

Characterization and thermal stability of nano eight arm copolymers synthesized by atom transfer radical polymerization

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Received 13 January 2017; revised 24 March 2017; accepted 24 March 2017

Available online 13 April 2017

Abstract

The synthesis of nano eight-armed poly{POSS lactide-b-N, N-(dimethylamino)ethyl methacrylate} copolymers is reported in this paper. Thio-click chemistry combined with living/controlled polymerization methods that allow the preparation of well-defined polymeric building block copolymers. This was carried out using Thio-Click reaction of octavinyl POSS with 2-mercapto ethanol to prepare Thiolate-POSS. Thiolate POSS-lactide polymers containing different L-Lactide repeated units (10, 25, 50 and 100) were synthesized by ring-opening polymerization of (L-lactide) in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a catalyst. The resulting polymers were copolymerized with N-hydroxyethyl-2-(dimethylamino) ethyl methacrylate (DMAEMA) via atom transfer radical polymerization. All the prepared polymers and copolymers are characterized by different spectroscopic and analytical techniques, such as infrared spectroscopy, nuclear magnetic resonance (^1H NMR and ^{13}C NMR) and by gel permeation chromatography (GPC), where all these analyses have verified the expected structure and compositions. On the other hand, images obtained from Scanning Electronic Microscopy (SEM) revealed the existence of nanostructures in the prepared copolymers due to the presence of the lactide array to give nanofiber within final compositions prepared, and with the presence of POSS in their structures, they enhance the copolymers thermal stability, and they are expected to be suitable for different applications as nano-carriers in the biomedical field.

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Keywords: Eight arms; Nanostructure; POSS; L-lactide; ATRP

1. Introduction

The recently reported controlled ring-opening polymerization (ROP) of cyclic monomers in the literature [1,2] is concerned with the coordination-

insertion, anionic, cationic, and nucleophilic polymerization. The coordination-inserts and nucleophilic polymerization are no doubt the most efficient and general methods reported so far for the ROP of lactones. Coordination-insertion polymerization uses metal alkoxides and related complexes as catalysts. In contrast, the organocatalytic ROP developed by Nederberg et al. [3], using amine-based catalysts, shows the extremely fast kinetics resulting in well-defined polymers and very high monomer conversion

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Peer review under responsibility of University of Kerbala.

levels. Since this discovery, a vast range of organo-catalysts based on pyridine, phosphine, and N-heterocyclic carbenes have been described in the literature [4].

DBU-catalyzed ROP of L-lactide was tested in CDCl_3 at room temperature at a 100:1:1 monomer/catalyst/initiator ratio by Pratt et al. [5], the resulting polymer was found to have M_n 21,000 g/mol and polydispersity ($\text{PDI} = M_w/M_n$) 1.05. The sampling of a polymerization reaction exhibited a linear increase of M_n with monomer conversion while the PDI stayed close to 1.05, even at nearly complete conversions, i.e. up to 99%. The molecular mass of the poly(lactide) could be controlled by varying the monomer/initiator ratio of 50:1 to 500:1 with good correlation of the targeted and experimental M_n values with PDI less than 1.1.

Among the developed, controlled radical polymerization processes, the Atom Transfer Radical Polymerization (ATRP) method is important where control happens with the aid of reversible redox reaction between alkyl halides and transition metal complexes. It is considered as an efficient method of forming carbon–carbon bonds between organic halides and alkenes. ATRP can be used to synthesize various polymers and copolymers with controlled molecular mass and polydispersity index close to unity. It can be carried out in a wide range of polymerization temperatures and is not very sensitive to the presence of oxygen and other inhibitors [6]. Many literature reports are found using ATRP for preparing N, N-(dimethylamino)ethyl methacrylate [7,8], N-isopropyl acrylamide [9] and styrene [10] homopolymers using Cu(I) halides and an organic ligand.

Pan et al. [11] have announced that the photoinduced metal-free atom transfer radical polymerization has been successfully stretched to the synthesis of polyacrylonitrile with predictable molecular weight and low dispersity. Moreover, Xue et al. [12] have managed to use ATRP without using Cu(I) catalyst to synthesize poly(n-butyl acrylate) homopolymer via activator generated by electron transfer ATRP using ethylene bis(2-bromoisobutyrate) (EBBiB). It seems that, compared to other controlled radical polymerization methods, ATRP is found a very versatile method of polymerization.

The first report describing the well-controlled copolymers that were prepared by ATRP copolymerization of caprolactone 2-(methacryloyloxy) ethyl ester (CLMA) with methyl methacrylate (MMA), was reported by Bury et al. [13]. This was followed by the synthesis of the triblock copolymer of poly(styrene-b-n-butyl acrylate-b-styrene) triblock copolymer [11].

Furthermore, copolymerization of N-isopropyl acrylamide monomer to the synthesis of poly(N-isopropyl acrylamide)-b-poly(L-lysine) and poly(N-isopropyl acrylamide-co-acrylamide)-b-poly(L-lysine) copolymers was accomplished by combining ATRP and ROP to study the influence of end group functionalization on thermal properties of the polymer obtained with lower polydispersity index [13].

