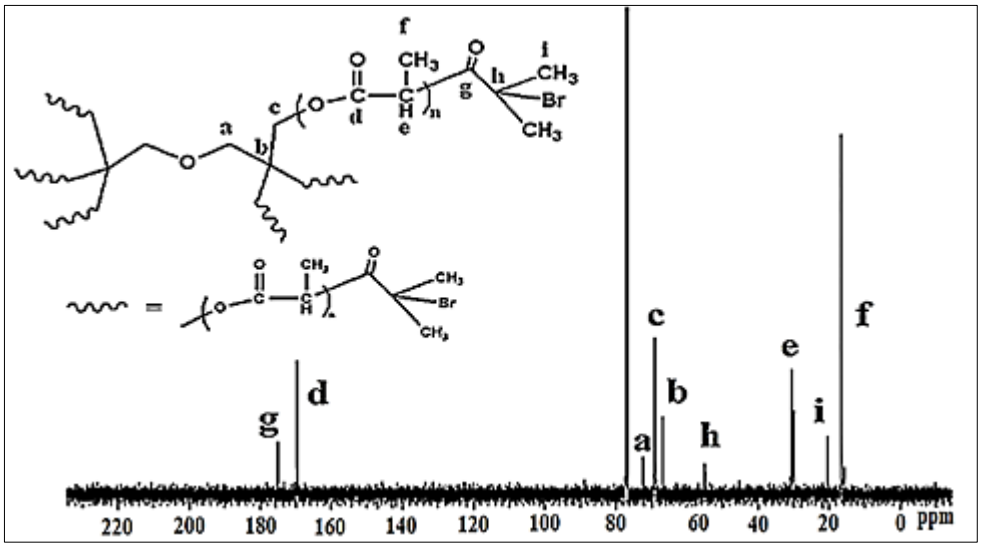


Figure 4. ^{13}C NMR spectrum of the ATRP initiators (D-PLLAnBr)

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13C NMR confirmed the copolymerization of D-PLLAnBr polymers with N-hydroxyethyl acrylamide. In Figure 5, the signals that appeared at 40 ppm (j) and 20 ppm (i) were assigned to the

carbon of the (CH_2) and (CH) groups in the repeating unit of N-hydroxyethyl acrylamide, respectively, and a signal at about 164 ppm (I) for its carbonyl carbon atom. While the carbon atoms in the CH_2 groups in the branched part of N-hydroxyethyl acrylamide (m and n) appeared at around 42 ppm and 66 ppm, respectively.

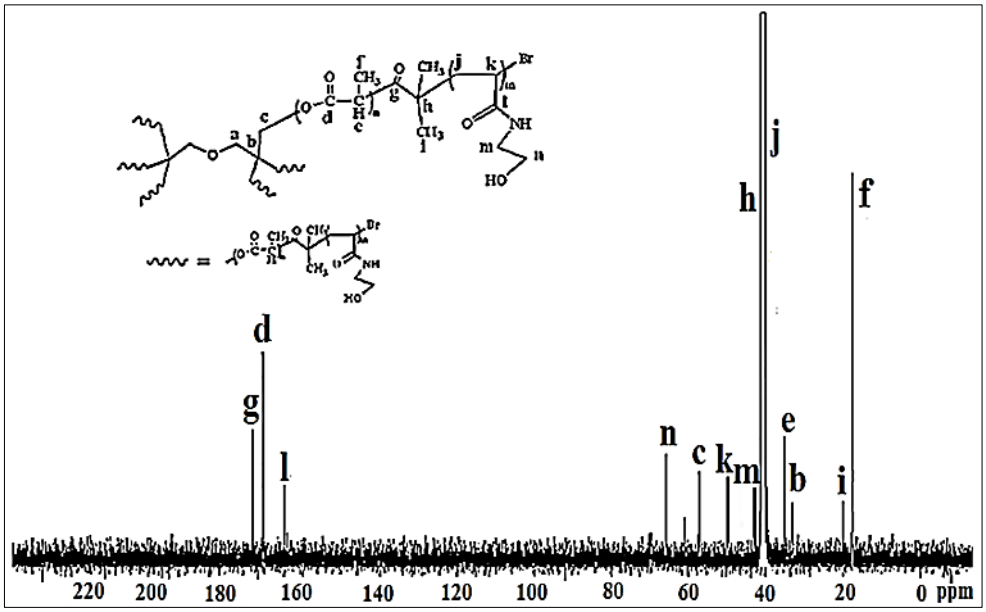

Figure 5. 13C NMR spectrum of the prepared copolymers (D-PLLAnBrNm)

Figure 6 shows the 13C NMR spectrum of the ATRP initiator with DMAEMA (D-PLLAnDBr). The signals corresponding to the C=O groups of the DMAEMA segments of the synthesized copolymers appear at approximately 167 ppm (m), while signals at 45 ppm (j) and 57 ppm (k) are assigned to the carbon of the (CH_2) and (CH) groups in the DMAEMA repeating unit, respectively. Also, the signals belonging to the OCH_2, NCH_2, and NCH_3 groups in the branched part of DMAEMA were shown at 68, 67, and 39 ppm, respectively.

