

# “Click” Chemistry as a Promising Tool for Side-Chain Functionalization of Polyurethanes

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**ABSTRACT:** Linear polyurethanes (PUs) having alkyne groups located along the backbone have been synthesized by reacting two different alkyne-functionalized diols with a diisocyanate compound.  $^1\text{H}$  NMR and FTIR proved the presence of these functional groups and the ability for the introduction of an elevated and controllable amount of functional groups that do not interfere with the PU chemistry. TGA measurements demonstrated that the incorporated alkyne diol in the PU materials strongly improves the final char yield. In the second part of the work, the copper catalyzed Huisgen 1,3-dipolar cycloaddition was undertaken between the alkyne-functionalized PUs and a variety of azide compounds such as benzyl azide and different fluorinated azide compounds, resulting in side-chain functionalized PUs with varying degree of functionalization.  $^1\text{H}$  NMR spectra clearly indicated the quantitative yields of the “click” reaction.

## Introduction

Since polyurethanes (PUs) have been discovered by Bayer in the 40s,<sup>1</sup> many academic and industrial research groups from all over the world have enlarged this field. PUs<sup>2</sup> are mostly, but not only, based on the reaction between diisocyanates, diols and polyols. The wide range of starting compounds leads to the synthesis of materials with different and unique properties. The targeted applications are numerous such as in the field of automobile, medicine, comfort, buildings, paintings, coatings, adhesives and packaging.<sup>3</sup> Additionally, the chemistry of polyurethanes allows for the synthesis of foams (flexible and rigid) or thermoplastic polymers, depending on their synthetic conditions. Nowadays, thermoplastic PUs have found a growing interest since the mechanical, thermal and chemical properties can be tailored by the choice and composition of the starting compounds. Actually, much research is focused on the degradability and the recycling of such materials due to their intense production.<sup>4</sup> More recently, much attention is shown for the development of functional polyurethanes because it is expected that they lead to applications that are outside of the PU market, thus giving rise to additional functionality to the end materials.

To introduce functionalities within the PU materials, few possibilities can be considered. One route to obtain functional polyurethanes is the use of monofunctional compounds (alcohol or isocyanate), which lead to polymer chain terminations with the functional group at the chain end and to a reduced molecular weight. The end-chain modification of the PU can also be performed after its formation. For instance, hydroxyethyl (meth)acrylate has been employed for the modification of a NCO-functionalized polyurethane leading to UV-cross-linkable polyurethane (meth)acrylate (PUA).<sup>5,6</sup> The UV-cured PUA coatings received considerable attention for their resistance to accelerated weathering or exposure to light for instance.<sup>7,8</sup> A similar strategy led to the elaboration of amino-functionalized PUs starting from the reaction between an excess of hexamethylene diisocyanate (HDI) and propylene glycol.<sup>9</sup> The isocyanate functions in the PU, located at the end-chains, were successively hydrolyzed with triphenylsilanol and water. These so-obtained amino-functionalized PUs may be afterward used for coatings, adhesives, sealants.<sup>9</sup> Surface modification of isocyanate-functionalized PUs was also reported in order to

incorporate different functional groups such as sulfonate or amine.<sup>10</sup>

Second, the functional group can be directly introduced during the process (one-pot procedure) by using a functional building block. Nevertheless, careful attention should be paid toward the inertness of the introduced functional groups during the polyurethane process to avoid secondary reactions, making the materials unusable for the desired final applications. For instance, the introduction of amino groups into PU requires protection/deprotection steps. Recently, the preparation of PUs bearing pendant amino groups starting from HDI, poly( $\epsilon$ -caprolactone) (PCL), and a modified poly(ethylene glycol) (PEG) has been described.<sup>11</sup> The approach consists in the reaction of dihydroxyl PEG with  $\text{NH}_2$ -protected aspartic acid (Asp) leading to a prepolymer PEG–Asp–PEG. Then, the consequent reaction between HDI, PCL and the amino-protected PEG–Asp–PEG allowed for the formation of PU with a low loading of pendant amino groups after an ultimate deprotection step. At the same time, Endo et al.<sup>12</sup> prepared PU bearing hydroxyl groups in the side chain (PHUs) by reacting a bifunctional cyclic carbonate with a diamine, after which the hydroxyl groups were converted into functionalized urethane groups with the help of functionalized isocyanates. In medicine, functional PUs are widely studied since it was established that PU shows relatively good *in vitro* blood compatibility in comparison to other polymeric films.<sup>13</sup> For example, Kim et al.<sup>14</sup> synthesized heparin-immobilized polyetherurethanes containing pendant ester groups from a NCO-prepolymer and diethyl bis(hydroxymethyl)malonate. The obtained ester-functionalized PU was then chemically modified to obtain either heparin or PEG–heparin as side groups. Another way that was largely explored consists of the functionalization of PUs by hydrogen removal of the urethane group (i.e., NH) of the material using for example, a drastic treatment based on sodium hydride (NaH).<sup>15–19</sup> In general, the chemical modification of such functional polymers can also suffer of a certain lack of efficiency since the reactivity of functional groups may be affected by the structure of the polymer and also by the efficiency of the chemical reactions used. For the past few years, this efficiency was intensively studied in the area of polymer chemistry since, in 2001, Sharpless and co-workers<sup>20</sup> introduced innovative approaches, named “click” chemistry, allowing quantitative reactions. Among the listed reactions, Huisgen 1,3-

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dipolar cycloadditions between an azide and an alkyne compound have been widely explored due to, among others, its efficiency, versatility and inertness toward other functional groups. The use of a copper catalyst leads to a tremendous acceleration of the reaction at room temperature.<sup>21,22</sup> Since the first report of "click" chemistry in polymer chemistry by Hawker, Sharpless and co-workers,<sup>23</sup> the construction of well-defined and complex macromolecular architectures *via* "click" chemistry has been a strongly growing field of research.<sup>24–27</sup> Relating to the PU field, Qin et al.<sup>28</sup> very recently reported the elaboration of polyurethanes using the combination of 2,4-toluene diisocyanate (TDI) and chromophore-functionalized diols. Nevertheless, the authors first synthesized these diols by the 1,3-dipolar azide–alkyne cycloaddition prior to their incorporation in the PU. These polymers were studied as organic second-order nonlinear materials for their further application in the field of high-speed electro-optic devices.

