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# Synthesis and Characterization of Comb-like Methoxy Polyethylene Glycol-grafted Polyurethanes via ‘Click’ Chemistry

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In this study, a series of comb-like methoxy polyethylene glycol (MPEG) functionalized polyurethanes (PUs) (PU-g-MPEG) were successfully prepared via ‘click’ chemistry and polyaddition reaction. The copper catalyzed Huisgen 1,3-dipolar cycloaddition was firstly carried out between 3,5-bis(hydroxymethyl)-1-propargyloxybenzene (PBM) and methoxy polyethylene glycol azide (MPEG-N<sub>3</sub>) to obtain MPEGylated diol PBM (MPEG-PBM). Then, the comb-like PUs having MPEG located on the backbones (PU-g-MPEG) were synthesized through the polyaddition of MPEGylated diol PBM and hexamethylene diisocyanate (HDI). Fourier transform infrared (FTIR), <sup>1</sup>H NMR spectroscopy, size exclusion chromatography (SEC), and thermo gravimetric analyses (TGA) were used to characterize these synthesized MPEG-functionalized comb-like PUs (PU-g-MPEG). Compared with PU without MPEG grafts, PU-g-MPEG show a better wettability.

**Keywords:** Polyurethane, ‘Click’ chemistry, comb-like polymer

## 1 Introduction

Polyurethanes (PUs) were usually prepared from the reaction between diisocyanates and diols or polyols, in which the repeating units contain a urethane moiety (1). It was first produced and investigated by Dr. Otto Bayer in 1937 (2). Since then, many academic and industrial research groups worldwide have been focusing on the PUs. Due to its extensive structure and property diversity, PUs materials was widely applied in many fields, such as medicine,

carrier for drugs release, coating, and adhesive (3, 4). Although PUs materials possess many excellent properties, such as durability, elasticity, fatigue-resistance, compliance, and acceptance or tolerance in the body during the healing (5), most of the conventional PUs can’t completely meet the requirement for either their surface or bulk properties when used as biomaterials. One of the major problems is the undesired interactions of foreign materials introduced into the body with the immune system (e.g., leukocytes, phagocytes) and biomolecules, such as lipids, proteins, fats, and enzymes. This problem is generally referred as bioincompatibility (6). An effective approach in developing a clinically applicable PU biomaterial is to modify the surface of PU which already has excellent biofunctionality and bulk properties. Two kinds of bio-compatibility are desired for PUs, namely the least foreign-body reactions and the cell- and tissue bonding capability (7).

Over the past two decades, using different methods, researchers grafted different biomacromolecules on the surface of PUs to functionalize PUs, such as fibronectin (8), peptides (9, 10), heparin (11, 12), and chitosan (13), etc. Among these biomacromolecules, the grafting of

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poly(ethylene glycol) (PEG) has been extensively investigated as the most common method of constructing non-fouling surfaces because PEG has good biocompatibility, low toxicity, nonimmunogenicity, and high water solubility (14–18). For example, it has been found that grafting PEG to solid surfaces reduces protein adsorption and cell adhesion, and at the same time does not show antigenic activity (19). Furthermore, it was demonstrated that PEG coatings can suppress platelet adhesion and resist protein adsorption both *in vitro* and *in vivo*, and therefore reduce the risk of thrombus formation, tissue damage, and other cytotoxic effects (20, 21). These inert characters of PEG are based on its molecular conformation in aqueous solution, where PEG exposes uncharged hydrophilic groups and shows higher surface mobility (steric exclusion). The excellent solubility of PEG in water is due to the strong hydrogen bonds between the oxygen in PEG and hydrogen in water. The unique features of PEG have been very attractive in the chemical, pharmaceutical, and material fields due to its excellent water solubility and biocompatibility.

Coating PU surface with PEG would render the surface fully biocompatible, while the physical/mechanical properties of the bulk materials remain largely unaffected. This would evidently result in the improved blood compatibility, without the need to invoke tissue engineering techniques including endothelial cell seeding. To achieve this objective, several major ways have been reported, such as, covalently grafting of PEG and plasma-induced polymerization of oligo(ethylene glycol) (OEG) precursors (22–26). Previous schemes used to attach PEG to surfaces involve either the functionalized derivatives of PEG or functionalized substrate surfaces in a two-step reaction or more (26). During the functionalization of polymer, the reactivity of functional groups may be affected by the functionalized moiety as well as the route of functionalization. Therefore, the careful attention needs to be paid to avoid the secondary reactions.

As a typical, high-efficiency, and quantitative ‘click’ chemistry reaction, Huisgen 1,3-dipolar cycloadditions between an azide and an alkyne compound, have been widely used in synthesis of functional polymer and surface modification (27–29). Du Prez et al. firstly prepared the linear PUs with a variable amount of “clickable” functions (alkyne), then employed Huisgen 1,3-dipolar cycloaddition to attach BzN<sub>3</sub>, amine and fluorinated compounds (TDFO-N<sub>3</sub> and Zonyl-N<sub>3</sub>) to the PUs, and finally obtained PUs with the new functionalities in the side-chain of the backbone (30). Musyanovych et al. synthesized the azide-functionalized polyurethane nanocapsules, subsequently clicked alkyne dye or propiolic acid to the above azide-functionalized polyurethane nanocapsules, and therefore provided a new kind of PU nanocapsules (31). Cho et al. obtained the mechanically robust antimicrobial nanocomposites by click coupling of azide moiety-containing hyper-

branched polyurethane (HBPU) and alkyne-functionalized multi-walled carbon nanotubes (MWCNTs) (32). Overall, the click chemistry is indeed a versatile tool in polymer synthesis.