There are several important areas of applications where this study can make an original contribution to combine three different methods of polymerization, namely thio-click, ring opening polymerization and atom transfer radical polymerization to prepare a series of poly(POSS lactide-b-N, N-dimethylamino ethyl methacrylate) copolymers containing eight arms. Therefore, this work will provide an important opportunity to advance the understanding of the synthesis of the new block copolymers and to demonstrate how they could introduce nanostructures in multiple large arm molecules.

2. Materials & methods

2.1. Materials

Octavinyl POSS was supplied by Hybrid Plastics company/USA, L-Lactide, 2-Mercapto ethanol N,N-dimethylamino ethyl methacrylate, Copper(I) bromide, N,N,N',N'',N'''-pentamethyldiethylenetriamine (PMDETA), diazabicyclo [5.4.0] undec-7-ene (DBU) (Assay $\geq 98\%$), 2-Bromoisobutyryl bromide (Assay $\geq 98\%$) 2,2-dimethoxy-2-phenylacetophenone, Diethyl ether (Assay $\geq 99\%$) and Magnesium sulfate were purchased from Sigma–Aldrich of USA, dichloromethane (DCM), dimethylformamide (DMF) (Assay $\geq 99.8\%$) and Triethylamine (Assay $\geq 99.5\%$), were supplied by MACRON Company/USA.

2.2. Instruments

All the spectroscopic and gel-permeation chromatography (GPC) measurements were carried out at Department of Chemistry/Michigan State University/USA. The FTIR spectra of the prepared polymers were recorded using Nicolet IR-42, Mid-IR spectrometer/Thermo Scientific-USA. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded using Agilent DDR2 500 MHz NMR spectrometers/Bruker US-based. Copolymers molecular weights and molecular weight distributions (M_w/M_n) were determined using a Waters 1515 gel permeation chromatography (GPC) calibrated with the poly(methyl methacrylate) standard.

The nanostructure of the prepared copolymers was examined under Scanning Electron Microscope type JEOL 7500F supplied by JEOL company available at the Center for Advanced Microscopy/Michigan State University/USA.

2.3. Methods

2.3.1. Preparation of Thiolate POSS by thio-click reaction of octavinyl POSS with 2-mercapto ethanol

Octavinyl POSS (6.33 g, 0.01 mol), 2-mercapto ethanol (7.0 ml, 0.09 mol) and trace amounts of the photoinitiator 2,2-dimethoxy-2-phenylacetophenone were dissolved in THF (20 ml) and added to a reaction round flask, the reaction was carried out at room temperature by irradiation with a UV-lamp (365 nm) for 1 h. The reactants were poured into 500 ml diethyl ether to precipitate the polymer, then filtered and washed with diethyl ether and then dried in a vacuum oven at 25 °C for 24 h (Viscous, yield 77%) (see [Scheme 1](#)).

2.3.2. Preparation of (Thiolate POSS-lactide) polymer (polymer TL₁₀)

This polymer was synthesized by ring-opening polymerization of (L-lactide) with Thiolate POSS in the presence of 1,8-Diazabicyclo [5.4.0] undec-7-ene (DBU) as a catalyst. Thiolate POSS (2.516 g, 0.002 mol) and L-lactide (11.5304 g, 0.08 mol) were dissolved in dichloromethane (25 ml). After stirring for 5 min under nitrogen atmosphere, DBU (150 μl) was added and the mixture was stirred for 24 h at 25 °C under a nitrogen atmosphere. The reaction was worked up by the slow addition of the reactants to 500 ml diethyl ether to precipitate the polymer, which was then filtered on a Buchner funnel and washed with diethyl ether. The polymer was dried in a vacuum oven at 25 °C for 24 h. (Viscous, yield 72%). The same procedure was repeated three times to prepare the polymers TL₂₅, TL₅₀ and TL₁₀₀, [Table 1](#) lists the quantities of reactants used in the preparation of those

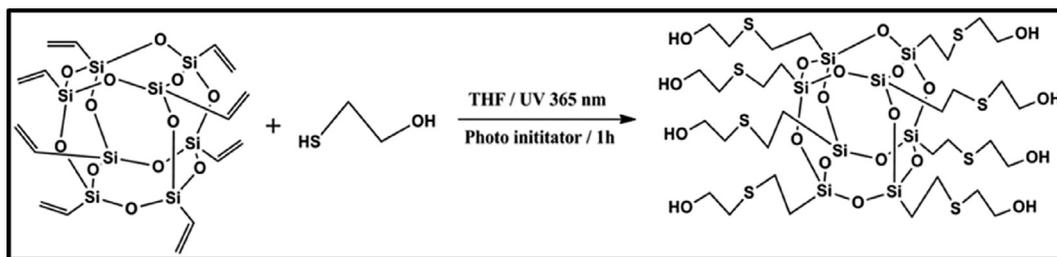
polymers and [Scheme 2](#) illustrate the chemical reaction route of the preparation.