The aim of the present work was to develop an efficient way for the elaboration of alkyne-containing PUs by the introduction of alkyne diols during the PU process. Because of the resistance of the alkyne group toward the usual reaction conditions and functional groups during the PU synthesis, it was foreseen that an universal class of functionalized PU materials could be prepared. The ultimate step is the functionalization of the PUs *via* "click" chemistry with the help of functional azide compounds, leading to a wide range of properties starting from the same compounds. To achieve this goal, two different alkyne-containing diols have first been synthesized. Then, alkyne-functionalized linear PUs with controllable alkyne loadings and variable molecular weight have been prepared. Finally, the postmodification has been done using the Huisgen 1,3-dipolar cycloadditions with several azide compounds in order to obtain new PU materials with properties that are directed *via* the azide compound.

## Experimental Section

**Materials.** Sodium azide (99%, Acros), copper(I) bromide (99.99%, Aldrich), copper(II) sulfate, 5H<sub>2</sub>O (99+%, Acros), L-ascorbic acid sodium salt (Na<sub>asc</sub>, 99%, Acros), *N*-2-(bromoethyl)phthalimide (98%, Alfa Aesar), *N,N,N',N',N''*-pentamethylethylenetriamine (PMDETA, 99+%, Fluka), butane-1,4-diol (BDO, 99+%, Acros), Zonyl FSO-100 (Aldrich), hexamethylene diisocyanate (HDI, 98%, Aldrich), dibutyltin dilaureate (95%, Fluka), methane sulfonyl chloride (99.5%, Acros), hydrazine monohydrate (98%, Acros), dimethylformamide (DMF, HPLC grade, Fisher) and dimethyl sulfoxide (DMSO, HPLC grade, Acros) were used as received. The compounds benzyl azide (BzN<sub>3</sub>),<sup>29</sup> 3,5-bis(hydroxymethyl)-1-propargyloxybenzene (PBM),<sup>30</sup> 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-azidoctane,<sup>31</sup> and 2,2-di(prop-2-ynyl)propane-1,3-diol (DPPD)<sup>32</sup> were synthesized according to the literature. Triethylamine (HPLC grade, Aldrich), tetrahydrofuran (THF, HPLC grade, Aldrich) and ethyl acetate (EtOAc, HPLC grade, Aldrich) were distilled prior to use.

**Instrumentation.** <sup>1</sup>H NMR spectra were recorded at 25 °C, with a Bruker Avance 300 spectrometer. Thermogravimetric analysis (TGA) was performed with a Mettler Toledo TGA/SDTA851e instrument under air atmosphere at a heating rate of 20 °C/min between 25 and 800 °C. Infrared spectra were obtained with ReactIR 4000 instrument (Mettler Toledo AutoChem ReactIR™) using a silicone probe (SiComp, optical range = 4400–650 cm<sup>-1</sup>). Molecular masses and molecular mass distributions were measured using gel permeation chromatography (GPC) using *N,N*-dimethylacetamide (DMA) as solvent and LiBr (0.42 g/L) with a flow rate fixed at 1 mL/min and a temperature of 50 °C (with poly(methyl methacrylate) standards).

**Synthesis of *N*-2-(Azidoethyl)phthalimide (PHT–N<sub>3</sub>).** *N*-2-(Bromoethyl)phthalimide (10 g, 40.97 mmol) in a mixture of DMF/water (120 mL, 9/1 v/v) was charged in a round-bottom flask. Then, 1.5 equivalent of sodium azide (59 mmol, 3.84 g) was introduced

and the reaction mixture was allowed to stir at 60 °C for 1 day. The mixture was then cooled to room temperature and a minimum of 5 extractions against ether was done. The combined ether layers were dried with magnesium sulfate and the solvent removed in vacuum, yielding a yellowish powder that was further dried under vacuum overnight (yield = 95.0%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 3.57 ppm (t, 2H, CH<sub>2</sub>–CH<sub>2</sub>–N<sub>3</sub>), 3.87 ppm (t, 2H, CH<sub>2</sub>–CH<sub>2</sub>–N<sub>3</sub>), 7.71 ppm (dd, 2H, Ar–H), 7.84 ppm (dd, 2H, Ar–H). FTIR (ATR): ν(N<sub>3</sub>) = 2111 cm<sup>-1</sup>, ν(C=O) = 1710 cm<sup>-1</sup>.

**Synthesis of Zonyl–N<sub>3</sub>.** Zonyl–N<sub>3</sub> was synthesized in two steps from hydroxyl chain terminated fluorinated surfactant Zonyl–FSO-100 (*M*<sub>w</sub> ~725 g/mol, with (CF<sub>2</sub>)<sub>n</sub>, *n* ~ 8 and (CH<sub>2</sub>CH<sub>2</sub>O)<sub>x</sub>, *x* ~ 8 from <sup>19</sup>F and <sup>1</sup>H NMR analysis).<sup>33,34</sup> In a 250 mL round-bottom flask, Zonyl (20 g, 1 equiv) was dissolved in freshly distilled THF (100 mL). Then, freshly distilled triethylamine (4.22 mL, 1.1 equiv) was added and the temperature fixed at 0 °C. Methane sulfonyl chloride was introduced dropwise (3.65 g, 1.15 equiv). After the addition, the reaction mixture was allowed to stir at room temperature overnight. Triethylamine salt was filtered off and the filtrate was evaporated under vacuum. This intermediate compound was not further purified and in a second step, it was dissolved in ethanol (100 mL) containing sodium azide (2.69 g, 1.5 equiv). The reaction was stirred overnight at reflux. Then, solvent was removed and both ether and water were added to the mixture allowing extractions. The combined organic layers were dried with magnesium sulfate and the solvent removed in vacuum, yielding a brown liquid (yield = 85%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 2.41 ppm (m, CF<sub>2</sub>–CH<sub>2</sub>–), 3.39 ppm (t, CH<sub>2</sub>–N<sub>3</sub>), 3.5–3.8 ppm (m, O–CH<sub>2</sub>–CH<sub>2</sub>–O). FTIR (ATR): ν(N<sub>3</sub>) = 2100 cm<sup>-1</sup>.

