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

Baqer A. Al-Mayyahi, Athir M. Haddad, Hadi S. Al-Lami*

Department of Chemistry, College of Science, University of Basrah, Basrah, Iraq

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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 (^{1}H 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.

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

* Corresponding author. Fax: +964 7707377488.
E-mail address: hadisalman54@yahoo.com (H.S. Al-Lami).
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levels. Since this discovery, a vast range of organocatalysts 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 ($PDI = M_w/M_n$) 1.05. The sampling of a polymerization reaction exhibited a linear increase of Mn 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 Mn 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(1) 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 ≥ 98%), 2-Bromoisobutyryl bromide (Assay ≥ 98%) 2,2-dimethoxy-2-phenylacetophenone, Diethyl ether (Assay ≥ 99%) and Magnesium sulfate were purchased from Sigma–Aldrich of USA, dichloromethane (DCM), dimethylformamide (DMF) (Assay ≥ 99.8%) and Triethylamine (Assay ≥ 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}H-NMR and ^{13}C-NMR spectra were recorded using Agilent DDR2 500 MHz NMR spectrometers/Bruker US-based. Copolymers molecular weights and molecular weight distributions (Mw/Mn) were determined using a Waters 1515 gel permeation chromatography (GPC) calibrated with the poly(methyl methacrylate) standard.

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