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Synthesis and Thermal Properties of Poly(Poss Lactide-B- N-Hydroxyethyl Acrylamide) Nanostar-Shape Block Copolymers

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Abstract

A series of star-shaped poly(POSS lactide-b-N-hydroxyethyl acrylamide) block copolymers with different L-Lactide repeated units were synthesized in this work via atom transfer radical polymerization of N-hydroxyethyl acrylamide with POSS Lactide using Thiolate POSS-lactideisobutyryl bromide as ATRP initiator. Their syntheses were confirmed by Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (^{1}H NMR and ^{13}CNMR), gel permeation chromatography (GPC). The characterization of the copolymers was verified the expected structure and composition with the presence of nanofibre structure as examined by scanning electron microscope, and it was found that their size decreased with increasing L-lactide monomer chain length. This was positively reflected on their thermal stabilities determined from TGA micrographs like decomposition temperature at 50% loss of the sample weight, decomposition rate, and the char content at the end of the decomposition process.

Keywords

Nanostructure; Star copolymer; L-Lactide; POSS; Hydroxyethyl acrylamide

Introduction

Over the recent few years, mechanistic developments in the field of Controlled "Living" Radical Polymerization (CRP) are reviewed, and have undergone notable development and has become one of the most capable and vigorous synthetic methods in modern polymer chemistry [1]. CRP is interesting from both scientific and industrial viewpoints, as the discovery of these reactions opened up a whole new world of possibilities regarding the design of novel polymeric architectures and compositions [2]. CRP means that a polymerization reaction, where no unwanted side reaction such as transfer or termination takes place, and where all polymer chains initiate simultaneously. Thus, the growing ends of the polymer chains are active indefinitely, and an ideal living system should yield polymers with predetermined molecular weight and narrow molecular weight distribution (Polydispersity Index, PDI = M_w/M_n) close to unity.

Among the controlled radical polymerization processes, Atom Transfer Radical Polymerization (ATRP) was the most successful approach [3]. It controls via a reversible redox reaction between alkyl halides and transition metal complexes. The first report in ATRP was announced by Kato et al. using dichlorotris (triphenylphosphine) ruthenium (II), $RuCl_2(PPh_3)_3$ as a catalyst system for the polymerization of methyl methacrylate (MMA) monomer initiated by carbon tetrachloride (CCl_4).The second system reported by concerning polymerization of styrene catalyzed by CuCl/2,2'-bipyridyl (bpy) in the presence of 1-phenylethyl chloride as an initiator [4,5].

Moreover, Teodorescu and Matyjaszewski have studied the polymerization of methacrylamide using model R-haloamide based initiators to obtain well-defined block copolymers [6]. Furthermore, 2-chloropropionamide as an initiator was used in the polymerization of N-isopropylacrylamide monomers with a small polydispersity index to study the influence of end group functionalization on thermal properties of polymers [7]. A five-arm star-shaped poly(ethylene oxide) with terminal bromide groups was synthesized by and used as a macroinitiator for the atom transfer radical polymerization of tert-butyl acrylate (tBA), resulting in five-arm star-shaped poly(ethylene oxide)-blockpoly(tert-butyl acrylate) block copolymers, PEO-b-PtBA [8]. The polymerization proceeded in a controlled way using a copper (I) bromide/pentamethyldiethylenetriamine catalytic system in acetonitrile as solvent. The hydrolysis of the tBA blocks of the amphiphilic star-shaped PEO-b-PtBA block copolymer resulted in dihydrophilic star structures.

Herein, the work is demonstrating a synthesis of well-defined star-shaped block copolymers having eight armpoly(POSS lactide-b-N- hydroxyethyl acrylamide) inorganic/organic polymers prepared by atom-transfer radical polymerization with the increasing of N-hydroxyethyl acrylamides (HEA).Thus, we believe that increasing the number HEA polymer chains of arms will reflect positively on the thermal stabilities of the copolymers and to improve their different application efficiencies since they appear to have nanofiber structures.

Experimental Section

Materials

N-hydroxyethyl acrylamide, copper(I) bromide, N,N,N′,N′′,N′′-pentamethyldiethylenetriamine,and diethyl ether (Assay ≥ 99 %) Anhydrous N,N-Dimethylformamide (DMF) (Assay ≥ 99.8%) were purchased fromSigma-Aldrich Company.