The aim of the present work is to prepare the comb-like MPEG grafted PUs by using ‘click’ chemistry and polyaddition reaction. Here, a series of comb-like MPEG-functionalized PUs were successfully synthesized and characterized.

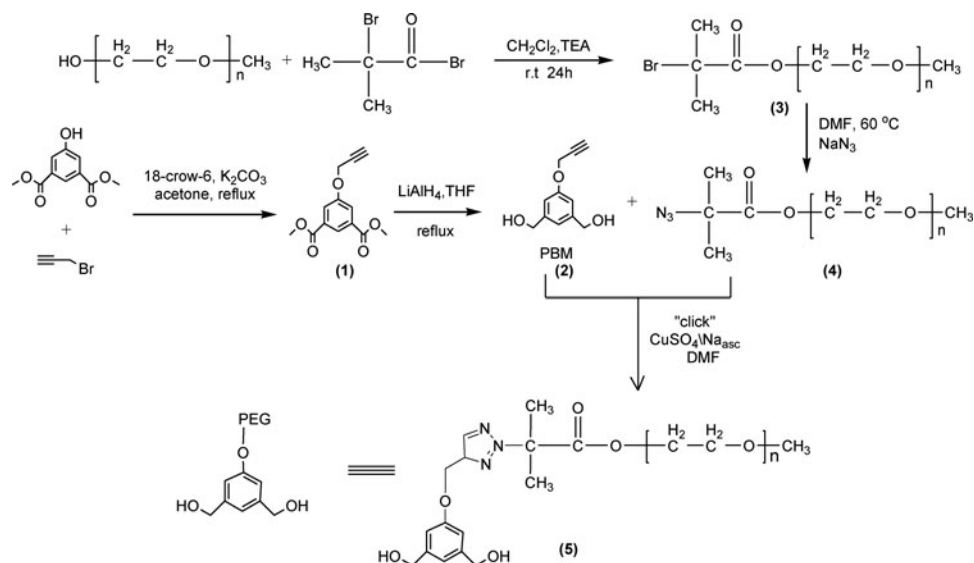
## 2 Experimental

### 2.1 Materials

Dimethyl 5-hydroxyisophthalate, 18-crown-6, propargyl bromide (80%) in xylene, LiAlH<sub>4</sub>, methoxy poly(ethylene glycol) (CH<sub>3</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OH, MPEG) (*M<sub>n</sub>* = 1299 (*n* = 30), 2945 (*n* = 67) and 8347 (*n* = 190), which are denoted as MPEG<sub>1K</sub>, MPEG<sub>3K</sub>, and MPEG<sub>8K</sub>, respectively), 2-bromoisobutyl bromide (BrIB, 98%, Aladdin), copper (II) sulfate·5H<sub>2</sub>O (+99%), L-ascorbic acid sodium salt (Na<sub>asc</sub>, +99%), hexamethylene diisocyanate (HDI, 99%), dibutyltin dilaurate, and sodium azide were purchased from Aladdin and were used as received. Triethylamine (TEA) was dried with CaH<sub>2</sub> for two hours and filtrated before use. Methylene dichloride (CH<sub>2</sub>Cl<sub>2</sub>) and ethyl acetate (EtOAc) were refluxed with calcium hydride (CaH<sub>2</sub>) and magnesium sulfate anhydrous (MgSO<sub>4</sub>), respectively, and distilled prior to use. The commercial PU sample (Type: PU58277) was kindly donated by Lubrizol Specialty Chemicals (Shanghai) Co., Ltd., China.

### 2.2 Instruments

<sup>1</sup>H-NMR spectra were recorded with a Bruker DPX-300 spectrometer. FTIR spectra were recorded using Fourier transform spectrometer (Nicolet 6700), and all samples were mixed with KBr powders, and the mixture was pressed into a tablet. Size exclusion chromatography (SEC) was performed at room temperature on a Waters 515 equipped with a Waters 2487 Ultraviolet absorbance detector and Wyatt Technology Optilab rEX refractive index detector. The columns were STYRAGEL HR3, HR4 and HR5 (300 × 7.8 mm) from Waters. HPLC grade THF was used as eluent at a flow rate of 1 mL/min. Samples in THF were filtered over a filter with pore size of 0.45 μm (Nylon, Millex-HN 13 mm Syringes Filters, Millipore, US). The columns were calibrated by using polystyrene standards with molecular weights in the range of 900 and 1.74 × 10<sup>6</sup> g/mol. The thermal property of products was determined with simultaneous thermogravimetric analysis (TGA) and differential thermal analysis (DTA) apparatus (Netzsch STA449F3) in a nitrogen atmosphere with a heating rate of 20°C/min from 25 to 800°C.



Sch. 1. Synthesis of alkyne-functionalized diol PBM (2), azide-terminated MPEG (4), and MPEG-PBM (5).

## 2.3 Synthesis of Comb-Like Polyurethane

The synthesis strategy was illustrated in Schemes 1 and 2.

### 2.3.1 Synthesis of Propargyl Ether of Dimethyl 5-Hydroxyisophthalate (1), 1-Propargyloxybenzene-3, 5-Dimethanol (PBM) (2), Methoxypolyethylene Glycol, 2-Bromoisobutyrate (MPEG-Br) (3), and Methoxy polyethylene Glycols Azide (MPEG-N<sub>3</sub>) (4)

The compounds 1, 2, 3, and 4 were synthesized according to the references (33–35). The synthesis conditions and structure characterizations were described in Supporting Information.