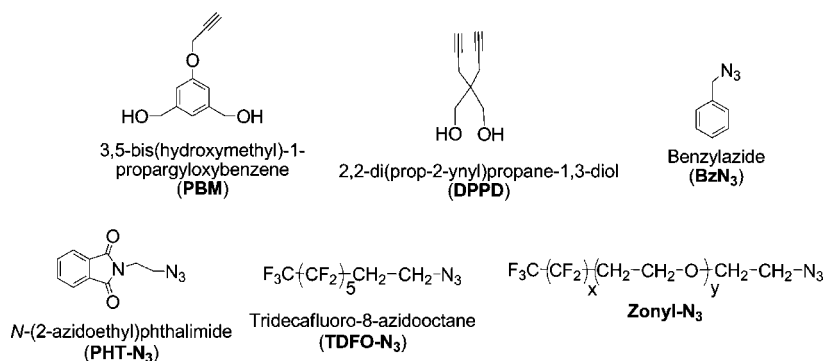
**Typical Synthesis of Linear Alkyne-Containing Polyurethane.** In a round-bottom flask were introduced 1 equiv of HDI, 1 equiv of a diol (or a predetermined mixture of two diols), and freshly distilled EtOAc. The mixture was degassed by bubbling nitrogen for 15 min and heated at 50 °C in a preheated oil bath. Then, dibutyltin dilaureate (approximately 20–30 μL) was added, and the reaction was allowed to stir under inert atmosphere for 2 h. During its formation, the PU slowly precipitates in the medium, and the obtained polymer was then filtered off and extensively washed with EtOAc and acetone to remove all unreacted compounds. The synthesized material was dried under vacuum overnight prior to further characterizations such as GPC or NMR.

**Typical Huisgen 1,3-Dipolar Cycloaddition onto Linear Polyurethane.** In a round-bottom flask, the alkyne-functionalized PU (1 equiv of alkyne functions) was charged with the azide compound (2 equiv), the solvent (DMSO or DMF) and the copper catalyst based on either CuBr/PMDETA (0.1 equivalent each according to the alkyne content) or CuSO<sub>4</sub>, 5H<sub>2</sub>O/Na<sub>asc</sub>. (0.05 and 0.1 equiv, respectively). The reaction was performed overnight under nitrogen atmosphere at 50 °C. The resulting modified material was precipitated in diethyl ether and dried under vacuum overnight prior to further characterizations.

**Deprotection of Phthalimide-Functionalized PU.** In a round-bottom flask, the phthalimide-functionalized PU (1 eq.) was dissolved in DMF. A solution of hydrazine monohydrate in DMF was slowly added to the reaction mixture. Then, the temperature was fixed at 70 °C for 4 h. The reaction mixture was cooled down to room temperature and the PU was precipitated into diethyl ether. The polymer was filtered off and dried under vacuum prior to characterizations.

## Results and Discussion

**Synthesis of Alkyne-Functionalized Polyurethanes.** Since their discovery, the functionalization of PU materials has been a challenge in order to elaborate new highly interesting materials that are finding their applications in various fields. In this study, linear alkyne-functionalized PUs have been synthesized and characterized by conventional characterization techniques, after which they are modified *via* "click" chemistry. The described strategy consists in incorporating alkyne functions in the PU by the introduction of alkyne-functionalized diols in the feed

**Chart 1. Diols Involved during the PU Process and Azide Compounds Used for the Copper-Catalyzed Huisgen 1,3-Dipolar Cycloaddition****Table 1. Synthesis of Linear PUs Starting from HDI and the Building Block PBM**

entry	reference <sup>a</sup>	composition (mol %) <sup>b</sup> PBM/BDO/HDI	$M_n^c$ (g/mol)	PDI <sup>c</sup>	$T_{5\%}^f$ (°C)	char yield <sup>d</sup> (%)
1	PU-PBM-50	50/0/50	8100	1.33	302	23.9
2	PU-PBM-25	25/25/50	14700	2.58	303	12.8
3	PU-PBM-8	8/42/50	6000 <sup>d</sup>	<i>d</i>	304	5.1
4	PU-PBM-0	0/50/50	<i>e</i>	<i>e</i>	299	1.4

<sup>a</sup> Indicated values relate to the amount of incorporated PBM (mol %) in the final material. <sup>b</sup> Final composition determined by <sup>1</sup>H NMR in DMSO-*d*<sub>6</sub>. <sup>c</sup> Determined by GPC calibrated with PMMA standards. <sup>d</sup> The resulting trace is out of the calibration window, and only the peak weight ( $M_p$ ) could be determined. <sup>e</sup> Not soluble in GPC solvent. <sup>f</sup> Temperature at 5% weight loss and final char yield, as determined by TGA. Heating ramp: 20 °C/min under air from 25 to 800 °C.

of the polycondensation. For this purpose, one monoalkyne diol, 3,5-bis(hydroxymethyl)-1-propargyloxybenzene (PBM) and a dialkyne diol, 2,2-di(prop-2-ynyl)propane-1,3-diol (DPPD), were synthesized according to the literature<sup>30,32</sup> (Chart 1).

First, the monoalkyne diol (PBM) was mixed with hexamethylene diisocyanate (HDI) in ethyl acetate. According to the desired PBM loading, a predetermined amount of butane-1,4-diol (BDO) is added to the mixture. Then, the temperature was fixed at 50 °C and one drop of tin catalyst was added. As a result of the use of ethyl acetate as solvent, the PU polymer is precipitating during its formation after few minutes, leading to macromolecules having a low molecular weight, which facilitates the characterization by <sup>1</sup>H NMR. Table 1 summarizes the results of the synthesized PUs with varying amounts of PBM (50, 25, and 8 mol %, entries 1–3, Table 1) and also a blank PU (0 mol % of PBM) synthesized from HDI and BDO (entry 4, Table 1).

Figure 1 shows a typical <sup>1</sup>H NMR spectrum obtained from PU-PBM-25. The typical resonance of the alkyne proton appears at 3.55 ppm proving that the functionalized diol has been incorporated in the polymer without any side reaction. 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, either from the BDO, the PBM, or the diisocyanate. Moreover, by taking into account the integration of peaks at 4.75 ppm (2H, –CH<sub>2</sub> from PBM), 3.9 ppm (4H, –O–CH<sub>2</sub> from BDO) and 2.9 ppm (4H, –NH–CH<sub>2</sub> from HDI), the molar ratio between BDO and PBM could be determined.