Instruments

The FTIR spectra were obtained by Nicolet IR-42, Mid-IR spectrometer using KBr pellets. 1H NMR and 13C NMR spectra were recorded by nuclear magnetic resonance spectroscopy using an Agilent DDR2 500MHz NMR spectrometer with dimethyl sulfoxide-d6 (Sigma-Aldrich, 99.9 atom % D) as a solvent. Copolymer 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 the poly(methyl methacrylate) standard.

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Computer controlled thermal analysis Instrumentals, TGA-Q500 V20.10 was used with heating rate 25°C/min under a nitrogen atmosphere. Microscope images were taken to the prepared copolymers using Scanning Electron Microscopy type JEOL 7500F.

Methods

Preparation of thiolate POSS-lactideisobutyryl bromide (TLnBr)

Thiolate POSS-lactideisobutyryl bromide (TLnBr where n= 10, 25, 50 and 100) was prepared asdescribed in our previous work [9]. It was used as an ATRP initiator.

General procedure for synthesis of poly(POSS lactide-b-N-hydroxyethyl acrylamide) ($TL_{10}BrN_m$)

Thiolate POSS-lactide-isobutyryl bromide (0.4g, 0.00005mole), N-hydroxyethyl acrylamide (HEA) (0.8 g, 0.007 mole), copper (I) bromide (0.05g) and N,N,N′,N″,N″-pentamethyldi-ethylenetriamine (PMDETA) (20 µl) were dissolved in DMF (15 ml) at 60ºC. After stirring for one hour under a nitrogen atmosphere, the reaction was stirred for a further 14 hours at 60ºC. Afterward, the product is 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(15ml). The copolymer was recovered through column chromatography on silica gel (200-400 mesh), DMF was removed by rotary evaporator and the copolymer was dried in vacuum oven at 25ºC for 24 hours (Solid, 71% yield).

The same procedure was carried out to prepare the other block copolymers ($TL_{25}BrN_m$), ($TL_{50}BrN_m$) and ($TL_{100}BrN_m$). Table 1 shows the quantities of reactants used in the preparation and the chemical equations can be represented by the Scheme 1 of these copolymers.

Results and Discussion

Characterization

The FT-IR spectra of the new block copolymers($TL_{10}BrNm$, $TL_{25}BrNm$, $TL_{50}BrNm$, and $TL_{100}BrNm$)are shown in Figure 1. The IR spectra of polymers that are prepared to have Thiolate POSS and L-lactide in their structure exhibited characteristic absorption bands due to the hydroxyl groups in the region of (3510 cm^{-1}), and intense bands due to the (C=O) groups around (1750 cm^{-1}). The spectra demonstrated an interestingabsorption peak at 1650 cm^{-1} assigned to the carbonyl of the amide group, and bands at around (3060 cm^{-1}) assigned to (N-H) bonds indicating that the prepared macro initiator polymer reacted with N-hydroxyethyl acrylamide. It is also designatedthe characteristic absorption intense bands due to the C-Br bonds at (680 cm^{-1}).

