Solvent free microwave assisted preparation of new telechelic polymers based on poly(ethylene glycol)

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Abstract. Poly(ethylene glycol) bis (methylimidazolium chloride) (PEGBMIM) with average molecular weights of 600 and 1000 g/mol and poly(ethylene glycol) bis (2-oxazoline) (PEGBOX) with average molecular weight of 600 g/mol have been prepared using microwave irradiation under solvent-free condition. The method described herein is a very good, safe, clean, economical and environmentally friendly alternative to the classical procedures. The resulted products have been characterized by common spectroscopic methods, such as FT-IR (Fourier transform infrared spectroscopy), ¹H NMR (Nuclear magnetic resonance of proton) and elemental analysis. Also, the effects of power levels and irradiation time on the yield of reactions and solubility of products have been studied.

Keywords: polymer synthesis, molecular engineering, green chemistry, microwave, ionic liquid

1. Introduction

Telechelic compounds have found considerable interest as versatile intermediates in many fields. Among these poly(ethylene glycol)-based telechelic compounds due to their salient properties are dominant for many applications in peptide synthesis, modification of enzymes and pharmaceutical industry and so on. Most of these applications require certain end-groups. Therefore, telechelic modification is an important prerequisite for the practical use of such basis telechelics as poly(ethylene glycol) [1–7].

The development of cleaner technologies is a major emphasis in green chemistry. Among the several aspects of green chemistry, using efficient and less hazardous energy sources such as microwave energy is recommended. Polymer synthesis assisted by microwave (MW) has seen spectacular growth over the last few years, specially when this new

technique has been coupled with solvent-free procedures, resulting in clean, easy-to-perform, cheap, safe and environmentally friendly conditions which are widely used as synthetic tools under ‘Green Chemistry’ conditions [8–13]. Therefore, we decided to prepare poly(ethylene glycol) containing imidazolium, which is an ionic liquid, and oxazoline end groups using such a green condition.

Ionic liquids are emerging as a set of new green solvents, mainly as a replacement for conventional volatile organic solvents. Ionic liquids containing 1,3-disubstituted imidazolium cations have shown great promise as an attractive alternative to conventional solvents. The important properties of these ionic liquids are low volatility, negligible vapor pressure, ease of handling, accelerated reaction rates and potential for recycling [13–19]. The preparation of the 1,3-dialkylimidazolium halides via conventional heating method in refluxing the

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solvents requires long time to afford reasonable yields and also need to use a large excess of alkyl halides/organic solvents as the reaction medium in contrast with a few minutes of reaction time using microwave [13, 14, 19]. Although for many years oxazoline and its derivatives played an important role in organic chemistry. They were used, for example as chiral catalysts or optically active reagents. Among all of the possible isomers 1,3-oxazoline (2-oxazoline) was the most frequently used [20].

The last few years have brought a growing interest in oxazoline compounds among polymer chemists. Polymer chemistry profits from very high reactivity of oxazoline groups in many ways [21–24]. The examples of using oxazoline functionality for grafting [21], ring opening polymerization [25] or introducing double bonds into polymer [26] are described. Bis-oxazoline compounds were applied as linear chain extenders for polyesters [27, 28] and polyamides [28]. Oxazoline macromonomers [29–31] were used to synthesize hyperbranched polymers of various structures [32]. Oxazoline-grafted polymers were used as a nonionic hydrogel for metal complexation [33].

Polymers with oxazoline ring functionality could be obtained by several methods. Reaction between polymer functional groups (acidic, amine) with oxazoline derivatives or bis-oxazoline compounds [26] is one of those. In the present work we have prepared the functional polymer using poly(ethylene glycol) 600 diacid (PEGDA) and α,α,α -tris(hydroxymethyl)methylamine. The direct condensation of carboxylic acids with β -hydroxylamines requires high temperatures and strongly acidic conditions [34] and therefore is not a synthetically valuable method to access these heterocycles. Here we report the preparation oxazoline ring at the end of a poly(ethylene glycol) under solvent-free condition using microwave irradiation.

