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 pentamerthyl-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 nanostucture 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)3 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 Dhamodaran [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(pentaerythritolactide-b-N,N-dimethylaminoethyl methacrylate) 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″-pentamethyldiethylenetriamine, magnesium sulfate, CDCl3 and dimethyl sulfoxide-d6 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 PLxBrDm, PLxBrDm, and PLx10BrDm copolymers.

<table>
<thead>
<tr>
<th>Copolymer Code</th>
<th>Amount of PLxBr (g)</th>
<th>No. of moles</th>
<th>Weight of DMAEMA (g)</th>
<th>No. of moles</th>
<th>Weight of CuBr (g)</th>
<th>Volume of DMF / PMDETA (µL)</th>
<th>Yield (%)</th>
<th>Physical state</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLx25BrDm</td>
<td>0.4</td>
<td>0.00003</td>
<td>0.8</td>
<td>0.005</td>
<td>0.05</td>
<td>20</td>
<td>67</td>
<td>Solid</td>
</tr>
<tr>
<td>PLx50BrDm</td>
<td>0.4</td>
<td>0.00003</td>
<td>0.8</td>
<td>0.005</td>
<td>0.05</td>
<td>20</td>
<td>71</td>
<td>Solid</td>
</tr>
<tr>
<td>PLx100BrDm</td>
<td>0.4</td>
<td>0.00001</td>
<td>0.8</td>
<td>0.005</td>
<td>0.05</td>
<td>20</td>
<td>69</td>
<td>Solid</td>
</tr>
</tbody>
</table>

Figure 1. Synthesis of prepared the copolymers PLxBrDm, PLxBrDm, and PLx10BrDm (m = 10, 25, and 50).

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

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

Copolymer PLx10Br: Color: White. Yield: 70%. FT-IR (KBr, ν, cm⁻¹): 2991 (C-H), 1741 (C=O), 1195 (C-O), 649 (C-Br). H NMR (500 MHz, CDCl₃, δ, ppm): 5.3 (O-CH), 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 (0-CH-CH₃ group in repeating unit of L-lactide segments).

Copolymer PLx25Br: Color: White. Yield: 70%. FT-IR (KBr, ν, cm⁻¹): 2996 (C-H), 1746 (C=O), 1197 (C-O), 647 (C-Br). H NMR (500 MHz, CDCl₃, δ, ppm): 5.3 (O-CH), 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 PLx50Br: Color: White. Yield: 76%. FT-IR (KBr, ν, cm⁻¹): 2998 (C-H), 1751 (C=O), 1198 (C-O), 641 (C-Br). H NMR (500 MHz, CDCl₃, δ, ppm): 5.3 (O-CH), 5.17 (O-CH groups of repeating unit of L-lactide).

2.4. Synthesis of four arms poly(pentaerythritol-lactide-b-N,N-dimethylaminoethylmethacrylate) (PL₁₀BrDm)

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‴-pentamethyldiethylenetriamine (PMDETA) (20 µL) were dissolved in 15 mL dimethylformamide (DMF) at 60 °C. After stirring for 1 h under nitrogen atmosphere, the reaction was stirred for 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 PL₁₀BrDm, PL₁₀BrDm, and PL₁₀BrDm. 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 PL₁₀BrDm: Color: Light green. Yield: 65%. FT-IR (KBr, ν, cm⁻¹): 1741 (C=O), 1133 (N-C). H NMR (500 MHz, DMSO-d₆, δ, ppm): 5.19 (O-CH groups in branched part of DMAEMA), 4.2 (O-CH, 4.3 (O-CH), 3.4 (N-CH₂ groups in branched part of DMAEMA), 2.9 (N-CH₂ 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).
1H NMR (500 MHz, DMSO-d6, δ, ppm): 178 (C=O), 174 (C=O), 170 (C=O), 69 (CH=O), 63 (CH2=O), 59 (CH=O), 56 (C-quat.), 50 (CH3), 47 (CH=O), 44 (C-quat.), 32 (CH3), 20 (CH3), 17 (CH). 