### 2.3.2 Synthesis of MPEGylated diol PBM (MPEG-PBM) (5) via Click Chemistry

A typical procedure for the synthesis of MPEGylated diol PBM was started with the feed ration of reagents [2, PBM]:[4, MPEG-N<sub>3</sub>]:[CuSO<sub>4</sub>·5H<sub>2</sub>O]:[Na<sub>asc</sub>] = 1:1:0.5:1. The Huisgen 1,3-Dipolar Cycloaddition reaction between PBM (0.1225 g, 0.654 mmol) and MPEG-N<sub>3</sub> (0.719 g, 0.654 mmol) was conducted at 60 °C in a 25 mL round-bottom flask charged with 10 mL of DMF as solvent and CuSO<sub>4</sub>·5H<sub>2</sub>O/Na<sub>asc</sub> as catalyst. After 24 h, the polymer solution was filtered and the solution was dried under vacuum overnight. Then the resulting copolymer was diluted with CH<sub>2</sub>Cl<sub>2</sub> and passed through a basic alumina column to remove click catalyst. The resulting solution was concentrated, and then the MPEG-PBM was precipitated into excess diethyl ether and dried under vacuum overnight prior to further characterizations such as NMR and FTIR.

### 2.3.3 Typical Synthesis of MPEG Grafted Polyurethane (PU-g-MPEG) (6)

A two-neck 25 mL round-bottom flask was charged with HDI (55.4 μL, 0.343 mmol), 5 (446 mg, 0.343 mmol) and freshly distilled EtOAc (6 mL). The mixture was deoxygenated by three freeze-pump-thaw cycles before maintained at 60 °C in a preheated oil bath. Then, dibutyltin dilaureate (approximately 10–20 μL) was added, and the reaction was allowed to stir under nitrogen atmosphere overnight. During its formation, the PU slowly precipitated in the medium, and the obtained polymer was then filtered off and extensively washed with EtOAc and acetone respectively to remove all unreacted compounds. The synthesized material PU-g-MPEG was dried under vacuum at 40 °C overnight for further characterizations such as NMR and FTIR.

### 2.3.4 The Hydrophilicity of Polyurethanes

To characterize the hydrophilicity of these polyurethane materials, the sessile drop method was used for contact angle measurements at 25 °C using a commercial contact angle meter (Solon Tech, Shanghai, China). All four PU samples, PU, PU-g-MPEG<sub>1K</sub>, PU-g-MPEG<sub>3K</sub>, and PU-g-MPEG<sub>8K</sub>, were first prepared into flat films, respectively, and then ultra-pure water droplets (the diameter of about 2 mm.) were placed at six different positions for one sample. Finally, the average value was obtained. The experimental error of the measurements was ± 1°.

### 2.3.5 The Measurement of Mechanical Properties of Polyurethanes

To compare the mechanical properties of polyurethanes, the modulus of stretch was measured.

**Table 1.** Characterization of the starting MPEGs

Sample	M <sub>w</sub>	M <sub>n</sub>	PDI <sup>a</sup>	T <sub>10%</sub> <sup>b</sup> (°C)	Char yield <sup>b</sup> (%)
MPEG <sub>1K</sub>	1650	1299	1.27	358	2.1
MPEG <sub>3K</sub>	3283	2945	1.11	376	1.7
MPEG <sub>8K</sub>	8709	8347	1.04	389	1.4

<sup>a</sup>determined by SEC using THF as solvent, calibrated using polystyrene standards.

<sup>b</sup>Temperature at 10% weight loss and final char yield, as determined by TGA. Heating ramp: 20°C/min under nitrogen atmosphere from 25 to 800°C.

The tensile properties of the polyurethane were determined using an Instron 4204 Universal Testing Machine at room temperature and humidity. The sample was prepared as film (10 mm × 15 mm × 1 mm) for A stretch speed is 1.0 cm/min. The tensile amplitude of 3% was used to ensure a linear elastic region.

### 3 Results and Discussion

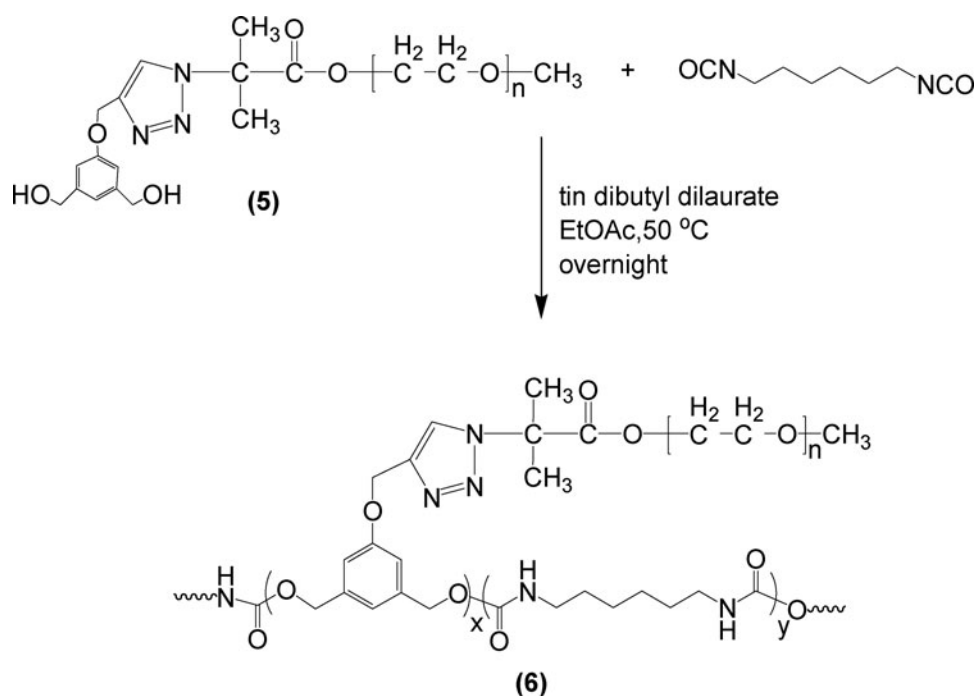
#### 3.1 Preparation of Methoxy Polyethylene Glycol Azides (MPEG-N<sub>3</sub>)