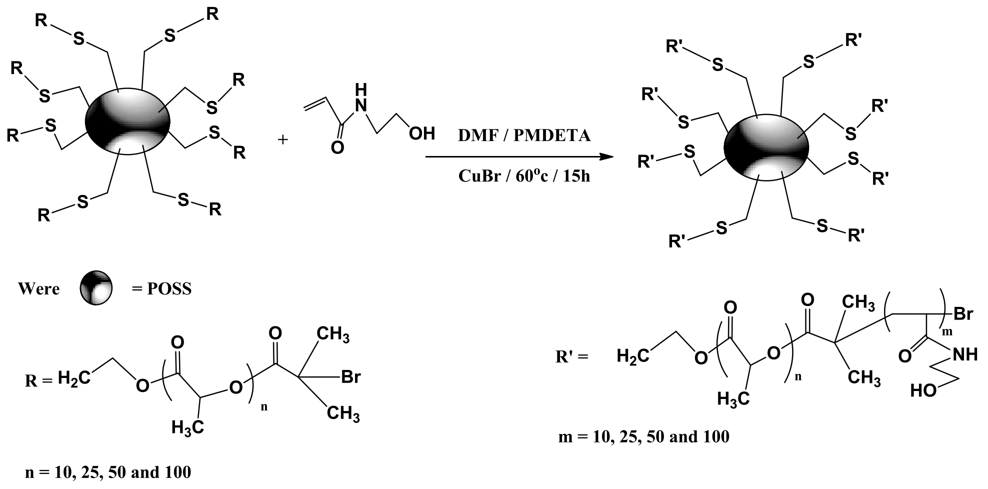
^1H NMR and ^{13}C NMR of ($TL_{10}BrN_m$, $TL_{25}BrN_m$, $TL_{50}BrN_m$, and $TL_{100}BrN_m$) copolymers were recorded on Agilent DDR2 500MHz NMR spectrometer using dimethyl sulfoxide-d6 (Sigma-Aldrich, 99.9 atom % D) as a solvent. Figures 2 and 3 represent ^1H NMR and ^{13}C NMR spectra for these synthesized star-shaped multi-armed block copolymers.

The ^{13}CNMR spectra of copolymers are shown in Figure 3. The peaks at 18 (g), 68 (f) and 164 (e) ppm were assigned to the poly(L-Lactide) blocks. The peaks appeared at 42 (n), 49 (k) were attributed to two methylene units and at 55 (l) ppm for methane, carbon and at 169 (m) for carbonyl carbon of N-hydroxyethylacrylamide. All these spectroscopic examinations of the prepared copolymers verified the suggested structure of the prepared copolymers.

Copolymers molecular weights and molecular weight distributions (Mw/Mn) were determined using a Waters 1515 gel

Table 1: The quantities of reactants used in the preparation of the copolymers.

Copolymer Code	Amount of TL_nBr		Amount of HEA		Wt. of CuBr (g)	Volume of PMDETA (µl)	Yield (%)	Physical state
	Weight (g)	No. of moles	Weight (g)	No. of moles				
$TL_{25}BrN_m$	0.4	0.00002	0. 8	0.007	0.05	20	70	solid
$TL_{50}BrN_m$	0.4	0.00001	0. 8	0.007	0.05	20	68	solid
$TL_{100}BrN_m$	0.4	0.000007	0. 8	0.007	0.05	20	72	solid



Scheme 1: Representative chemical equation of preparation the copolymers (TL10BrNm), (TL25BrNm), (TL50BrNm) and (TL100BrNm) Where (n= 10, 25, 50 and 100), (m≈ 10, 25, 50 and 100).

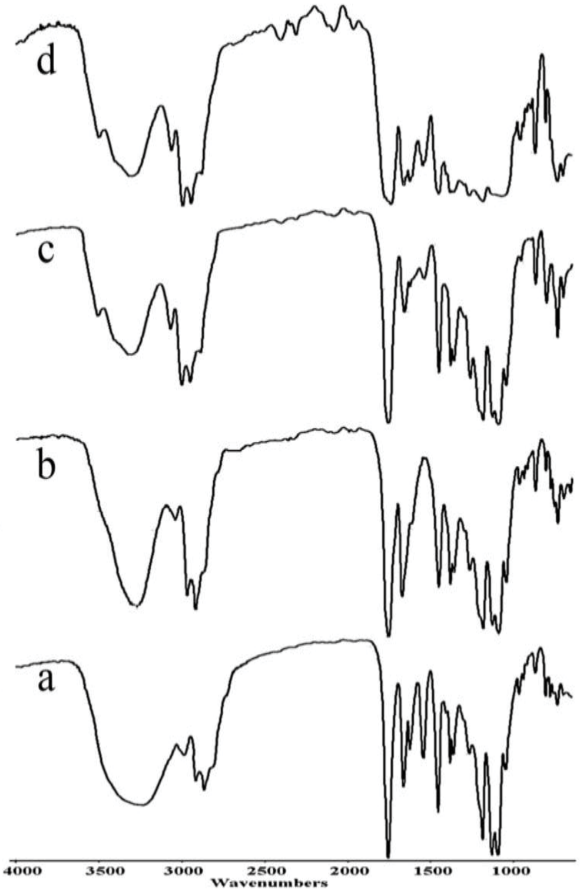


Figure 1: FT-IR spectra of: (a) TL10BrNm, (b) TL25BrNm, (c) TL50BrNm and (d) TL100BrNm.