Although new hydrophilic ionic liquids, based on poly(ethylene glycol), which are potentially important due to their applications in molecular engineering, secondary batteries, sensors and electrochromic displays have been prepared using the same method.

2. Experimental

2.1. Materials

1-Methylimidazolium, α,α,α -tris(hydroxymethyl)methylamine, thionyl chloride, and poly(ethylene glycol) with average molecular weights of 600 and 1000 (Merck) and poly(ethylene glycol) diacid with average molecular weights of 600 was purchased from Fluka.

2.2. Instruments

The ^1H NMR spectra of the products recorded on a FT.NMR-Bruker (400 MHz) spectrometer. The FT-IR spectra obtained on a Bruker FT-IR, Tensor 270 spectrometer. Elemental analysis performed using an Elementar, Vario EL III. Reactions were performed in a domestic microwave oven Butan.

2.3. General Procedure

2.3.1. PEGBMIM (a, b)

Dichloro poly(ethylene glycol) (PEGCl) with different average molecular weights (5 mmol) which were prepared from related poly(ethylene glycol) and thionylchloride [6] and 1-methylimidazole (11 mmol) were placed in a an open glass container. The mixture was irradiated and stirred intermittently in an unmodified household microwave oven under reaction conditions which are outlined in Table 1 (During the reaction the temperature of the mixture reached 115°C). After it was allowed to cool to room temperature, diethylether (5 ml) was added into the mixture to remove excessive starting materials. The residue was washed with diethylether several times and it was vacuum-dried in a desiccator.

Poly(ethylene glycol) bis (methylimidazolium chloride) 1000 g/mol (a)

IR (KBr, cm^{-1}): $\nu = 3107\text{--}3150$ (aromatic C–H stretching), 1633 (aromatic C=N stretching), 1469, 1350 (CH_2 bending), 1136 (C–O stretching), 625, 655 (aromatic C–H oop). ^1H NMR (400 MHz, CDCl_3 , ppm): $\delta_{\text{H}} = 3.55$ (m, O– CH_2 – CH_2 –O), 3.77 (2H, t, O– CH_2 – CH_2 –N), 3.94 (3H, s, N– CH_3), 4.48 (2H, t, N– CH_2 – CH_2 –O), 7.44, 7.64 (2H, C(4,5)–H), 9.87 (1H, C(2)–H).

Elemental analysis: Calculated for $\text{C}_{52}\text{H}_{100}\text{Cl}_2\text{N}_4\text{O}_{21}$ (1217 g/mol): 51.20 (C%), 8.61 (H%), 4.60 (N%).

Table 1. The yield of the obtained products under different reaction conditions

Product name	Reaction condition: MW/time [W/min]	Yield [%]
a	(300/2)+(300/5) ¹	20
a	(300/2)+(300/5)+(300/5)	36
a	(300/2)+(300/5)+(300/5)+(300/5)	57
a	(300/2)+(300/5)+(300/5)+(300/5)+(300/5)	70
a	(300/2)+(300/5)+(300/5)+(300/5)+(300/5)+(300/5)	83
b	(300/5)+(300/5)	28
b	(300/5)+(300/5)+(300/5)	34
b	(300/5)+(300/5)+(300/5)+(300/5)	58
b	(300/5)+(300/5)+(300/5)+(300/5)+(300/5)	67
b	(300/5)+(300/5)+(300/5)+(300/5)+(300/5)+(300/5)	76
c	(600/2)+(600/5)	30
c	(600/2)+(600/5)+(600/5)	45
c	(600/2)+(600/5)+(600/5)+(600/5)	64
c	(600/2)+(600/5)+(600/5)+(600/5)+(600/5)	67
c	(600/2)+(600/5)+(600/5)+(600/5)+(600/5)+(600/5)	79

¹Irradiation at 300 W for 2 min, stirring for 1 min out of oven, again irradiation at 300 W for 5 min ...