Table 1 summarizes the molecular weights and molecular distributions of the starting MPEGs (MPEG<sub>1K</sub>, MPEG<sub>3K</sub>, and MPEG<sub>8K</sub>) and also their thermal property.

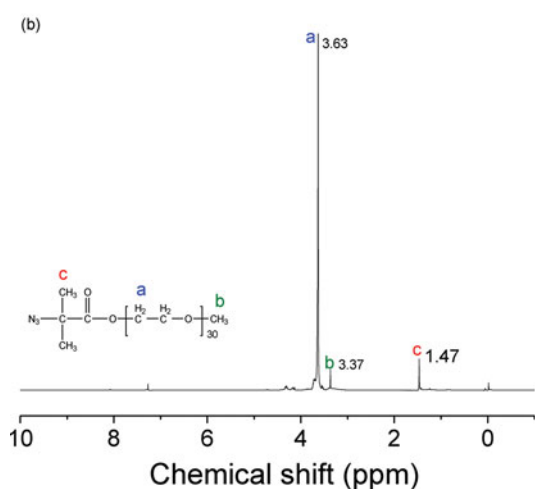
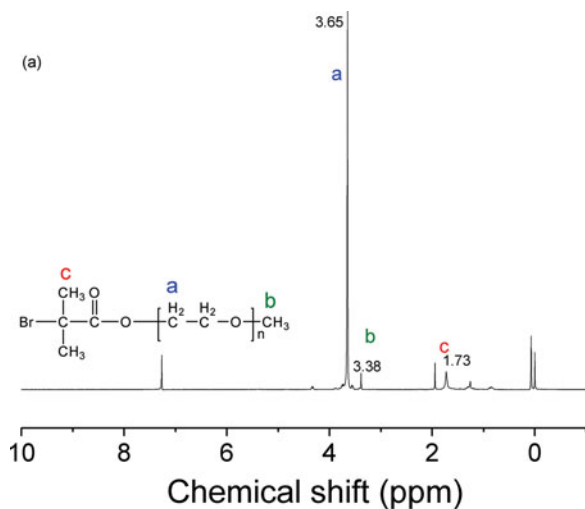
Take MPEG<sub>1K</sub>-N<sub>3</sub> as an example. In the first step of synthesis of MPEG<sub>1K</sub>-N<sub>3</sub>, the methoxy poly (ethylene glycol)

2-bromoisobutyrate was prepared by reacting MPEG<sub>1K</sub> with 2-bromoisobutyryl bromide [34, 35]. The <sup>1</sup>H NMR spectrum obtained from MPEG<sub>1K</sub>-Br is shown in Figure 1a and demonstrates the successful reaction. The typical peak at 3.65 ppm is attributed to the methylene proton of the repeat units (-CH<sub>2</sub>-CH<sub>2</sub>-O-) of the MPEG and the signal at 3.38 ppm is assigned to the terminal methyl in the MPEG<sub>1K</sub>. The new peak at 1.73 ppm corresponding to the protons of 2-bromoisobutyryl bromide clearly proves that the hydroxyl group has been substituted by ester. Moreover, the complete substitution of the hydroxyl groups is confirmed by the peak area integration calculation.

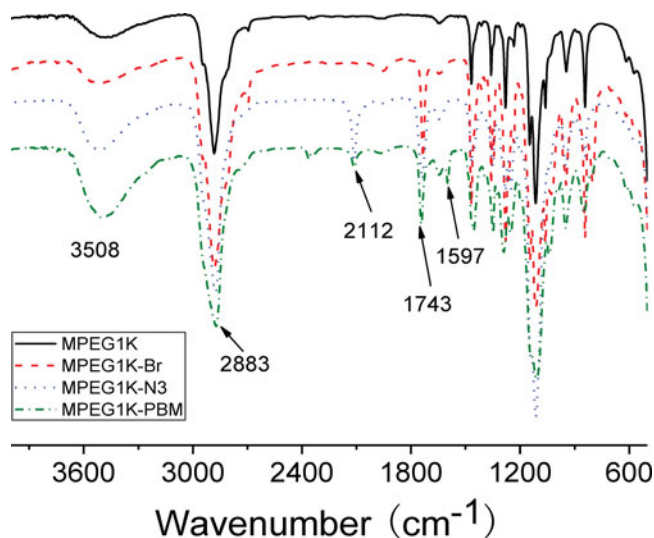
According to Scheme 2, the terminal group bromides of MPEG<sub>1K</sub>-Br, whose synthesis was previously accomplished, must be converted into azides by reaction with sodium azide. MPEG<sub>1K</sub>-Br was thus reacted with 1.5 equiv. of sodium azide in DMF at 60°C for 2 days. <sup>1</sup>H-NMR spectrum in Figure 1(b) confirms that the conversion of the terminal bromides into azides is quantitative. Indeed, the resonance peak at 1.73 ppm corresponding to the hydrogens of 2-bromoisobutyryl bromides completely shifted to 1.47 ppm. The product was also characterized by IR spectroscopy, which clearly illustrated the terminal group transformation, as shown in Figure 2. Compared with MPEG<sub>1K</sub>, two new strong peaks were observed for MPEG<sub>1K</sub>-N<sub>3</sub>. The typical band at 1743 cm<sup>-1</sup> corresponding to the carbonyl function due to the ester substitution and the band at 2112 cm<sup>-1</sup> owing to conversion of the bromide termini into azide groups both appeared as expected.