2.3.3. Preparation of ATRP initiator (TL₁₀Br)

Thiolate POSS-lactide (4.7 g, 0.0007 mol) and triethylamine (TEA) (0.37 ml, 0.003 mol) were dissolved in DCM (15 ml) at 0 °C. After stirring for 15 min under nitrogen atmosphere, 2-bromoisobutyryl bromide (BIBB) (0.33 ml, 0.003 mol dissolved in 5 ml from DCM) was added drop-wise into the mixed solution. The reaction was kept in a nitrogen atmosphere and in an ice-bath for 1 h. The reaction was stirred for a further 24 h at room temperature. The reaction was stirred for a further 24 h at room temperature. Afterward, the product was washed with 1 M HCl, saturated sodium bicarbonate, and distilled water three times, then dried over magnesium sulfate and filtered; DCM was evaporated by rotary evaporator. (Viscous, yield 65%). The same procedure was carried out to prepare the polymers (TL₂₅Br), (TL₅₀Br) and (TL₁₀₀Br). [Table 2](#) exhibits the quantities of reactants used and [Scheme 3](#) shows the chemical equations of preparation of ATRP initiators.

2.3.4. ATRP of (Thiolate POSS-Lactide bromide) (TL₁₀Br) with N,N-Dimethylamino ethyl methacrylate (DMAEMA): (TL₁₀BrD_m)

Thiolate POSS-lactide bromide (0.4 g, 0.00005 mol), N,N-(dimethylamino)ethyl methacrylate (0.8 g, 0.005 mol), Copper(I)bromide (0.05 g) and N,N,N',N'',N'''-pentamethyldiethylenetriamine (20 μl) were dissolved in DMF (15 ml) at 60 °C. After stirring for 1 h under a nitrogen atmosphere, the reaction was stirred for a further 14 h at 60 °C. Then, the product was added slowly to 500 ml cold diethyl ether to precipitate the copolymer. It was 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 silica gel (200–400 mesh) column chromatography. DMF was removed by rotary evaporator. The copolymer obtained was dried in

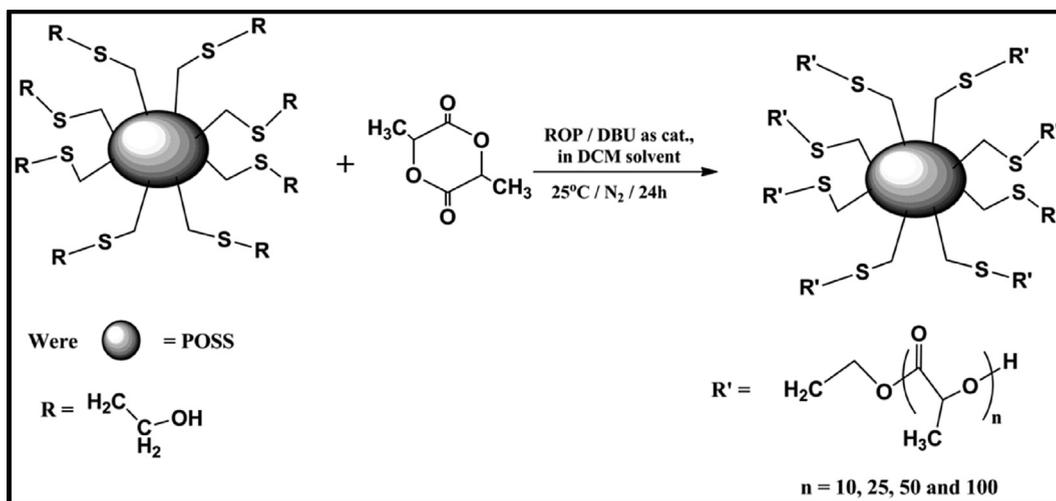


Scheme 1. Chemical equations of preparation of Thiolate POSS.

Table 1

The quantities of reactants used in the preparation of TL₂₅, TL₅₀ and TL₁₀₀ polymers.

Polymer code	Amount of Thiolate POSS		Amount of L-lactide		DBU (μl)	Yield (%)	Physical state
	Weight (g)	No. of mole	Weight (g)	No. of mole			
TL ₂₅	0.7548	0.0006	8.6478	0.06	100	75	Viscous liquid
TL ₅₀	0.3774	0.0003	8.6478	0.06	90	78	Viscous liquid
TL ₁₀₀	0.2516	0.0002	11.5304	0.08	120	84	Solid

Scheme 2. Chemical equations of preparation of the polymers TL₁₀, TL₂₅, TL₅₀ and TL₁₀₀ by ROP to L-Lactide with Thiolate POSS.

vacuum oven at 25 °C for 24 h (Solid, yield 70%). The same procedure was carried out to prepare the copolymers (TL₂₅BrD_m), (TL₅₀BrD_m) and (TL₁₀₀BrD_m). Table 3 shows the quantities of reactants used and the chemical equations of the preparing those copolymers are illustrated in the Scheme 4.