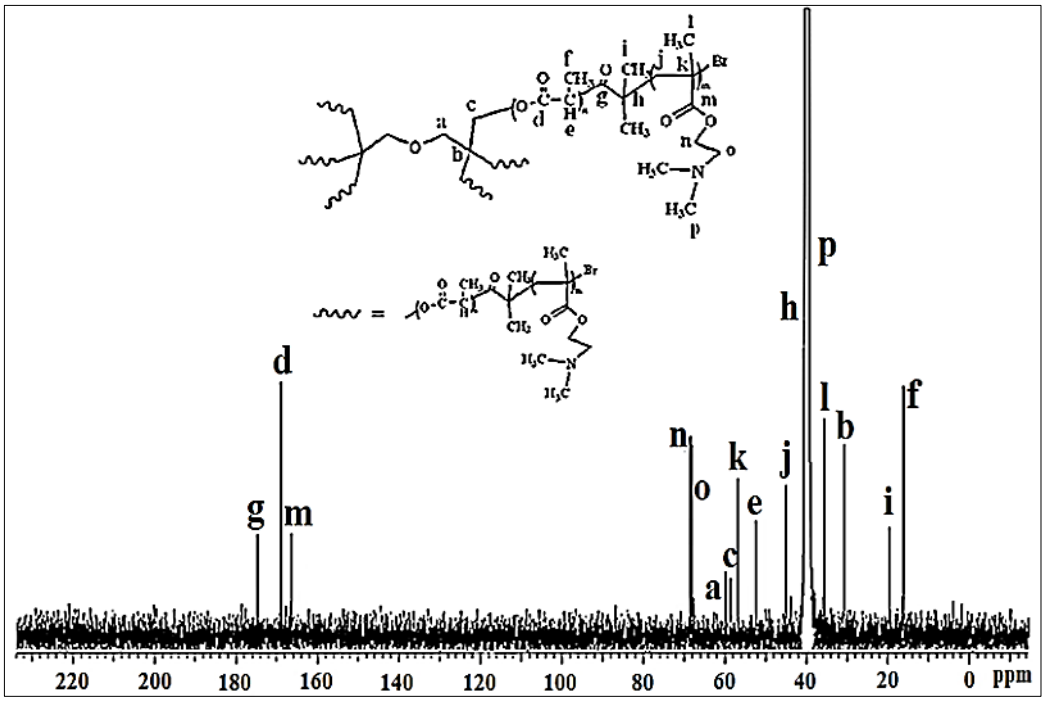

Figure 6. ^{13}C NMR spectrum of the prepared copolymers (D-PLLAnBrDm)

Estimation of the copolymer polydispersity index

The molecular weight distributions (Mw/Mn) were determined for all prepared copolymers, and the obtained results are shown in Table 4. The PDI is ranging between 1.02-1.07, implying that the copolymer molecular weight distribution is closely monodisperse or of a narrow distribution type. All of these findings support the expected structure and composition of the produced copolymers with high precision. The results of GPC were significantly close to the theoretical calculations of molecular weight, and the result in the awesome polydispersity index (PDI) was near to one.

Table 4. GPC results of the prepared copolymers

Copolymer Code	Value of (m)*	M_n Found (Daltons)	M_w Found (Daltons)	Polydispersity Index (PDI)
D-PLLA$_{10}$BrN$_m$	14	15183	15767	1.03
D-PLLA$_{25}$BrN$_m$	27	30576	32672	1.06
D-PLLA$_{50}$BrN$_m$	61	64939	68737	1.05
D-PLLA$_{100}$BrN$_m$	114	123072	127766	1.03
D-PLLA$_{10}$BrD$_m$	13	17788	18312	1.02
D-PLLA$_{25}$BrD$_m$	29	39376	41248	1.04
D-PLLA$_{50}$BrD$_m$	57	76451	82180	1.07
D-PLLA$_{100}$BrD$_m$	117	154521	163446	1.05

* m = number of HEAA and DMAEMA repeating unit found practically by GPC.

Characterization of Nanostructures of synthesised copolymers by scanning electron microscopy (SEM)

The morphology and geometry of the obtained D-PLLA$_{100}$BrNm and D-PLLA$_{100}$BrDm as a representative of the prepared copolymers were studied using scanning electron microscopy. The presence of a nanostructure with a mean diameter of roughly 56 nm for D-PLLA$_{100}$BrNm and 58 nm for D-PLLA$_{100}$BrDm, as measured by the Image-J program, is shown in Figures 7 and 8, respectively. This shows that copolymer nanoparticles were successfully formed. As a result, these copolymers could be used in a variety of technical and pharmaceutical applications.