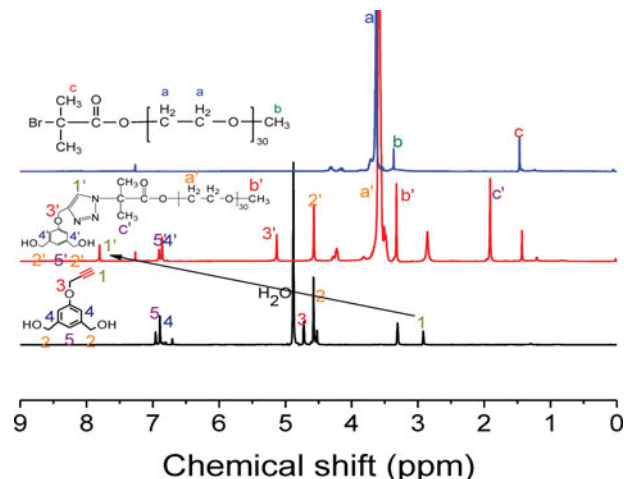
**Sch. 2.** Synthesis of MPEG grafted polyurethane (PU-g-MPEG) based on HDI and MPEG-PBM.



**Fig. 1.**  $^1\text{H-NMR}$  spectra (300MHz,  $\text{CDCl}_3$ ) of  $\text{MPEG}_{1\text{K}}\text{-Br}$  and  $\text{MPEG}_{1\text{K}}\text{-N}_3$ .



**Fig. 2.** IR spectra of the starting  $\text{MPEG}_{1\text{K}}$ ,  $\text{MPEG}_{1\text{K}}\text{-Br}$ ,  $\text{MPEG}_{1\text{K}}\text{-N}_3$ , and  $\text{MPEG}_{1\text{K}}\text{-PBM}$ .

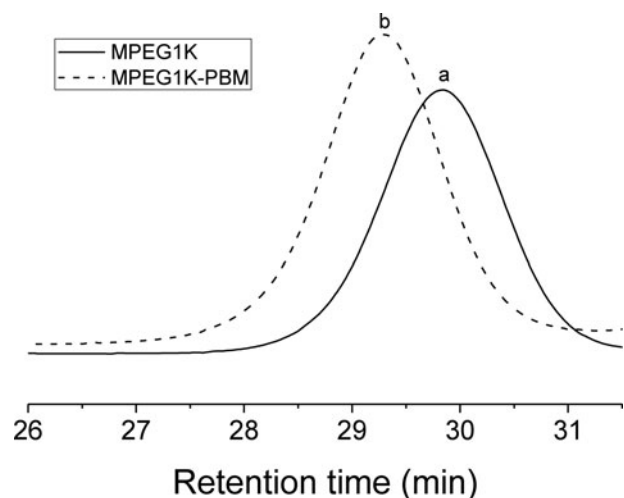


**Fig. 3.**  $^1\text{H-NMR}$  spectra (300MHz,  $\text{CDCl}_3$ ) of the starting PBM (lower spectrum),  $\text{MPEG}_{1\text{K}}\text{-N}_3$  (upper spectrum), and  $\text{MPEG}_{1\text{K}}\text{-PBM}$  (middle spectrum).

$^1\text{H-NMR}$  spectra of the  $\text{MPEG}_{3\text{K}}\text{-Br}$ ,  $\text{MPEG}_{3\text{K}}\text{-N}_3$ ,  $\text{MPEG}_{8\text{K}}\text{-Br}$ , and  $\text{MPEG}_{8\text{K}}\text{-N}_3$  were shown in Figures 3 and 4, respectively.

### 3.2 Synthesis of MPEGylated PBM (MPEG-PBM) through Click Reaction of Alkyne-Functionalized Diol PBM with $\text{MPEG-N}_3$

The click reactions were conducted in the presence of Cu (I) generated *in situ* from  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and sodium ascorbic acid (Sch. 2). Catalysis by Cu (I) ensured regioselective formation of the 1,4-disubstituted 1,2,3-triazole isomer, rather than a mixture with the corresponding 1,5-disubstituted 1,2,3-triazole isomer (36). Table 2 summarizes SEC data of synthesized MPEG-PBM compounds with varying molecular weight MPEGs.



**Fig. 4.** SEC traces of  $\text{MPEG}_{1\text{K}}$  (solid line, curve a) and the 'clicked'  $\text{MPEG}_{1\text{K}}\text{-PBM}$  (dashed line, curve b).