The elaborated PUs were also characterized by FT-IR spectroscopy to further prove the incorporation of the functionalized alkyne diol in the materials. In Figure 2, the IR spectra display the overlay of the starting alkyne diol PBM and the synthesized PU-PBM-25.

The spectrum corresponding to the PU-PBM-25 (upper spectrum, Figure 2) shows typical bands, on one hand at 1737 cm<sup>−1</sup> corresponding to the carbonyl function from the urethane groups and, on the other hand at 2220 cm<sup>−1</sup> (C≡C) and 3290 cm<sup>−1</sup> (C≡C–H) relating to the terminal alkyne functions present in the material. The thermal stability of the synthesized functionalized PU was studied by thermogravimetric analysis (TGA) measurements.

As shown in Figure 3 (top), all synthesized PUs are stable up to 300 °C. The initial decomposition temperature, defined as 5% weight loss (data in Table 1), are similar, showing that the incorporation of PBM in the material does not affect the thermal behavior at the early stage of the thermal decomposition process. However, it can be observed from the overlay that for a higher PBM content in the PU, the overall final char yield is increasing up to 25%. Thus, PBM may act at the same time as a stabilizer agent as already reported elsewhere. Indeed, alkyne groups are known to act as a cross-linker upon heating by creation of reticulated alkenes and can participate in a reaction of cyclotrimerization making the materials flame-retardant.<sup>35,36</sup> This is ascribed to the formation of char on the upper part of the material, which prevents the formation of volatile compounds from the inner part. In addition, terminal alkynes have also been used to elaborate high-performance polymers and composites.<sup>37</sup> When final char yields were plotted against the amount of incorporated PBM (Figure 3, bottom), a linear relationship was surprisingly observed, meaning that a structure–property relationship may exist that can justify the above-mentioned explanation about the thermal stability of alkyne-functionalized materials. Moreover, the stability of the materials has been studied after heating them at 200 °C for 30 min. <sup>1</sup>H NMR measurements (data not shown) after this degradation study showed no change meaning that the PUs are stable in these conditions and especially that the alkyne functions are still available for further reactions.

The same strategy has been employed to incorporate in the PU a diol bearing two alkyne functions per repeating unit (Scheme 1).

The reactivity of DPPD was examined by elaborating a soluble PU starting from DPPD and HDI (entry 1, Table 2) as shown in Scheme 1. Then, BDO was introduced in the feed of the polycondensation to obtain a PU with 15 mol% of DPPD (entries 2 and 3, Table 2).

Figure 4 shows the overlay of the starting diol DPPD and the PU-DPPD-15.

The IR spectrum of DPPD (upper spectrum) indicates the presence of the alkyne function due to the low intense band at 2120 cm<sup>−1</sup> (C≡C) and the shoulder at approximately 3270 cm<sup>−1</sup> (C≡C–H) next to the intense OH stretching. Additionally, the spectrum corresponding to the PU-DPPD-15 shows the appearance of three intense bands at 1700 cm<sup>−1</sup> from amide I



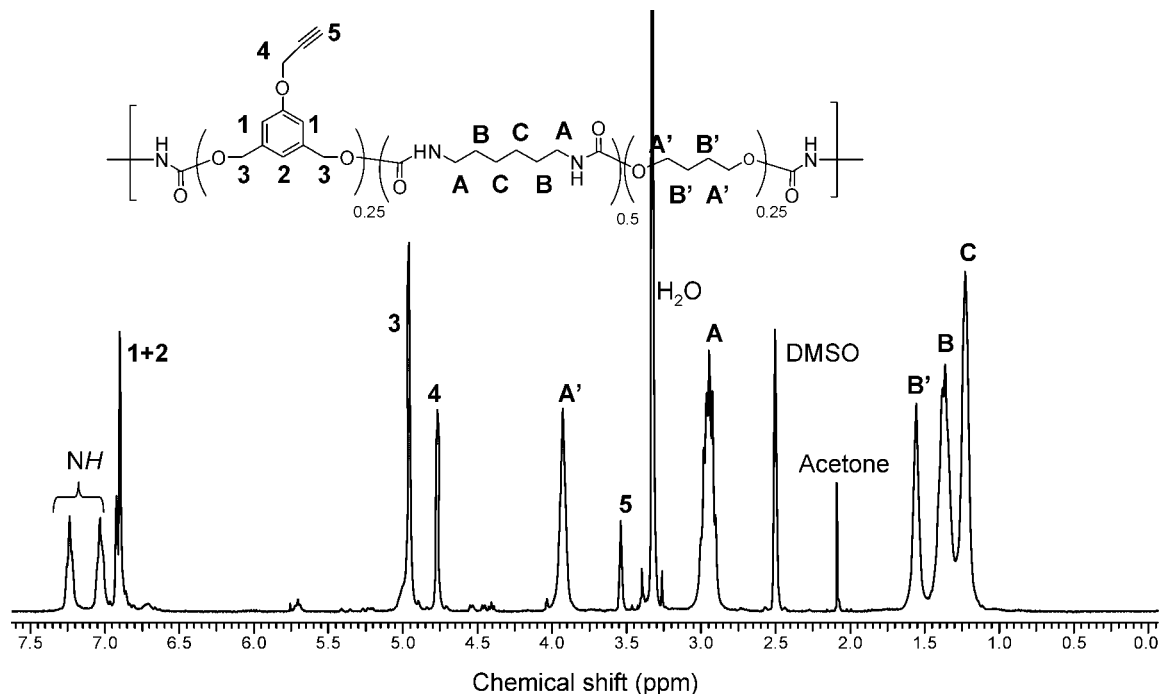


Figure 1.  $^1\text{H}$  NMR spectrum (300 MHz,  $\text{DMSO}-d_6$ ) of PU-PBM-25.