3. Results and discussion

3.1. FTIR characterization of the new prepared polymers and copolymers

Polymers that were prepared from Thiolate POSS with L-lactide (TL₁₀, TL₂₅, TL₅₀ and TL₁₀₀) exhibit absorption bands in the IR region (3508, 3505, 3510

and 3507 cm⁻¹ respectively), assigned to the hydroxyl groups and intense bands due to the (C=O) groups (1744, 1745, 1749 and 1753 cm⁻¹ respectively). The copolymers that were prepared from TL_nBr with DMAEMA (TL₁₀BrD_m, TL₂₅BrD_m, TL₅₀BrD_m and TL₁₀₀BrD_m) show additional characteristic absorption bands due to the (C–N) stretching at (1136, 1133, 1134 and 1134 cm⁻¹, respectively).

3.2. Characterization of new polymers and copolymers by NMR

¹H NMR and ¹³C NMR spectra of Thiolate POSS and (TL₁₀BrD_m, TL₂₅BrD_m, TL₅₀BrD_m and TL₁₀₀BrD_m) copolymers were recorded by using dimethyl sulfoxide-

Table 2

The reactant amounts used in the preparation of (TL₂₅Br), (TL₅₀Br) and (TL₁₀₀Br) ATRP initiators.

Polymer code	Amount of TL _n		Amount of TEA		Amount of BIBB		Yield (%)	Physical state
	Weight (g)	No. of moles	Volume (ml)	No. of moles	Volume (ml)	No. of moles		
TL ₂₅ Br	3.9	0.00025	0.14	0.001	0.13	0.001	66	Viscous liquid
TL ₅₀ Br	3.76	0.000125	0.07	0.0005	0.06	0.0005	71	Viscous liquid
TL ₁₀₀ Br	4.2	0.00007	0.04	0.0003	0.035	0.0003	69	Solid

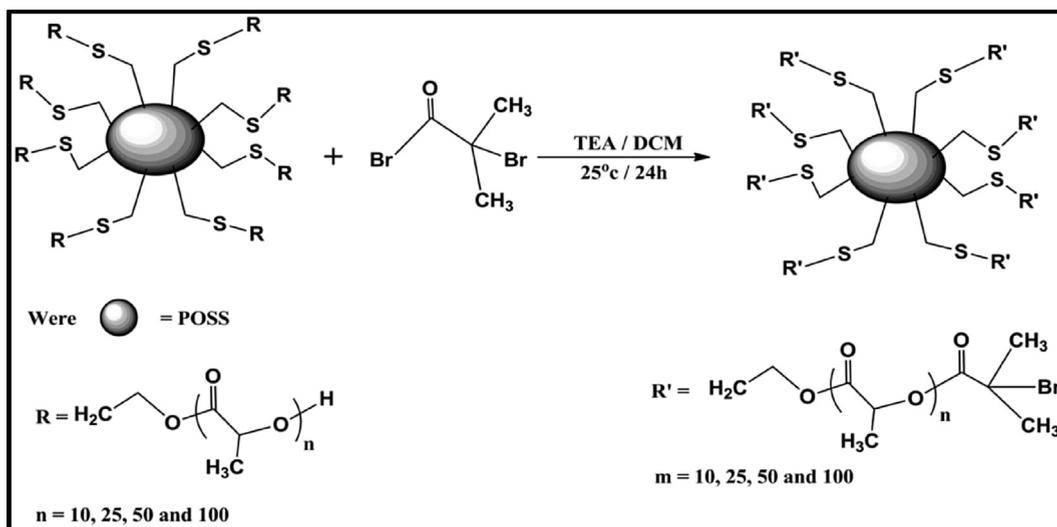
Scheme 3. Chemical equations of preparation the ATRP initiators TL₁₀Br, TL₂₅Br, TL₅₀Br and TL₁₀₀Br.

Table 3

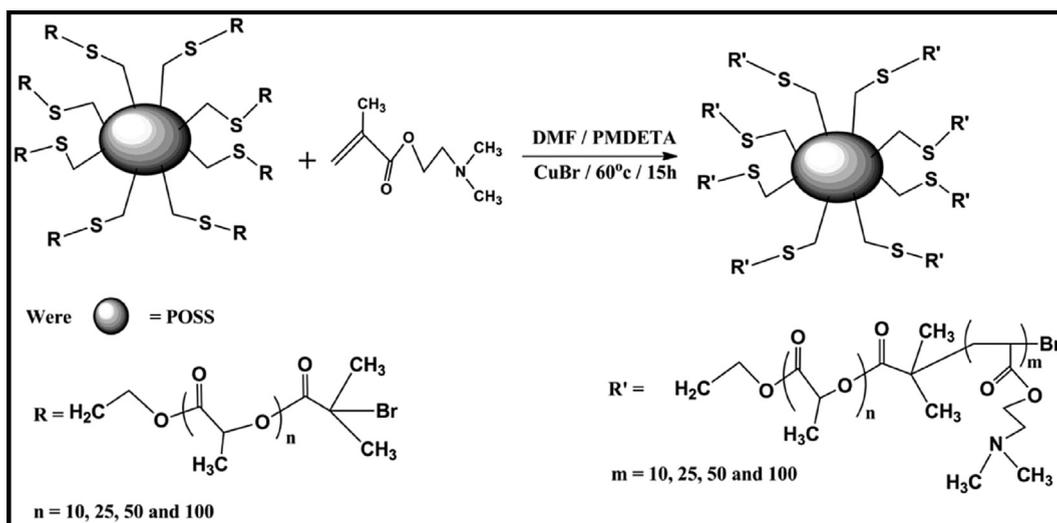
The quantities of reactants used in the preparation of (TL₂₅Br-D_m), (TL₅₀Br-D_m) and (TL₁₀₀Br-D_m) copolymers, where n = 10, 25, 50 and 100.