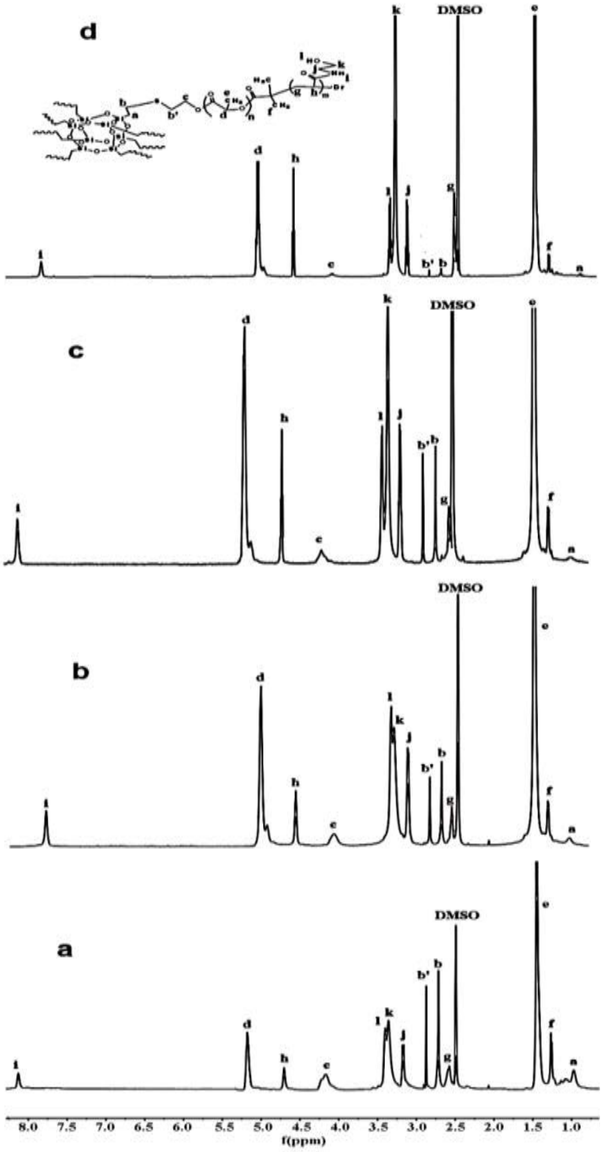


Figure 2: ^{1}H NMR spectra of: (a) $TL_{10}BrNm$, (b) $TL_{25}BrNm$, (c) $TL_{50}BrNm$ and (d) $TL_{100}BrNm$.

permeation chromatography (GPC) equipped with a refractive index detector (Waters 2412). DMF was used as the eluent solvent at a flow rate of 1.0 mL/min and calibrated with poly(methyl methacrylate) standard and the results obtained are shown in Table 2. These results revealed that nearly monodisperse copolymers with polydispersity indices (PDI) close to one were prepared, and demonstrated the convergence between the theoretical and practical values of polymers and block copolymers molecular weights.

Microstructure

Morphologicalexamination of the preparedness copolymers was performed by using scanning electron microscope type JEOL 7500F supplied by JEOL company/USA. Figures 4 and 5 show the SEM micrographs of examining copolymers.The micrographs exhibited the presence of poly(L-lactide) nanofibers in a size ranging from (49.7-61.1) nm, Figure 4, and in a range of (40.1-49.3) nm, Figure 5, depending on the number of the lactide repeated units in the polymer chains, 25 and 100 units respectively.

Thermal Stability

Thermal stability of the prepared copolymers was studied using computer controlled thermal analysis instrument type TGA-Q500 V20.10. Figure 6 shows the resulted thermograms and the calculated thermal functions obtained from the thermal analysis like initiation and final decomposition temperatures, T_i and T_f, the rate of decomposition, the activation energy of the decomposition, 50% weight loss temperature T_{50} and char content for first decomposition and second decomposition are listed in Table 3. Thermal gravimetric analysis indicates that the initial decomposition temperature (T_i) ranges between 169-200°C for the first decomposition and between 239-318°C for the second decomposition.