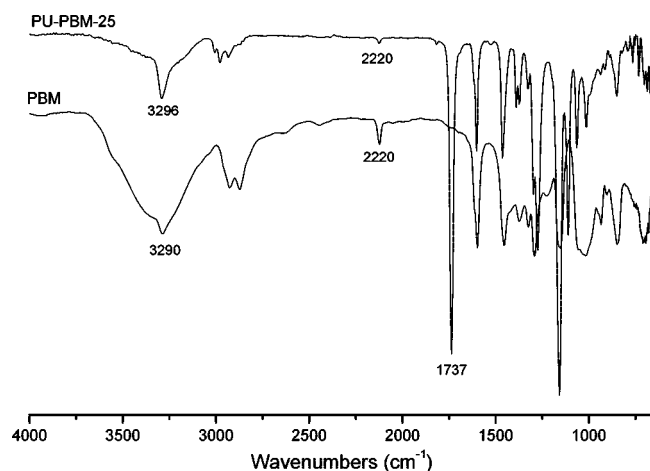


Figure 2. FT-IR spectra of the starting diol PBM and PU-PBM-25.

( $\text{C}=\text{O}$  stretching vibrations) of the urethane, at  $1540\text{ cm}^{-1}$  from the amide II ( $\text{C}-\text{N}$  stretching vibrations) and at  $1258\text{ cm}^{-1}$  belonging to the amide III ( $\text{C}-\text{N}$  deformation).

The thermal stability of such materials was also examined by TGA. It reveals that all synthesized PU-DPPD are stable up to  $250\text{ }^\circ\text{C}$  or higher. In contrast to the previous series (PU-PBM), at the early stage of the degradation process ( $250\text{--}350\text{ }^\circ\text{C}$ ), the incorporation of DPPD makes the material more sensitive to the heating as observed in Figure 5.

Nevertheless, as observed in the case of PBM-functionalized PUs, the incorporation of the dialkyne diol DPPD leads to high char-yielding materials. The most notable difference between both series (PU-PBM and PU-DPPD) is the decomposition temperature at about  $300\text{ }^\circ\text{C}$  for the series PU-PBM and at  $250\text{ }^\circ\text{C}$  for the series PU-DPPD. This can be ascribed to the presence of an aromatic compound (PBM), which affords more rigidity to the whole structure compared to the aliphatic compound DPPD. The thermal behavior of the alkyne-containing PUs is promising since it shows that the yields of flammable and volatile components from the thermal degradation of the

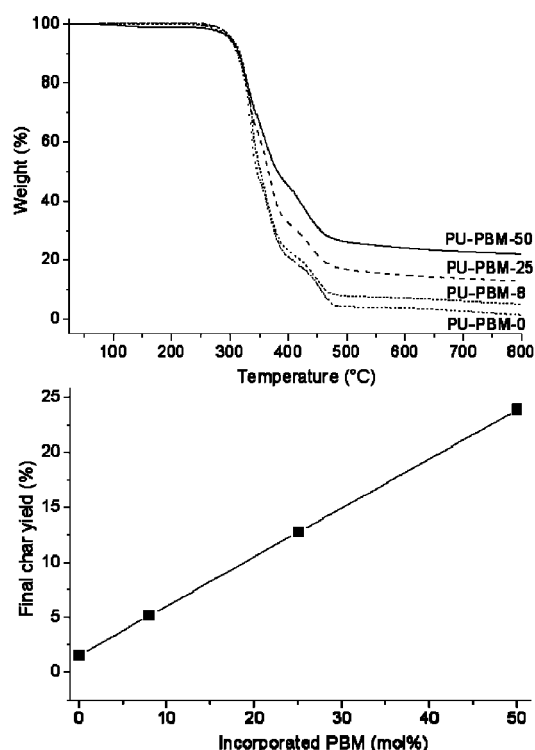


Figure 3. Top: TGA curves of the PU-PBM (heating ramp:  $20\text{ }^\circ\text{C}/\text{min}$  under air from  $25$  to  $800\text{ }^\circ\text{C}$ ). Bottom: Final char yield of the PU-PBM series versus the mol % of PBM incorporated in the material.

PUs are low and may satisfy the requirements for acting as flame retardants.

**"Click" Reactions onto Alkyne-Functionalized Linear PUs.** The postmodification of PU side-chains, allowing to tune the properties of the resulting polymers, has been a great challenge due to quite low conversions that are mainly caused by the steric hindrance or the nature of the reaction involved. Therefore, the quantitative copper(I) catalyzed azide-alkyne cycloadditions appears to be a promising approach to achieve

Scheme 1. Synthesis of PU–DPPD Based on HDI, BDO, and DPPD.

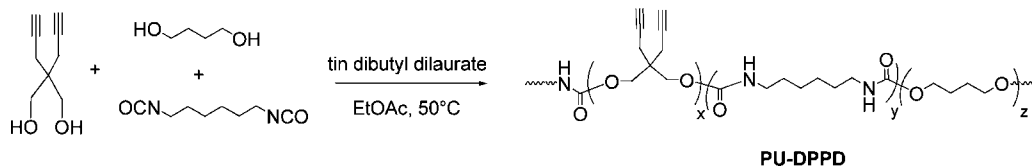


Table 2. Synthesis of Linear PUs Starting from HDI and the Building Block DPPD

entry	reference	composition <sup>a</sup> (mol %) DPPD/BDO/HDI	$M_n^b$ (g/mol)	PDI <sup>b</sup>	$T_{5\%}^d$ (°C)	char yield <sup>d</sup> (%)
1	PU–DPPD-50	50/0/50	4800	2.66	258	9.9
2	PU–DPPD-15	15/35/50	8800	1.86	287	5.5
3	PU–DPPD-0	0/50/50	<i>c</i>	<i>c</i>	299	1.4

<sup>a</sup> Final composition determined by <sup>1</sup>H NMR in DMSO-*d*<sub>6</sub>. <sup>b</sup> Determined by GPC calibrated with PMMA standards. <sup>c</sup> Not soluble in GPC solvent. <sup>d</sup> Temperature at 5% weight loss, determined by TGA. Heating ramp: 20 °C/min under air from 25 to 800 °C.