**Table 2.** SEC data of MPEGylated diol PBMs (MPEG-PBM).

Sample	$M_w$	$M_n$	PDI
MPEG <sub>1K</sub> -PBM	2403	1905	1.26
MPEG <sub>3K</sub> -PBM	4197	3823	1.10
MPEG <sub>8K</sub> -PBM	8635	8387	1.03

determined by SEC using THF as solvent, calibrated using polystyrene standards.

The quantitative character of the 'click' reaction could be determined by <sup>1</sup>H-NMR in CDCl<sub>3</sub>. Figure 3 shows the comparison of <sup>1</sup>H-NMR spectra of the starting materials PBM (lower spectra) with the final material MPEG<sub>1K</sub>-PBM (middle spectra) obtained after the dipolar cycloaddition with MPEG<sub>1K</sub>-N<sub>3</sub> (upper spectra). The arrow in Figure 3 clearly indicates the shift of the alkyne proton at 2.92 ppm (1, lower spectra) to 7.80 ppm (1', middle spectra), which corresponds to the proton linked to the formed triazole ring. Also, new peaks appear at 3.58 ppm (a', repeat unites -CH<sub>2</sub>-CH<sub>2</sub>-O- from MPEG), at 3.30 ppm (b', terminal CH<sub>3</sub> from MPEG) and at 1.91 ppm (c', two CH<sub>3</sub> from MPEG), prove the success of the reaction. The complete disappearing of the alkyne proton at 2.92 ppm (1, lower spectra) reveals that the reaction is quantitative.

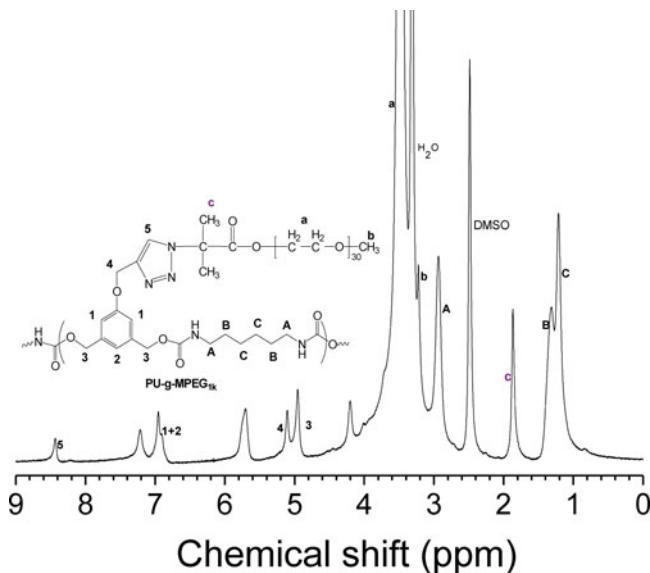
The IR spectrum of MPEG<sub>1K</sub>-PBM in Figure 2 indicates the adsorption at 2112 cm<sup>-1</sup> characteristic of the azide almost disappears in favor of a new absorption at 1597 cm<sup>-1</sup> characteristic of the triazole unsaturations. Additionally, the alcohol termini of PBM gives rise to a characteristic broad and strong stretch from 3620 to 3100 cm<sup>-1</sup>. The band at 1743 cm<sup>-1</sup> corresponds to the carbonyl function from the ester groups in MPEG<sub>1K</sub>-Br, and MPEG<sub>1K</sub>-N<sub>3</sub>.

IR spectra of MPEG<sub>3K</sub>, MPEG<sub>3K</sub>-Br, MPEG<sub>3K</sub>-N<sub>3</sub> and MPEG<sub>3K</sub>-PBM were shown in Figure 5. IR spectra of MPEG<sub>8K</sub>, MPEG<sub>8K</sub>-Br, MPEG<sub>8K</sub>-N<sub>3</sub> and MPEG<sub>8K</sub>-PBM were shown in Figure 6. The similar IR absorption characters can be found in Figure 5 and Figure 6.

It can be noted from Table 2 that the functionalized MPEGs have a higher number average molecular weights than the starting materials in Table 1, showing the success of the grafting reaction. On the other hand, Figure 4 illustrates the comparison of the SEC traces of the resulting MPEG<sub>1K</sub>-PBM with number average molecular weight and polydispersity index (PDI), and their PDIs are still very narrow, similar to the starting MPEGs, which prove the chain structures of the MPEG are not remarkably influenced during the reaction. The similar SEC traces can be found in Figure 9s.

### 3.3 Typical Synthesis of Comb-like MPEG Grafted Polyurethane (PU-g-MPEG)

In this part, comb-like MPEG-functionalized polyurethanes were synthesized by the conventional techniques

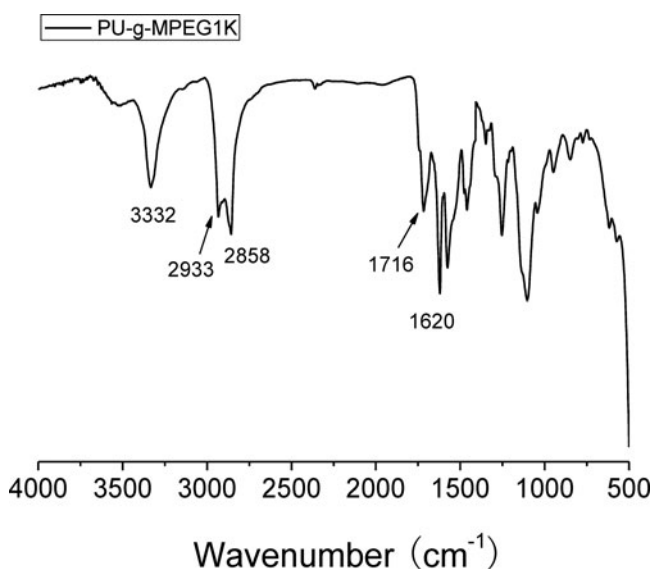


**Fig. 5.** <sup>1</sup>H-NMR spectrum (300MHz, DMSO-D<sub>6</sub>) of the PU-g-MPEG<sub>1K</sub>.

after which it was characterized by <sup>1</sup>H-NMR, FTIR, and TGA.