Examining the TG curves obtained, Figure 6, has shown that the copolymers are composed of two segment types with very distinct thermal stabilities that can be ascribed to the poly(L-Lactide) and N-hydroxyethyl acrylamide segments. All the copolymers showed dual-step decomposition. The first stage of ~20 % weight loss around 160-180°C can be attributed to the elimination of water and formaldehyde molecules as a result of the cross linking reaction between free hydroxyl groups present in the polymer chains into

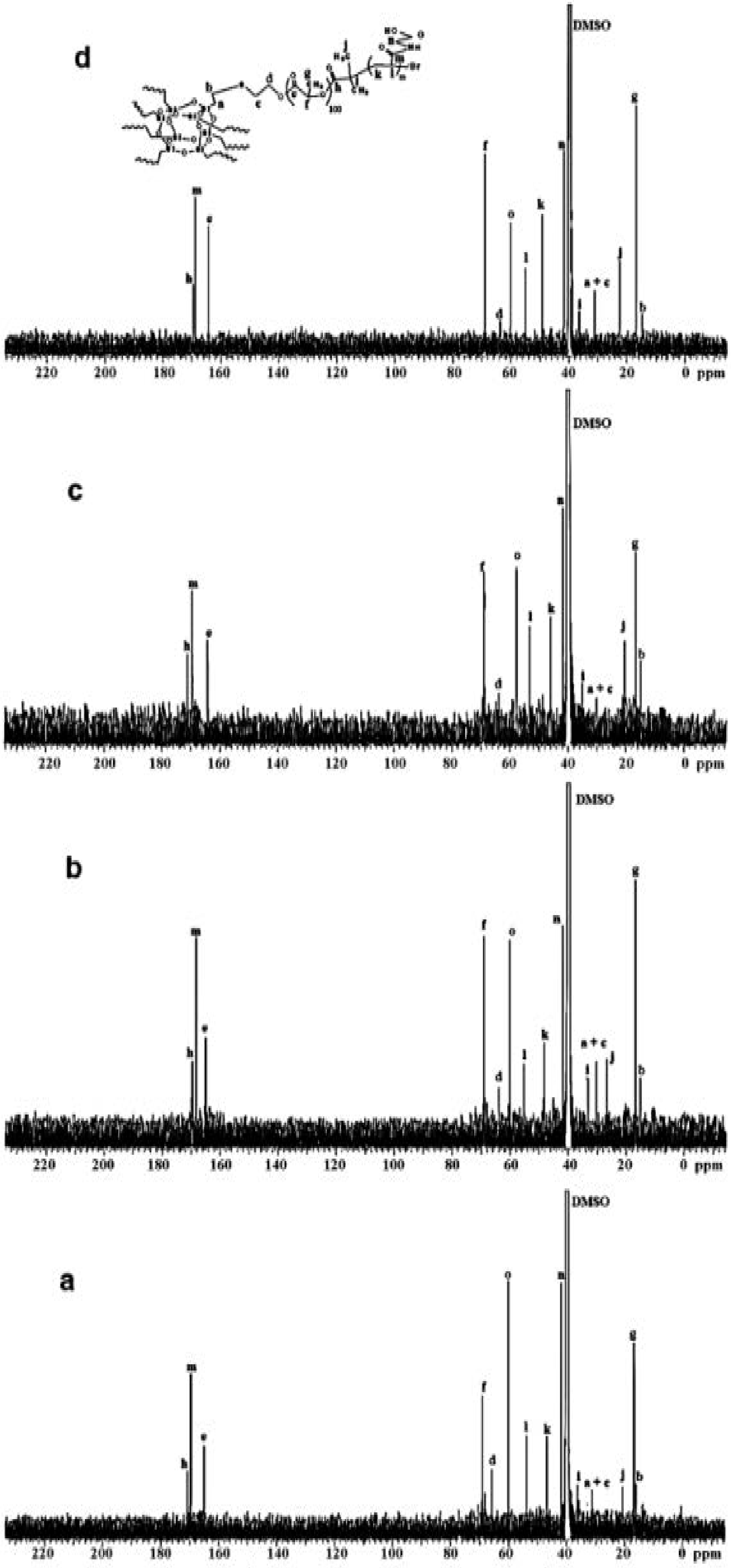


Figure 3: ^{13}C NMR spectra of: (a) $TL_{10}BrN_m$, (b) $TL_{25}BrN_m$, (c) $TL_{50}BrN_m$ and (d) $TL_{100}BrN_m$.