Found: 52.21 (C%), 8.74 (H%), 4.09 (N%). Conversion: 87.7%.

Poly(ethylene glycol) bis (methylimidazolium chloride) 600 g/mol (b): IR (KBr, cm⁻¹): ν = 3073–3145 (aromatic C–H stretching), 1568 (aromatic C=N stretching), 1456, 1352 (CH₂ bending), 1107 (C–O stretching), 627, 655 (aromatic C–H oop).

¹H NMR (400 MHz, CDCl₃, ppm): δ _H = 3.59 (m, O–CH₂–CH₂–O), 3.83 (2H, t, O–CH₂–CH₂–N), 4.01 (3H, s, N–CH₃), 4.54 (2H, t, N–CH₂–CH₂–O), 7.60, 7.74 (2H, C(4,5)–H), 9.99 (1H, C(2)–H).

Elemental analysis: Calculated for C₃₄H₆₄Cl₂N₄O₁₂ (791 g/mol): 51.58 (C%), 8.09 (H%), 7.07 (N%). Found: 49.67 (C%), 7.81 (H%), 6.51 (N%). Conversion: 95%.

2.3.2. PEGBOX (c)

Poly(ethylene glycol) 600 diacid (1 mmol) and α,α,α -tris(hydroxymethyl)methylamine (2.2 mmol) were placed in an open glass container in such a way as to occupy only 10% of the overall volume. The mixture was irradiated intermittently in an unmodified domestic (multimode) microwave oven at the power levels indicated in Table 1 (During the reaction the temperature of the mixture reached 138°C). When the irradiation terminated and all of the starting materials disappeared, the mixture was allowed to cool to room temperature. Then, dichloromethane (5 ml) was added at room temperature and the mixture was stirred for some minutes to precipitate unreacted α,α,α -tris(hydroxymethyl)methylamine. The resulted mixture was filtered and

the obtained clear solution was added into diethyl ether to precipitate the expected functional polymer.

Poly(ethylene glycol) bis (2-oxazoline) 600 g/mol (c)

IR (KBr, cm⁻¹): ν = 3362 (O–H stretching), 2880 (aliphatic C–H stretching), 1658 (C=N stretching), 1462, 1352 (CH₂ bending), 1107 (C–O stretching).

¹H NMR (400 MHz, DMSO-d₆, ppm): δ _H = 3.62 (m, OCH₂O–(CH₂CH₂O)_{n-2}–CH₂O), 3.96 (4H, s, C(3)–CH₂OH), 4.20 (2H, C(4)–H), 4.59 (2H, b, C(3)–CH₂OH).

Elemental analysis: Calculated for C₃₀H₅₆N₂O₁₆ (700 g/mol): 51.40 (C%), 8.00 (H%), 4.00 (N%). Found: 49.25 (C%), 7.88 (H%), 3.80 (N%). Conversion: 99%.

3. Results and discussion

According to Figure 1 derivatives of poly(ethylene glycol) with different average molecular weights have been reacted with 1-methylimidazole and α,α,α -tris(hydroxymethyl)methylamine as reactants, separately. The reactions have been performed using microwave irradiation under solvent-free condition. So poly(ethylene glycol) bis(3-methylimidazolium chloride) and poly(ethylene glycol) containing oxazoline end groups have been prepared. These reactions have been performed in a good yield, quickly and without using chemical solvents.

In the process of preparation of ionic liquids it is observed that at elevated power levels partial decomposition/charring of the ionic liquid occurs possibly owing to the localized overheating of ionic liquid, which eventually results in lower yields. To avoid this problem, the reactions are conducted with intermittent heating and mixing at a moderate power level to obtain better yields and cleaner ionic liquid formation. So, we tried to irradiate samples in various conditions at different power levels for different period of times to obtain an optimized condition.