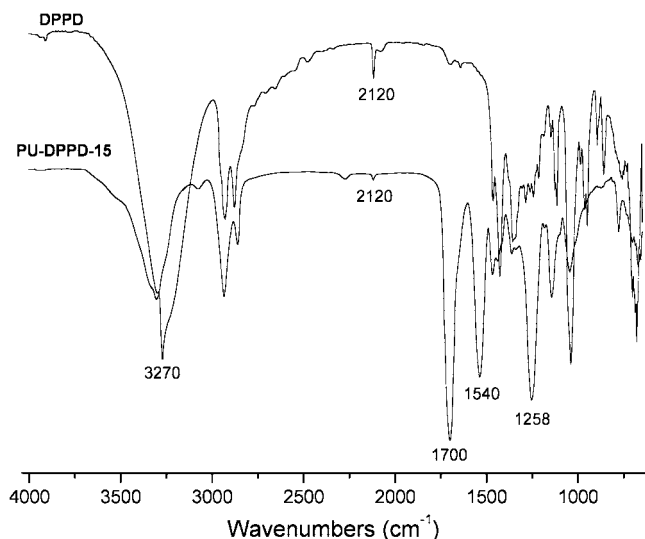


Figure 4. FT-IR spectra of the starting diol DPPD (up) and the PU–DPPD-15 (down).

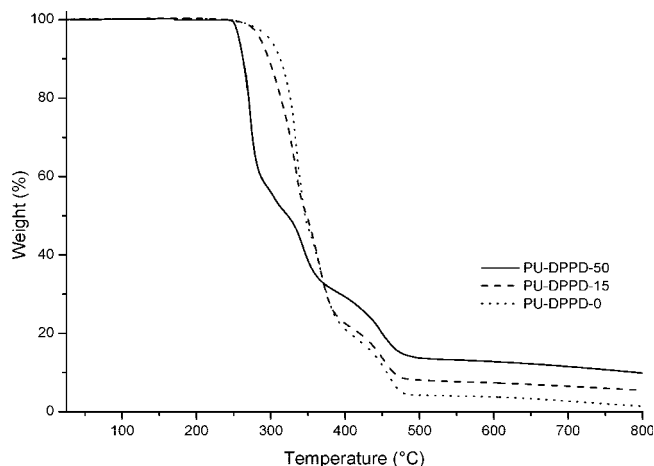
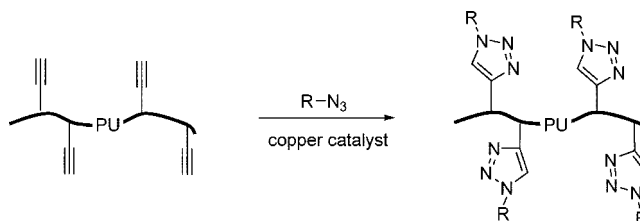


Figure 5. TGA curves of the polyurethanes functionalized with the dialkyne diol DPPD (heating ramp: 20 °C/min under air from 25 to 800 °C).

such modifications.<sup>24–27</sup> The availability of the alkyne functions present in the previously synthesized PUs has been studied by carrying out the “click” reaction with several azides (Scheme 2).

Scheme 2. General Scheme of the Huisgen 1,3-Dipolar Cycloadditions between Alkyne Containing PU and Azide Compound



The “click” reactions were carried out either in DMSO at 50 °C or in DMF at 60 °C in combination with common copper catalyst systems such as Cu<sup>I</sup>Br/PMDETA or CuSO<sub>4</sub>/Na<sub>asc</sub>. These solvents were used in order to maintain the PU solubility, while the copper catalysts were chosen as a function of their efficiency toward the “click” reaction. In this study, several azide compounds (Chart 1) were used in a 2-fold excess such as benzyl azide (BzN<sub>3</sub>), *N*-(azidoethyl)phthalimide (PHT–N<sub>3</sub>), tridecafluoro-8-azidoctane (TDFO–N<sub>3</sub>) or Zonyl–N<sub>3</sub>. The results of the coupling reactions between PBM-based PUs and the organic azide compounds are reported in Table 3.

A first screening was performed with PU–PBM-50 in different reaction conditions. First, the reaction of BzN<sub>3</sub>, which can be considered as a model compound, was undertaken and the precipitated PU was then analyzed by <sup>1</sup>H NMR in DMSO-*d*<sub>6</sub>. Figure 6 shows the overlay of the <sup>1</sup>H NMR spectra of the starting material PU–PBM-50 (lower spectrum, Figure 6) and the final material obtained after the dipolar cycloaddition with benzylazide (PU–PBM-50–Bz) (upper spectrum, Figure 6).

The arrow in Figure 6 clearly indicates the shift of the alkyne proton at 3.5 ppm (5, lower spectrum) to 8.2 ppm (5', upper spectrum), which corresponds to the proton linked to the formed triazole ring. Also, new peaks appear at 5.5 ppm (6', CH<sub>2</sub> from BzN<sub>3</sub>) and at 7.3–7.4 ppm (7', aromatic protons from BzN<sub>3</sub>), proving the success of the reaction. The complete disappearance of the alkyne proton at 3.5 ppm (Figure 6, lower spectrum) reveals that the reaction was quantitative. The same conclusions could be drawn from the reaction between BzN<sub>3</sub> and PU–PBM-25. Also, *N*-(azidoethyl)phthalimide (PHT–N<sub>3</sub>) was allowed to react with PBM-based PUs using CuSO<sub>4</sub>/Na<sub>asc</sub> as copper catalyst in DMF at 60 °C. As shown in Table 3, the “click” reactions with PU–PBM-50 and PU–PBM-25 occurred in a quantitative way since no peak from the starting alkyne proton could be detected in the final material by <sup>1</sup>H NMR.

Phthalimide-based compounds are often used as an amine-protecting group<sup>38–40</sup> and a simple deprotection step *via* hydrazine treatment is performed<sup>41</sup> (Scheme 3). For instance, O'Shea et al.<sup>42</sup> prepared bromo-terminated polystyrene (PS–Br) by ATRP, which was then treated with potassium phthalimide followed by the hydrazinolysis in order to obtain amino-terminated polystyrene (PS–NH<sub>2</sub>). In the present case, it can be a very promising way to obtain PUs functionalized with reactive primary amino groups. PU–PBM-25 was reacted with a solution of hydrazine in DMF at 70 °C. The <sup>1</sup>H NMR spectra are shown in Figure 7.