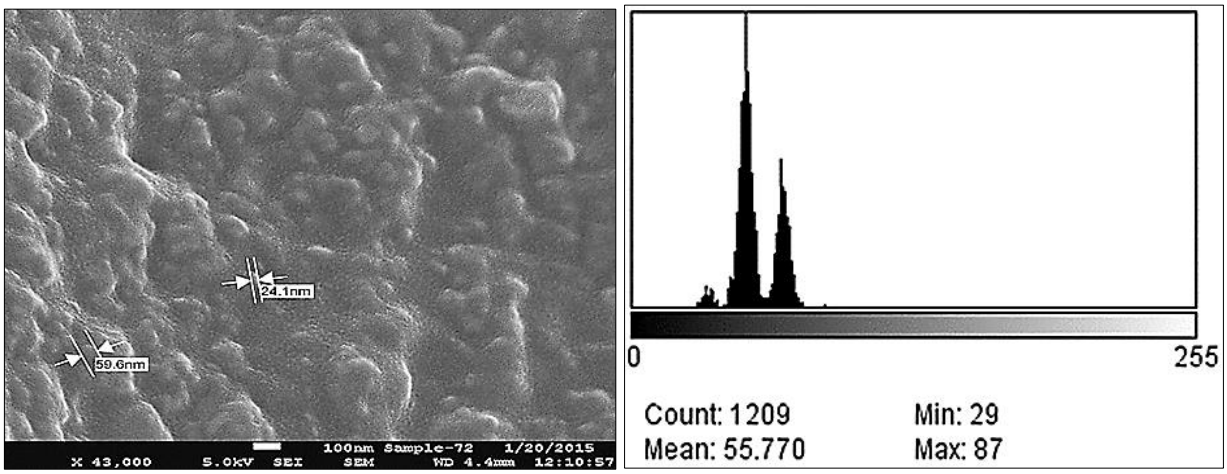

Figure 7. SEM micrographs and the image-J result of D-PLLA$_{100}$BrNm

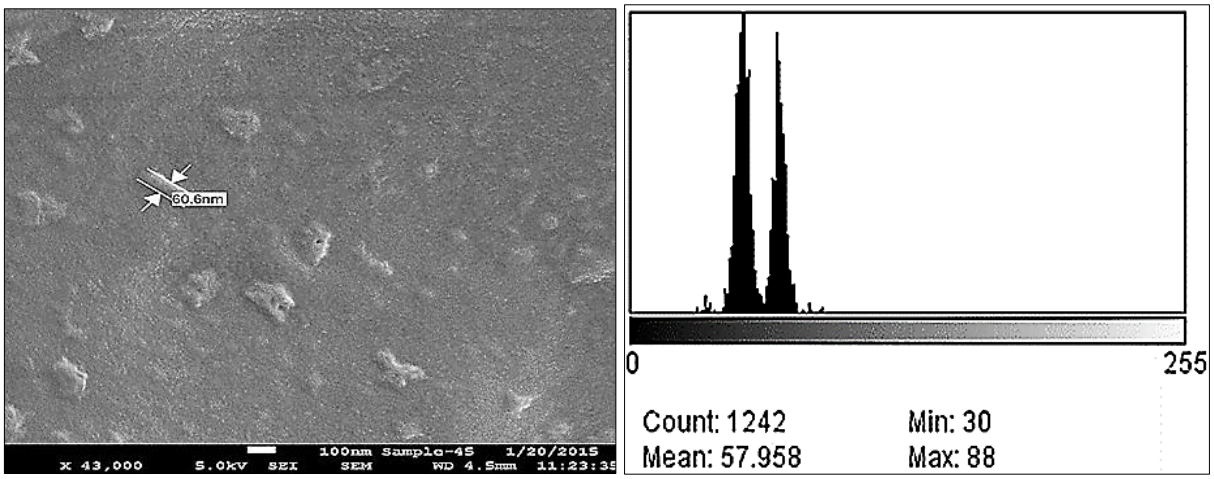

Figure 8. SEM micrographs and the Image-J result of D-PLLA$_{100}$BrDm

4. Conclusions

Using copper (I) bromide (CuBr) and N,N,N′,N″,N″-pentamethyl-diethylenetriamine (PMDETA) as the catalyst system, six arms of D-PLLAnBrNm and D-PLLAnBrDm were successfully synthesized from distinct monomers, N-hydroxyethyl acrylamide (HEAA) and N-dimethylamino ethyl methacrylate (DMAEMA). Furthermore, the GPC results showed that the expected copolymer molar masses have a narrow molecular weight distribution (PDIs ≤ 1.07), and that the prepared copolymer structures were confirmed as examined by FT-IR, 1H-NMR, and 13C-NMR spectroscopy. On the other hand, SEM images indicated the presence of nanostructures in the produced copolymers ranging from 56-58 nm. The molecular weight, content, chain length, and distribution of the molecules change come as a result of the controlled polymerization (ATRP).

Acknowledgments: The authors would like to thank Professor B. Borhan and Dr. K. Ashtekar of Michigan State University's Chemistry Department for their help and interesting conversation during their time at MSU.

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Manuscript received: 7.01.2022