In order to obtain MPEG-grafted polyurethane (denoted as PU-g-MPEG), in the feed of polyaddition, a predetermined mixture of MPEG-PBM and hexamethylene diisocyanate (HDI) were reacted in ethyl acetate at 50°C with dibutyltin dilaurate as catalyst (Sch. 2). The polyurethane precipitated in the solvent during its formation. In order to compare the characteristics of PUs, a series of PUs were synthesized as shown in Table 3.

Take PU-g-MPEG<sub>1K</sub> as example, <sup>1</sup>H NMR spectra of the MPEG-functionalized polyurethane (Fig. 5) demon-



**Fig. 6.** IR spectrum of the PU-g-MPEG<sub>1K</sub>.

**Table 3.** Synthesis of MPEG grafted polyurethane (PU-g-MPEG) based on HDI and MPEG-PBM.

Sample	Composition <sup>a</sup> (mol%) 50/50	T <sub>10%</sub> (°C)	Char yield <sup>b</sup> (%)
PU	PBM/HDI	293	6.4
PU-g-MPEG <sub>1K</sub>	MPEG <sub>1K</sub> -PBM/HDI	311	4.9
PU-g-MPEG <sub>3K</sub>	MPEG <sub>3K</sub> -PBM/HDI	320	3.7
PU-g-MPEG <sub>8K</sub>	MPEG <sub>8K</sub> -PBM/HDI	333	1.8

<sup>a</sup>Final composition determined by <sup>1</sup>H-NMR in DMSO-d<sub>6</sub>.

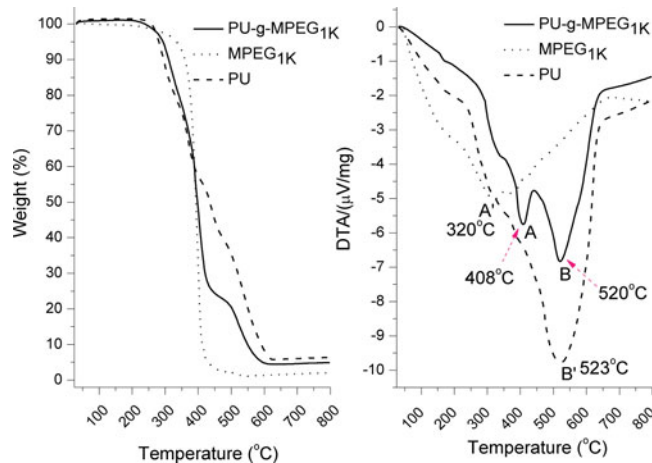
<sup>b</sup>Temperature at 10% weight loss and final char yield, as determined by TGA. Heating ramp: 20°C/min under nitrogen atmosphere from 25 to 800°C.

strate the successful polymerization. The typical resonance of the proton linked to the formed triazole ring appears at 8.43 ppm (5) and a high peak appears at 3.49 ppm (a, repeat units -CH<sub>2</sub>-CH<sub>2</sub>-O- from MPEG) proving that the functionalized diol has been incorporated in the polymer without any side reaction as confirmed by the integrations. Moreover, the peak at 7.2–7.3 ppm corresponds to hydrogens linked to the nitrogen atoms from the urethane groups. It clearly indicates that all expected peaks are present, both from the MPEG<sub>1K</sub>-PBM and diisocyanate.

Figure 6 presents the FT-IR spectra of the PU-g-MPEG<sub>1K</sub>. It can be seen from this figure that a narrow absorption peak appears at 3332 cm<sup>-1</sup> corresponds to the -N-H stretching vibration. The IR peaks at 2933 and 2858 cm<sup>-1</sup> correspond to aliphatic -C-H stretching. The absorption peaks at 1716 and 1620 cm<sup>-1</sup> correspond to -C=O in ester and C=C stretching, respectively, and the IR peak at 1500–1575 cm<sup>-1</sup> is due to -N-H bending. All of the absorption peaks prove that the reaction between -O-H group of diol MPEG<sub>1K</sub>-PBM and -N=C=O group of diisocyanate are completed successfully.

The elaborated PU is also characterized by simultaneously thermogravimetric analysis (TGA) and differential thermal analysis (DTA) (Fig. 7). From the TGA curves (left), it is found that the PU-g-MPEG<sub>1K</sub> (solid line) displays two rapid degradation processes, while both the linear PU (dash line) and MPEG<sub>1K</sub> (dot line) only show one degradation process, suggesting a two-step mechanism for the degradation of PU-g-MPEG<sub>1K</sub>. As seen from the DTA curves in the right picture, the two endothermic peaks of the PU-g-MPEG<sub>1K</sub> (solid line) appear at 408 and 520°C. It is possible that the degradation of the first stage is due to the pendant MPEG groups and the second stage is based on the degradation of the polyurethane backbone.