Table 2: GPC resultsof the prepared star shaped block copolymers.

Polymer Code	Value of (m)	M_n (Daltons)	M_w (Daltons)	Polydispersity Index (PDI)
$TL_{10}BrN_m$	13	20140	21670	1.08
$TL_{25}BrN_m$	30	44500	50770	1.14
$TL_{50}BrN_m$	60	86480	93180	1.08
$TL_{100}BrN_m$	115	165940	176660	1.06

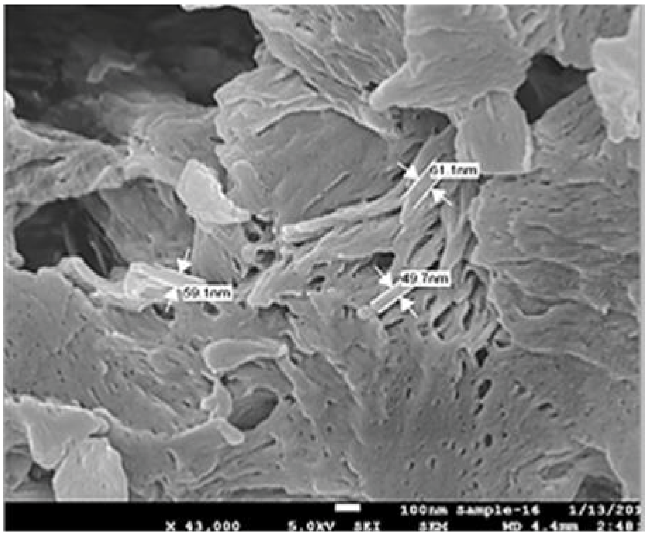


Figure 4: SEM micrograph of $TL_{25}BrN_m$.

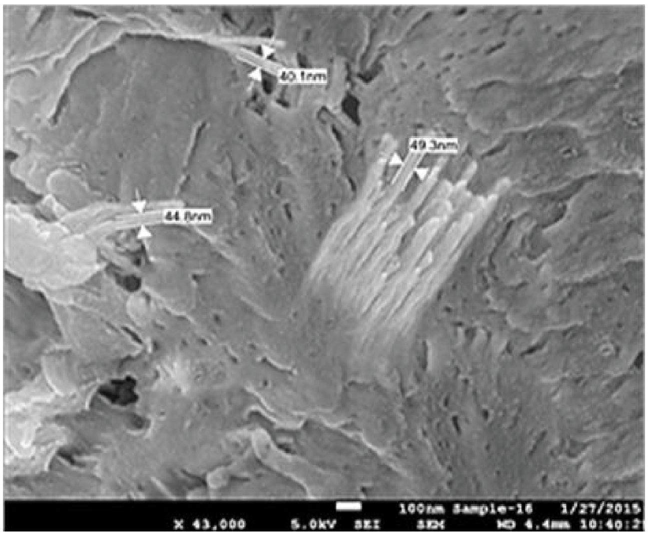


Figure 5: SEM micrograph of $TL_{100}BrN_m$.