In the case of condensation of acid with β -amino alcohol, once the amide are formed, subsequent intramolecular condensation between the amide and the free hydroxyl groups present in the molecule can afford 2-oxazoline. The presence of at least two hydroxyl groups in the amino alcohol seems to be crucial to promote the further condensation (Figure 2). In the absence of such a second hydroxyl group, the condensation needs a catalyst to proceed.

Because of the polar nature of the transition states involved in these processes, the microwave irradiation should help to drive the reaction to completion. Furthermore, the final temperature reached ($T \sim 140^\circ\text{C}$) implies that the formed water is removed from the reaction medium rendering the global process irreversible, irrespective of the mode of activation (MW irradiation or conventional heating).

It is believed [35] that the key role of the second hydroxyl group is to form an internal H-bond with the carbonyl group of the amide to provide some electrophilic assistance for the next condensation. This mechanism is also highly beneficial for MW specific effects as it involves a dipolar transition state from neutral reactants.

Figure 3 shows the FT-IR spectra of the products in comparison with their primary polymers. According to the spectrum the elimination of C–Cl stretch-

Figure 3. The FT-IR spectra of PEGCI, PEGBMIM (a,b), PEGBOX (c) and PEGDA

ing bands, and the appearance of aromatic C–H and C=N stretching bands confirm the formation of the expected ionic liquids. Furthermore the elimination of C=O stretching band in 1746 cm^{-1} and the appearance of C=N stretching band in 1658 cm^{-1} , confirm the formation of 2-oxazoline.

Table 2. The elemental analysis results of the products

		Content [%]			[C]/[N] [%]	Conversion [%]
		C	H	N		
PEGMIM(a)	calculated	51.20	8.61	4.60	13.00	87.8
	found	52.21	8.74	4.09	14.89	
PEGMIM(b)	calculated	51.58	8.09	7.07	8.50	95.0
	found	49.67	7.81	6.51	8.90	
PEGOX(c)	calculated	51.40	8.00	4.00	15.00	99.0
	found	49.25	7.88	3.80	15.12

Figure 4. The ^1H NMR spectra of PEGBMIM (a,b), PEGBOX (c) and PEGDA

Table 3. The solubility behavior of products in comparison with the primary polymers

Solvent	PEGCl	a	b	PEGDA	c
Water	+ ¹	+	+	+	+
DMF	+	+	+	+	+
Dichloromethane	+	+	+	+	+
Diethylether	+ ²	–	–	+ ³	–
n-Hexane	–	–	–	–	–
Toluene	+	+	+	±	–

¹+: soluble, –: insoluble, ±: slightly soluble

^{2,3}PEGCl and PEGDA are insoluble in diethylether below 0°C

Figure 4 shows the ^1H NMR spectra of the products. The appearance of the aromatic protons signals in **a** (7.44, 7.64, 9.87 ppm) and **b** (7.60, 7.74, 9.99 ppm), and the elimination of the peak of carboxylic acid groups (8.88 ppm) from PEGDA are evidences of formation of the **a**, **b** and **c** products. Also the elemental analysis results of the products are shown in Table 2. According to these results, functionalization of the primary polymers has been concluded.

The resulted data showed that, in the case of preparation PEGBMIM (**a,b**), the obtained dicationic salts generated from dichloro poly(ethylene glycol) are slightly contaminated with the corresponding monocationic intermediate.

The solubility of the synthesized polymers in water and in common organic solvents were studied and the results are shown in Table 3. The results showed that the solubility of the obtained polymers are similar to their parent polymers, but they became polar than primary polymers.

4. Conclusions

According to the obtained results poly(ethylene glycol) bis methylimidazolium chloride with average molecular weights of 600 and 1000 g/mol and poly(ethylene glycol) bis 2-oxazoline with average molecular weight of 600 g/mol have been prepared as a new telechelic polymers under solvent free condition using an unmodified household microwave oven, a method that precludes the usage of volatile organic solvents and is much faster, efficient, and eco-friendly.

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