Copolymer code	Wt. of TL _n Br (g)	Moles No. of TL _n Br (mole)	Wt. of DMAEMA (g)	Moles No. of DMAEMA (mole)	Wt. of CuBr (g)	Volume of PMDETA (μl)	Yield (%)	Physical state
TL ₂₅ BrD _m	0.4	0.00002	0.8	0.005	0.05	20	71	Solid
TL ₅₀ BrD _m	0.4	0.00001	0.8	0.005	0.05	20	69	Solid
TL ₁₀₀ BrD _m	0.4	0.000007	0.8	0.005	0.05	20	69	Solid

d6 (Sigma–Aldrich/USA, 99.9 atom % D) as solvent, and for (Thiolate POSS-lactide) polymers and (TL₁₀Br, TL₂₅Br, TL₅₀Br and TL₁₀₀Br) polymers were recorded by using CDCl₃ (Sigma–Aldrich/USA, 99.8% atom D)

as solvent. Figs. 1 and 2 represent the ¹H NMR and ¹³C NMR spectra of the prepared polymers and copolymers.

¹H NMR of (Thiolate POSS-lactide) polymers show the signals at about 5.2 ppm representing the methine

Scheme 4. Chemical equations of preparation the copolymers (TL₁₀BrD_m), (TL₂₅BrD_m), (TL₅₀BrD_m) and (TL₁₀₀BrD_m). Where (n = 10, 25, 50 and 100), (m ≈ 10, 25, 50 and 100).