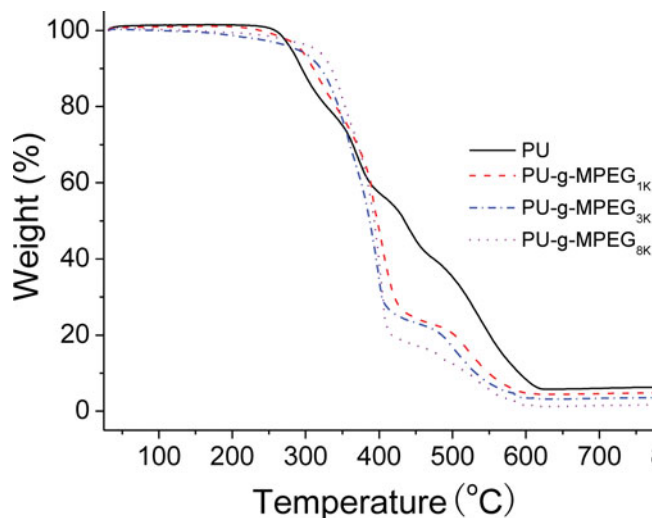
The TGA curves of all synthesized PUs are illustrated in Figure 8. As shown in the figure, the TGA curves for PU-g-MPEG<sub>1K</sub> (dash line), PU-g-MPEG<sub>3K</sub> (dash dot line) and PU-g-MPEG<sub>8K</sub> (dot line) in a nitrogen stream show a similar trend, containing two rapid degradation processes. The first stage of apparent weight losses



**Fig. 7.** TGA curves (left) and DTA curves (right) of the PU, MPEG<sub>1K</sub>, and PU-g-MPEG<sub>1K</sub> (heating ramp: 20°C/min under nitrogen atmosphere from 25 to 800°C).

lasts from 320 to 400°C and the second stage ranges from 500 to 580°C. If the criteria of stability are taken as the temperature at which 10% weight loss occurred, the temperature stability increases in the order: PU < PU-g-MPEG<sub>1K</sub> < PU-g-MPEG<sub>3K</sub> < PU-g-MPEG<sub>8K</sub> (Table 3). In contrast, the incorporation of the MPEG leads to low char-yielding materials (Fig. 8 and Table 3), which can be ascribed to the presence of the aliphatic compound MPEG.

Figure 8. TGA curves of PU, PU-g-MPEG<sub>1K</sub>, PU-g-MPEG<sub>3K</sub>, and PU-g-MPEG<sub>8K</sub> (heating ramp: 20°C/min under nitrogen atmosphere from 25 to 800°C).



**Fig. 8.** TGA curves of PU, PU-g-MPEG<sub>1K</sub>, PU-g-MPEG<sub>3K</sub>, and PU-g-MPEG<sub>8K</sub> (heating ramp: 20°C/min under nitrogen atmosphere from 25 to 800°C).



Combining the above results, it can be generally concluded that the polyurethanes with pendant MPEG groups were synthesized in a straightforward way.

### 3.4 The Hydrophilicity of Comb-like MPEG Grafted Polyurethane (PU-g-MPEG)

PU without the graft of PEG is moderately hydrophilic, and shows a water contact angle of 99.0°. The other three MPEG-grafted PU materials, namely, PU-g-MPEG<sub>1K</sub>, PU-g-MPEG<sub>3K</sub>, and PU-g-MPEG<sub>8K</sub>, show a higher hydrophilicity, and the water contact angle is 49.0°, 38.0°, and 23.0°, respectively. The grafting of MPEG remarkably contributes to the improvement of the wettability. Furthermore, the wettability increases with the chain length of grafted MPEG.

### 3.5 The Mechanical Properties of Comb-like MPEG Grafted Polyurethane (PU-g-MPEG)

The modulus of stretch is one of the most important mechanical properties of polyurethane, therefore, in this part, we compared the stretch modulus of synthesized comb-like MPEG grafted polyurethane (PU-g-MPEG) and a commercial available polyurethane (PU58277). The commercial polyurethane presents an excellent modulus of stretch, this value is 32.9 MPa. However, the synthesized three PU-g-MPEG samples, are extremely fragile materials and is difficult to prepare a film for the measurement of modulus of stretch. These results indicate that the significant increase of molecular weight of PU-g-MPEG is needed for the excellent modulus of stretch or other mechanical properties.

## 4 Conclusions

A series of comb-like poly(ethylene glycol)-functionalized polyurethanes have been achieved successfully via sequent 'click' chemistry and polyaddition reaction. This synthetic approach permits functionalization of PUs using MPEGs of different molecular weight, such as MPEG<sub>1K</sub>, MPEG<sub>3K</sub>, and MPEG<sub>8K</sub>. Moreover, it has been proved by TGA measurements that such functionalized PUs has a higher thermal stability and that the final char yields are proportional to molecular weight of the MPEGs in the synthesized material. The grafting of MPEG remarkably improved the wettability of polyurethane materials. In almost all cases, quantitative yields were obtained as observed by <sup>1</sup>H-NMR and FTIR measurements. These results confirmed that 'click' chemistry is a facile and versatile method for preparing functional polyurethanes. Furthermore, the synthetic strategy reported in this paper can be potentially considered as a universal route toward the design of other biocompatible materials such as block copolymers and functional poly (ester ether). At the same time, in order to obtain PU-g-MPEG with excellent mechanical properties, espe-

cially modulus of stretch, the synthesis method presented here needs to be improved to significantly increase molecular weights.

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