Table 3. Results of the "Click" Reactions onto PBM-Based Polyurethanes

PU sample	azide compound	catalyst	$M_n^d$ (g/mol)	yield <sup>e</sup> (%)	char yield <sup>g</sup> (%)
PU-PBM-50	BzN <sub>3</sub>	CuBr/PMDETA <sup>b</sup>	11600	>99	14.1
	PHT-N <sub>3</sub>	CuSO <sub>4</sub> /Na <sub>asc</sub> . <sup>c</sup>	11400	>99	15.6
	TDFO-N <sub>3</sub>	CuSO <sub>4</sub> /Na <sub>asc</sub> . <sup>c</sup>	7800	>99	22.0
	Zonyl-N <sub>3</sub>	CuSO <sub>4</sub> /Na <sub>asc</sub> . <sup>c</sup>	14100	<i>f</i>	2.16
PU-PBM-25	BzN <sub>3</sub>	CuBr/PMDETA <sup>b</sup>	24700	>99	18.5
	PHT-N <sub>3</sub>	CuSO <sub>4</sub> /Na <sub>asc</sub> . <sup>c</sup>	18300	>99	11.2
	TDFO-N <sub>3</sub>	CuSO <sub>4</sub> /Na <sub>asc</sub> . <sup>c</sup>	16000	>99	21.1

<sup>a</sup> Starting materials: PU-PBM-50:  $M_n$  = 8100 g/mol, PDI = 1.33. PU-PBM-25:  $M_n$  = 14 700 g/mol, PDI = 2.85. Reaction conditions: PU (1 equiv), azide (2 equiv), time = overnight. <sup>b</sup> CuBr/PMDETA: 0.1 equiv, DMSO, 50 °C. <sup>c</sup> CuSO<sub>4</sub>/Na<sub>asc</sub>: 0.05 and 0.1 equiv, respectively, DMF, 60 °C. <sup>d</sup> Determined by GPC calibrated with PMMA standards. <sup>e</sup> Determined by <sup>1</sup>H NMR in DMSO-*d*<sub>6</sub>. <sup>f</sup> Partially soluble in DMSO-*d*<sub>6</sub>. <sup>g</sup> Determined by TGA analysis. Heating ramp: 20 °C/min under air from 25 to 800 °C.

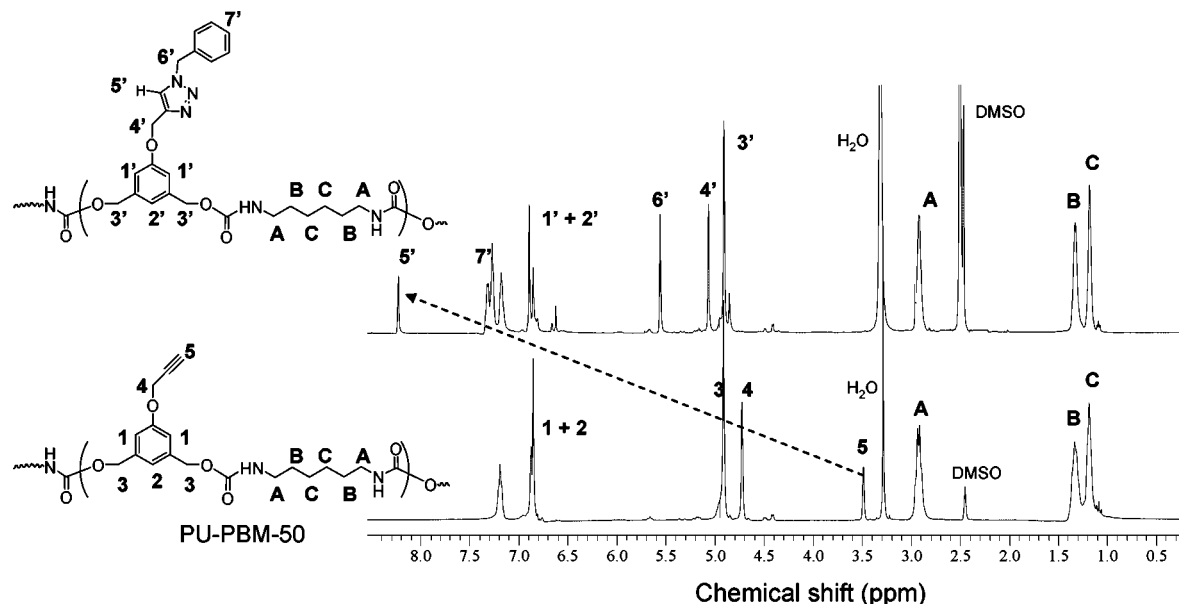
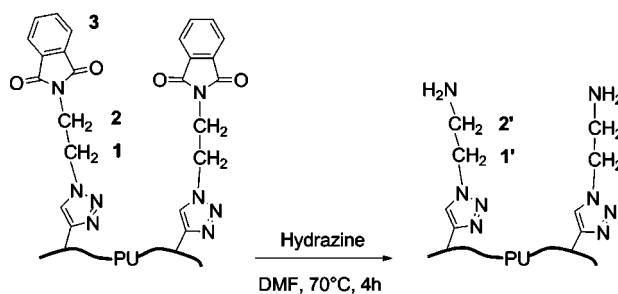


Figure 6. <sup>1</sup>H NMR spectra (300 MHz, DMSO-*d*<sub>6</sub>) of the starting polymer PU-PBM-50 (lower spectrum) and the final PU after the "click" reaction with BzN<sub>3</sub> (upper spectrum).

Scheme 3. General Scheme for the Hydrazinolysis of the Phthalimide-Based Materials



Between both <sup>1</sup>H NMR spectra, three major differences were observed, among which the clear disappearance of the peak at 7.8 ppm corresponding to the phthalimide groups of PU-PBM-25-PHT (3, lower spectrum, Figure 7). The other changes related to a chemical shift due to the change of the chemical environment of two methylene protons between the triazole ring and either the phthalimide group or amino group. As a consequence, the methylene protons at 4.65 ppm and 4.05 ppm (2 and 1 respectively, lower spectrum, Figure 7) were shifted to 4.45 ppm and 3.9 ppm respectively (2' and 1' respectively, upper spectrum, Figure 7). Thus, ethylamino-functionalized PU was obtained *via* the strategy in which the first step involves the "click" reaction of an amino precursor onto the PU and the second step is a deprotection step. A direct anchoring of an amine to the PU *via* the cycloaddition process could also be considered with the help of 1-azidoethylamine. Nevertheless, this azido compound is explosive and therefore difficult to obtain

because of the low C/N ratio<sup>20</sup> (i.e., 2/4). In principle, another safer azide containing the amino compound could be synthesized and used in the cycloaddition reaction to obtain amino-functionalized PUs in one step.