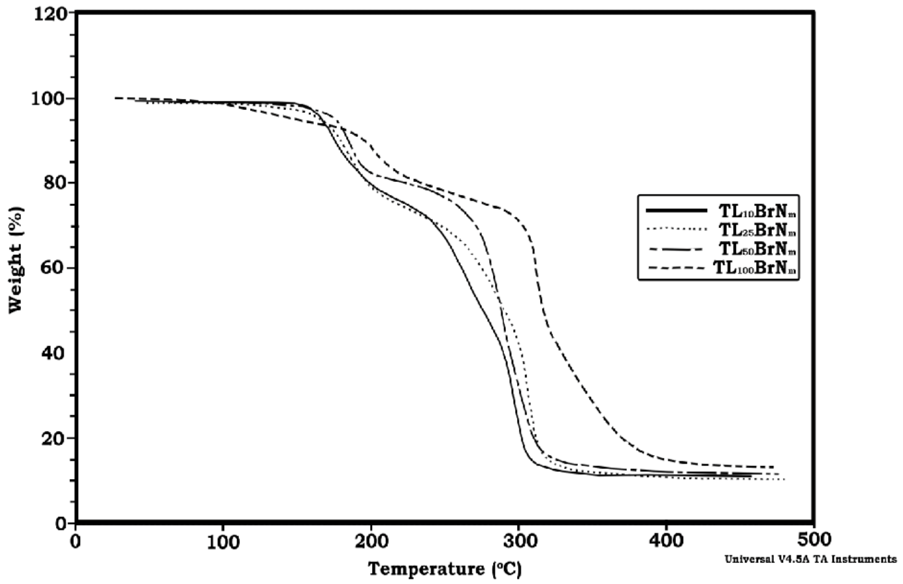


Figure 6: TGA thermograms of $TL_{10}BrNm$, $TL_{25}BrNm$, $TL_{50}BrNm$ and $TL_{100}BrNm$.

methylol groups[10,11]as illustrated in the following equation where (R) represents a polymer chain:

$$\left[2R-\overset{H}{N}-CH_2OH\xrightarrow[-H_2O]{Heat}R-\overset{H}{N}-CH_2O-CH_2.NH-R\xrightarrow[-HCHO]{Heat}R-\overset{H}{N}-CH_2-NH-R\right]$$

and the second degradation step at a higher temperature (higherthan 138°C) can be related to the PLLA segment chain end “unzipping” mechanism and to N-hydroxyethyl acrylamide [12].

The excellent thermal stability of poly(POSS lactide-b-N-hydroxyethyl acrylamide) Nano block copolymers obtained may enhance new applications for these Lactide copolymers in different Bioengineering applications, especially in drug delivery or in tissue engineering might be subjected to or undergo modification and manipulation process [13,14]. This means that they should have higher thermal stability because most previous modification processes need temperatures higher than 70°C to be completed.

Table 3: Thermal stability functions of ($TL_{10}BrNm$), ($TL_{25}BrNm$), ($TL_{50}BrNm$) and ($TL_{100}BrNm$) copolymers.

Copolymer Code	Decomp. Stage	T_i (ºC)	T_f (ºC)	Rate of Decomp. (%Wt/min)	Activation Energy (kJ.mol^{-1})	Temp. Range for Activation Energy (ºC)	Wt% Loss (%)	Temp. of 50% Wt. Loss (ºC)
$TL_{25}BrNm$	**1st decomp.**	169	202	0.78	0.020	161-175	21.18	275
	2nd decomp.	239	308	1.06	0.023	239-244	66.83	
$TL_{25}BrN_m$	**1st decomp.**	166	209	0.43	0.028	166-180	23.64	285
	2nd decomp.	251	317	0.87	0.024	251-265	64.13	
$TL_{50}BrN_m$	**1st decomp.**	176	214	0.43	0.031	175-190	18.86	290
	2nd decomp.	267	319	0.55	0.024	266-275	68.51	
$TL_{100}BrN_m$	**1st decomp.**	200	236	0.29	0.063	200-215	35.01	315
	2nd decomp.	318	379	0.32	0.079	317-328	45.93	

Conclusion

In summary, we reported for the well-defined new star shaped eight-armed block copolymers composed from POSS Lactide and N-hydroxyethyl acrylamide, and they were successfully prepared by atom transfer radical polymerization. Spectroscopic examination by FT-IR, ^{1}H NMR and ^{13}C NMR verified the suggested copolymer structures. GPC results also revealed that all the copolymers are of nearly monodisperse with very narrow distributions accompanied by nanofiber structures as shown by SEM micrographs and their sizes are affected by the length of lactide polymer chains. The thermal gravimetric results showed that the initial and final decomposition temperatures for the preparing block copolymers increased with the increasing of lactide repeated units, whereas the rate of decompositions decreased with the increasing of lactide repeated units.

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