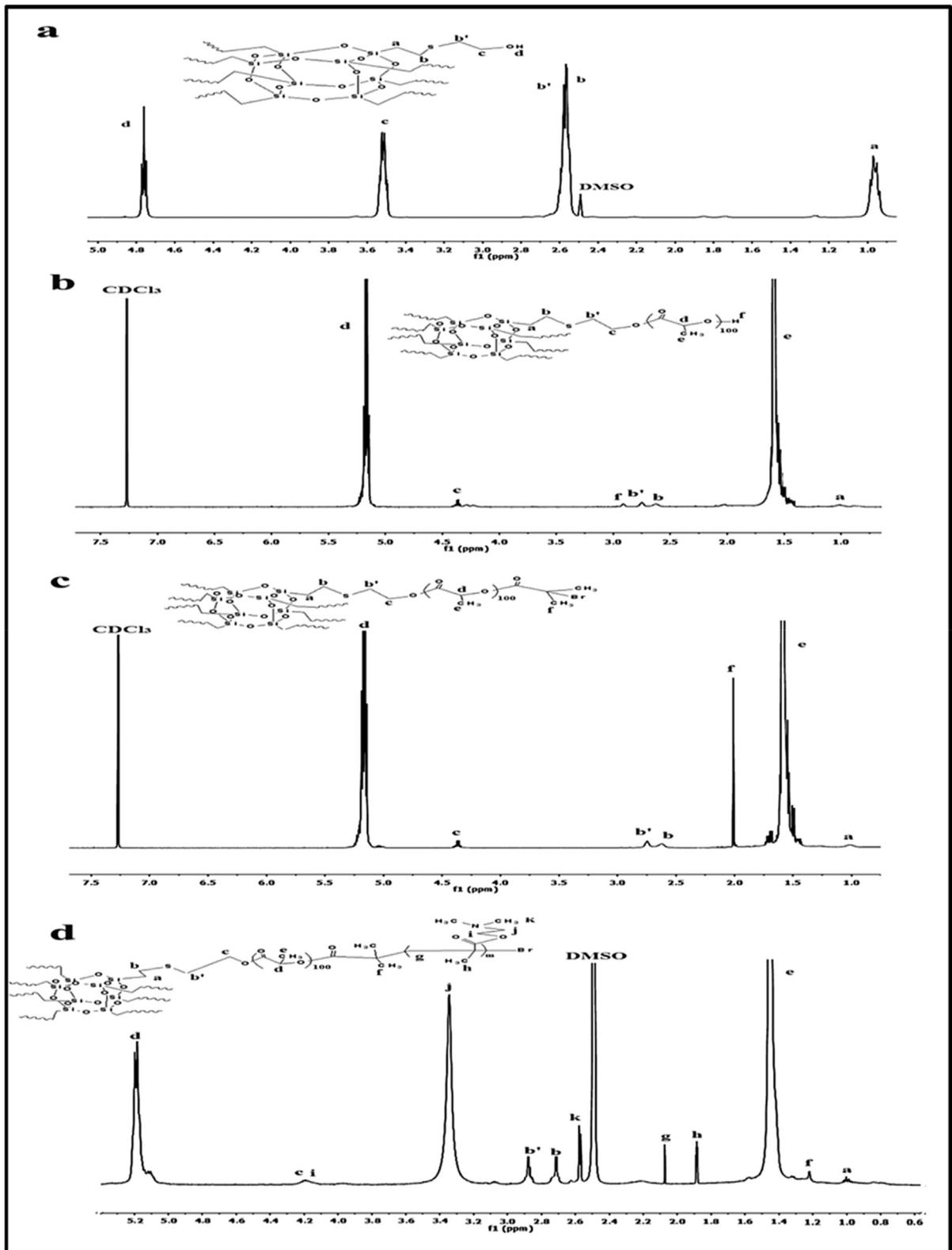


Fig. 1. ^1H NMR Spectra of: (a) Thiolate POSS, (b) TL₁₀₀, (c) TL₁₀₀ Br and (d) TL₁₀₀ BrD_m.

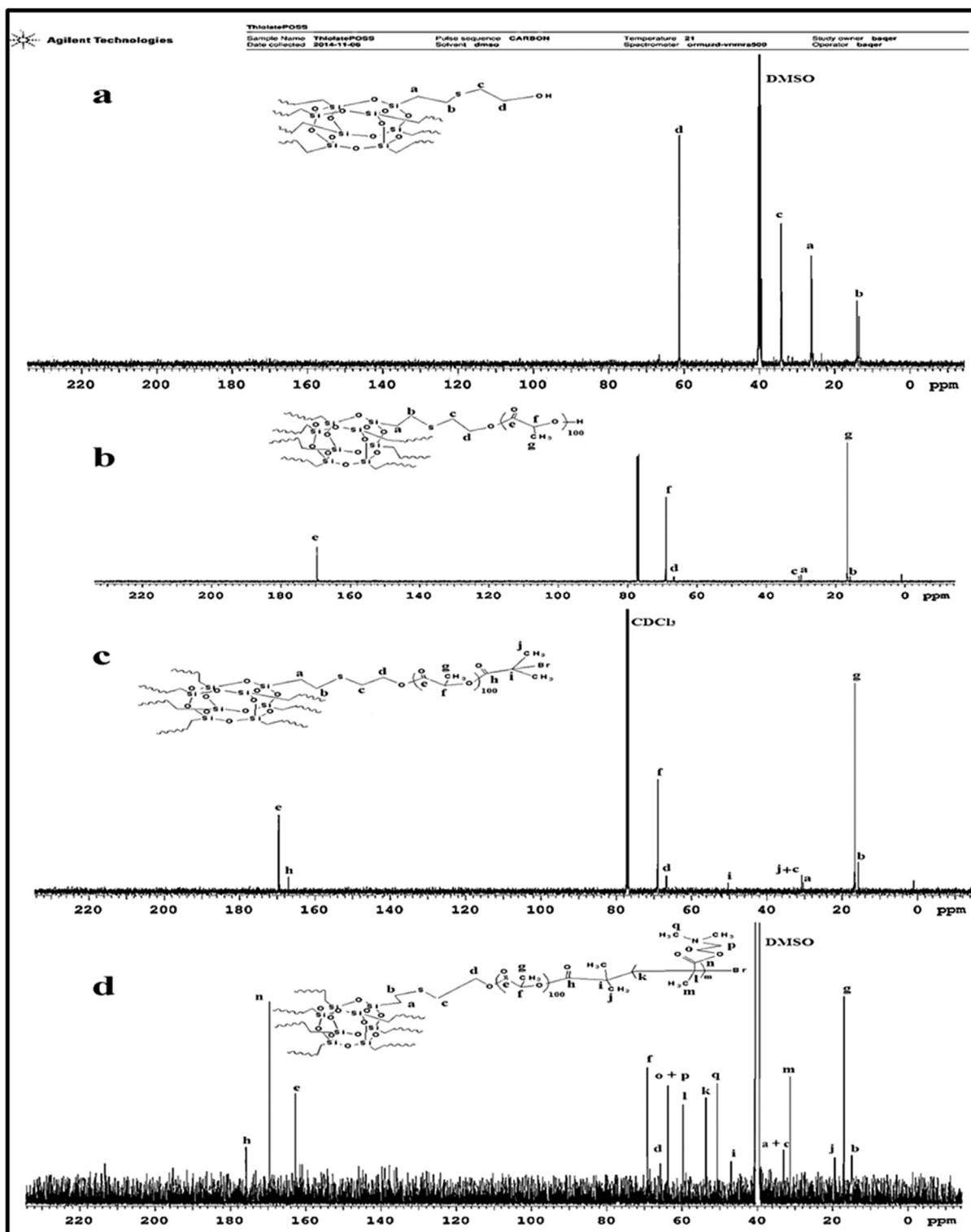


Fig. 2. ¹³C NMR Spectrum of: (a) Thiolate POSS, (b) TL₁₀₀, (c) TL₁₀₀ Br and (d) TL₁₀₀ BrDm.