**Copolymer Pl10BrDm**: Color: Light green. Yield: 67%. FT-IR (KBr, ν, cm⁻¹): 1746 (C=O), 1134 (N-C). 13C NMR (500 MHz, DMSO-d6, δ, ppm): 52 (O-CH groups in branched part of DMAEMA), 4.2 (O-CH3), 4 (O-CH3), 3.35 (N-CH2 groups in branched part of DMAEMA), 2.72 (CH2 groups of repeating unit of DMAEMA), 2.71 (CH2 groups of repeating unit of DMAEMA), 1.45 (O-CH2-CH3), 1.41 (CH). 1H NMR (500 MHz, DMSO-d6, δ, ppm): 177 (C=O), 170 (C=O), 169 (C=O), 69 (CH=O), 63 (CH2=O), 59 (CH=O), 56 (C-quat.), 50 (CH3), 47 (CH=O), 44 (C-quat.), 32 (CH3), 20 (CH3), 17 (CH).

**Copolymer Pl10BrDm**: Color: Light green. Yield: 71%. FT-IR (KBr, ν, cm⁻¹): 1751 (C=O), 1136 (N-C). 1H NMR (500 MHz, DMSO-d6, δ, ppm): 52 (O-CH groups in branched part of DMAEMA), 4.19 (O-CH3), 4.0 (O-CH3), 3.36 (N-CH2 groups in branched part of DMAEMA), 2.86 (N-CH2 groups in branched part of DMAEMA), 2.71 (CH2 groups of repeating unit of DMAEMA), 2.25 (CH groups of repeating unit of DMAEMA), 1.45 (O-CH2-CH3), 1.41 (CH). 13C NMR (500 MHz, DMSO-d6, δ, ppm): 176 (C=O), 174 (C=O), 170 (C=O), 69 (CH=O), 64 (CH2=O), 62 (CH3-CH-O), 60 (CH-O), 58 (C-quat.), 50 (CH3), 48 (CH=O), 44 (C-quat.), 30 (CH3), 22 (CH3), 17 (CH).

**Copolymer Pl10BrDm**: Color: Light green. Yield: 76%. FT-IR (KBr, ν, cm⁻¹): 1745 (C=O), 1133 (N-C). 1H NMR (500 MHz, DMSO-d6, δ, ppm): 5.19 (O-CH groups in branched part of DMAEMA), 4.19 (O-CH3), 4.1 (O-CH3), 3.34 (N-CH2 groups in branched part of DMAEMA), 2.86 (N-CH2 groups in branched part of DMAEMA), 2.72 (CH2 groups of repeating unit of DMAEMA), 2.26 (CH2 groups of repeating unit of DMAEMA), 1.45 (O-CH2-CH3), 1.41 (CH). 13C NMR (500 MHz, DMSO-d6, δ, ppm): 175 (C=O), 174 (C=O), 169 (C=O), 69 (CH=O), 64 (CH2=O), 62 (CH3-CH-O), 59 (C-quat.), 51 (CH3), 48 (CH=O), 44 (C-quat.), 31 (CH3), 20 (CH3), 17 (CH).

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 PL50BrDm, PL100BrDm, PL25BrDm and PL10BrDm showed characteristic intense absorption bands due to the v(N-C) groups at 1133, 1136 and 1133 cm⁻¹, respectively, and the v(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 PL50BrDm, PL100BrDm, PL25BrDm and PL10BrDm copolymers was recorded by using dimethyl sulfoxide-d6 as solvent. The signals belong to the O-CH=O, O-CH=CH2 and CHX3 groups in repeating unit of L-lactide segments of the synthesized all copolymers were 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 CH=CH2 and CHx2 groups in repeating unit of DMAEMA and O-CH2 N-CH2 N-CH2 groups in branched part of DMAEMA were showed around at δ 6.2, 3.4, 3.1 and 2.9 ppm, respectively.

3.3. Copolymers molecular weight and polydispersity index

The molecular weight and the polydispersity index (Mw/Mn) 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 PL50BrDm and PL100BrDm 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 T1 and Ti, rate of decomposition, the activation energy of the decomposition, temperature of 50% weight loss (T50), and char content for first and second decomposition step.
Thermal gravimetric results indicates that the initial decomposition temperature (T₁) 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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