protons (CH, d), at about 1.6 ppm representing the methyl (CH₃, e) protons of repeated unit of lactide segment, the signal at about (2.75–3, f) ppm for hydroxyl groups at the end chains of polymers. The ¹H NMR spectra of copolymers shows the proton of (CH₃) groups of DMAEMA (that is bonded to nitrogen atom) appears at around 2.55 ppm (k), the protons in (CH₂) and (CH₃) groups in the repeated unit of DMAEMA appear at around (2.05 and 1.9 ppm, respectively) (g and h), and the protons in (CH₂) groups in branched part of DMAEMA (i and j) appear at around (4.15 and 3.35 ppm, respectively).

¹³C NMR of the two polymers shows a signal at about 170 ppm representing the carbon atom of the carbonyl group of lactide repeated unit (e), a signal at about 69 ppm for the carbon atom of the methylene group (CH, f), and at about 17 ppm representing the carbon atom of a methyl group (CH₃) of L-lactide (g). The ¹³C NMR spectra of copolymers show the carbon atoms in (CH₃) groups of DMAEMA (that is bonded to nitrogen atom) appear at around 48 ppm (q), the carbon atoms in (CH₂) and (CH₃) groups in repeating unit of DMAEMA appear at around (54 and 58 ppm, respectively) (k and l), the carbon atoms in (CH₂) groups in branched part of DMAEMA (o and p) appear approximately at the same value at around (64 ppm respectively), while the carbon atom of a methyl group (CH₃) (which is near to the repeating unit of DMAEMA)(m) appears at about 27 ppm and the carbon atom of the carbonyl group of DMAEMA appears at about 170 ppm (n).

All these spectroscopic examinations of the prepared copolymers, i.e. FTIR, ¹H NMR and ¹³C NMR, verified the suggested structure for the prepared copolymers and promoted this matter to a great accuracy with the results of GPC and having polydispersity

index (PDI) close to unity. The molecular weight and polydispersity index (M_w/M_n) were determined for all prepared polymers and copolymers and Table 4 shows the GPC results.

3.3. Scanning electron microscopy (SEM)

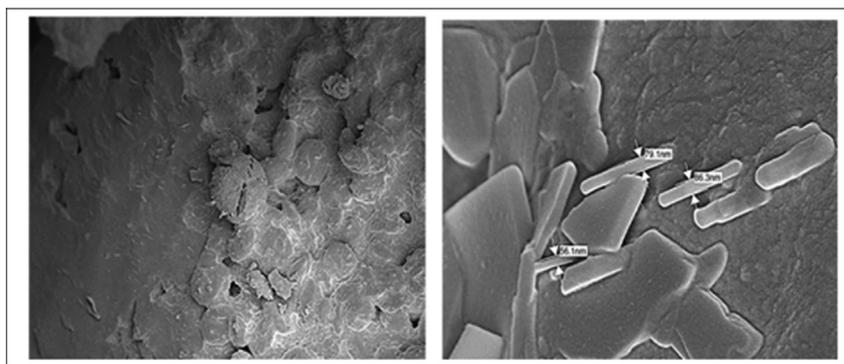
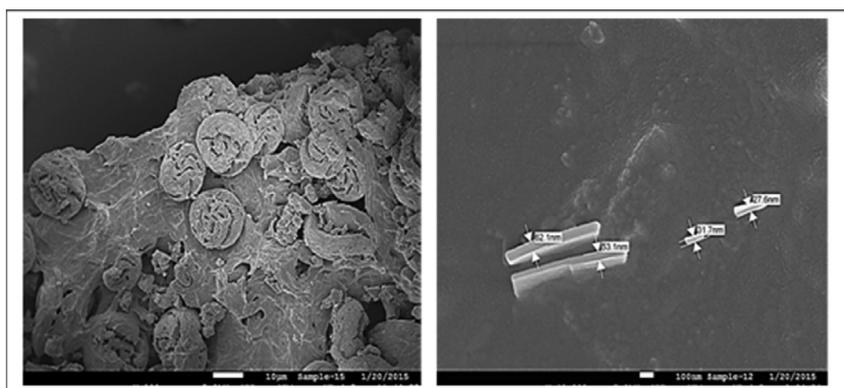
The examination of the morphology and the nanoparticles geometry of the prepared copolymers were performed by using SEM at different amplifications (10 μm and 100 nm). Figs. 3 and 4 manifest the SEM micrographs of the examining diblock copolymers, TL₂₅BrD_m and TL₁₀₀BrD_m, respectively. The micrographs obtained from scanning electron microscope exhibited the size of the nanoparticles, and it was found to be in a range of (27.6–86.3) nm and the images of SEM measurements showed the size of the nanoparticles decreased with increasing L-lactide monomers chain length in the copolymers.

3.4. Thermogravimetric analysis

Thermal stability functions of the prepared copolymers were determined from the obtained thermograms as tangential decomposition temperature (initial decomposition temperature T_i), the degree of decomposition temperature at 50% loss of the sample weight (T_{50%}), the temperature of the final decomposition (T_f), char content at the end of the decomposition process, the rate of decomposition process and the activation energy of the decomposition process which calculated when the weight loss ratios depending on the Arrhenius equation. The results obtained are shown in Table 5. As it can be seen, the copolymers appear to have two main degradation stages. The copolymers lost about (18–35)% of their weight in their first stage between

Table 4
GPC results for prepared polymers and copolymers.

Polymers				
Polymer code	M _n calculated (Daltons)	M _n found (Daltons)	M _w found (Daltons)	Polydispersity index (PDI)
TL ₁₀	7020	7100	8160	1.15
TL ₂₅	15,670	15,650	17,360	1.11
TL ₅₀	30,080	30,000	33,000	1.10
TL ₁₀₀	58,910	58,950	61,130	1.04
Copolymers				
Copolymer code	Value of (m)	M _n (Daltons)	M _w (Daltons)	Polydispersity index (PDI)
TL ₁₀ BrD _m	12	23,260	25,070	1.08
TL ₂₅ BrD _m	31	55,860	59,240	1.06
TL ₅₀ BrD _m	58	104,180	121,660	1.17
TL ₁₀₀ BrD _m	116	205,860	284,760	1.38

Fig. 3. SEM micrograph of TL₂₅BrDm.Fig. 4. SEM micrographs of TL₁₀₀BrDm.

(178–215) °C and about (47–64)% in their second stage between (290–330) °C depending on lactide units in the copolymer compositions. The first degradation stage was attributed to the loss of lactide monomer and the (dimethylamino) ethyl groups from PDEAEM, released at this stage while the weight loss associated with the second degradation stage was attributed to the elimination of CO₂ and CO groups and to the carbonization processes [14].

The high thermal stability obtained may lead to more applications for these Lactide copolymers, because it is known that the polymers used in tissue engineering applications, loading drug applications and biological applications, may undergo modification and manipulation process with biological covalent links or with certain medicines, and this needs better thermal stability at temperatures higher than 70 °C sometimes to complete modification operations, and some lactide

Table 5

Thermal stability functions of (TL₁₀BrDm), (TL₂₅BrDm), (TL₅₀BrDm) and (TL₁₀₀BrDm) copolymers.

Copolymer code	Decomp. stage	T _i (°C)	T _f (°C)	Rate of decomp. % wt/min	Activation energy kJ·mol ⁻¹	Temp. range for activation energy (°C)	Weight loss (%)	Temp. of 50% weight loss (°C)
TL ₁₀ BrDm	1st decomp.	178	204	0.39	0.034	178–190	18.20	305
	2nd decomp.	290	319	0.43	0.035	290–300	64.41	
TL ₂₅ BrDm	1st decomp.	187	264	0.38	0.053	187–205	24.94	310
	2nd decomp.	302	338	0.41	0.037	302–310	57.83	
TL ₅₀ BrDm	1st decomp.	191	255	0.33	0.055	191–210	21.94	319
	2nd decomp.	308	379	0.34	0.050	308–318	63.21	
TL ₁₀₀ BrDm	1st decomp.	200	236	0.29	0.063	200–215	35.01	310
	2nd decomp.	319	380	0.31	0.083	319–330	47.33	

copolymers may show less thermal stability, and for this reason they are not good enough to be used on their own [15].

4. Conclusions

Nano eight arm poly{POSS lactide-b-N,N-(dimethylamino)ethyl methacrylate} copolymers were successfully synthesized by combining thiol-ene click chemistry and ring-opening polymerization with atom transfer radical polymerization. The Thiolate POSS was prepared with success firstly by Thio-Click reaction of Octavinyl POSS with 2-Mercapto ethanol with 77% yield, which is considered very good, then it was successfully extended by ROP of L-Lactide in the presence of DBU to prepare Thiolate-POSS-Lactide having a different chain length with yields ranging from 75 to 84% and low polydispersity indices, i.e. $D < 1.15$. Diblock having eight arms copolymers were positively synthesized when the Octa-functional ATRP initiators had different lactide chain length and fixed amount of N,N-(dimethylamino)ethyl methacrylate in a controlled manner via ATRP copolymerization with good yields and lower polydispersity indices. Spectroscopic examination of the copolymers by FTIR, ^1H NMR, and ^{13}C NMR along with GPC results confirmed the suggested structures with dispersity close to one. Nanostructures were obtained as shown by SEM micrographs due to the presence of lactide polymer chains and they were positively reflected in the copolymers thermal stability.

Acknowledgment

The authors would like to thank Prof. B. Borhan and Dr. K. Ashtekar from Chemistry Department/Michigan State University/USA, for their help and the valuable discussion during the time period of the work at the MSU.

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