Last attempts of the series of PU-PBM were undertaken with fluorinated azide compounds in order to enlarge the concept of functionalized PUs by grafting hydrophobic pendant chains along the backbone of the PUs. TDFO-N<sub>3</sub>, which was synthesized from the iodide derivative, was allowed to react with both PU-PBM-50 and PU-PBM-25 using copper sulfate and sodium ascorbate (Table 3). In both cases, the <sup>1</sup>H NMR revealed the appearance of the triazole proton. Integrations of this specific peak and the others from the PU backbone fit well, proving again the quantitative character of the "click" reactions. Thus, the high hydrophobicity of the fluorinated compound did not affect the dipolar cycloaddition.

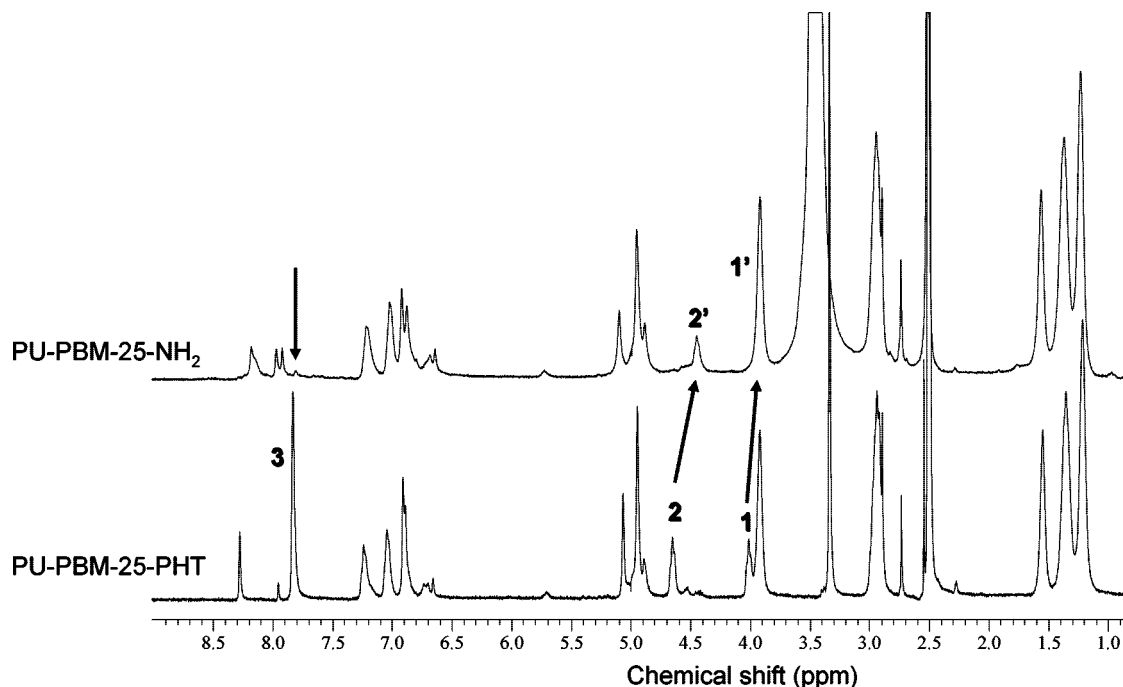


Figure 7.  $^1\text{H}$  NMR spectra (300 MHz,  $\text{DMSO}-d_6$ ) of PU-PBM-25-PHT (down) and PU-PBM-25- $\text{NH}_2$  (up).

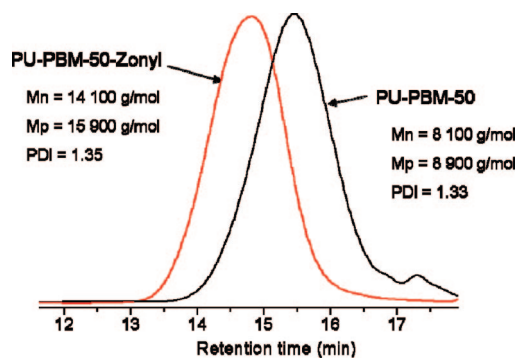


Figure 8. GPC traces of the starting material PU-PBM-50 and PU-PBM-50-Zonyl.

Finally, also another azide compound was used, namely Zonyl- $\text{N}_3$ . This compound was synthesized from commercially available hydroxy-functionalized Zonyl FSO-100, which is a low molecular weight block copolymer having a first block based on a perfluoroalkyl chain followed by a second poly(ethylene glycol) block (Chart 1). Zonyl FSO-100 is currently widely used in applications such as improved wetting agent, lubricant, antifogging and pigment compatibilizer in inks.<sup>43</sup> In the present work, Zonyl- $\text{N}_3$  was reacted with PU-PBM-50. As mentioned in Table 3, the resulting PU was only partially soluble in the NMR solvent, making the measurement not suitable. Nevertheless, the change of solubility may be an indirect proof of the grafting process by “click” chemistry. On the other hand, Figure 8 represents the overlay of the GPC traces of PU-PBM-50 and the resulting PU with their macromolecular characteristics such as number average and peak molecular weight and polydispersity index (PDI). A shift of the macromolecular species toward lower retention time is clearly shown. Also, the peak molecular weight is largely increasing proving that the fluorinated compound has been grafted to the PU backbone *via* the alkyne functions.

It can also be noticed from Table 3 that after the “click” reaction all the functionalized PUs have a higher number-average molecular mass than the starting PU-PBM-50 and PU-PBM-25, showing the success of the grafting reaction. As

Table 4. Results of the “Click” Reactions onto DPPD-Based Polyurethanes<sup>a</sup>

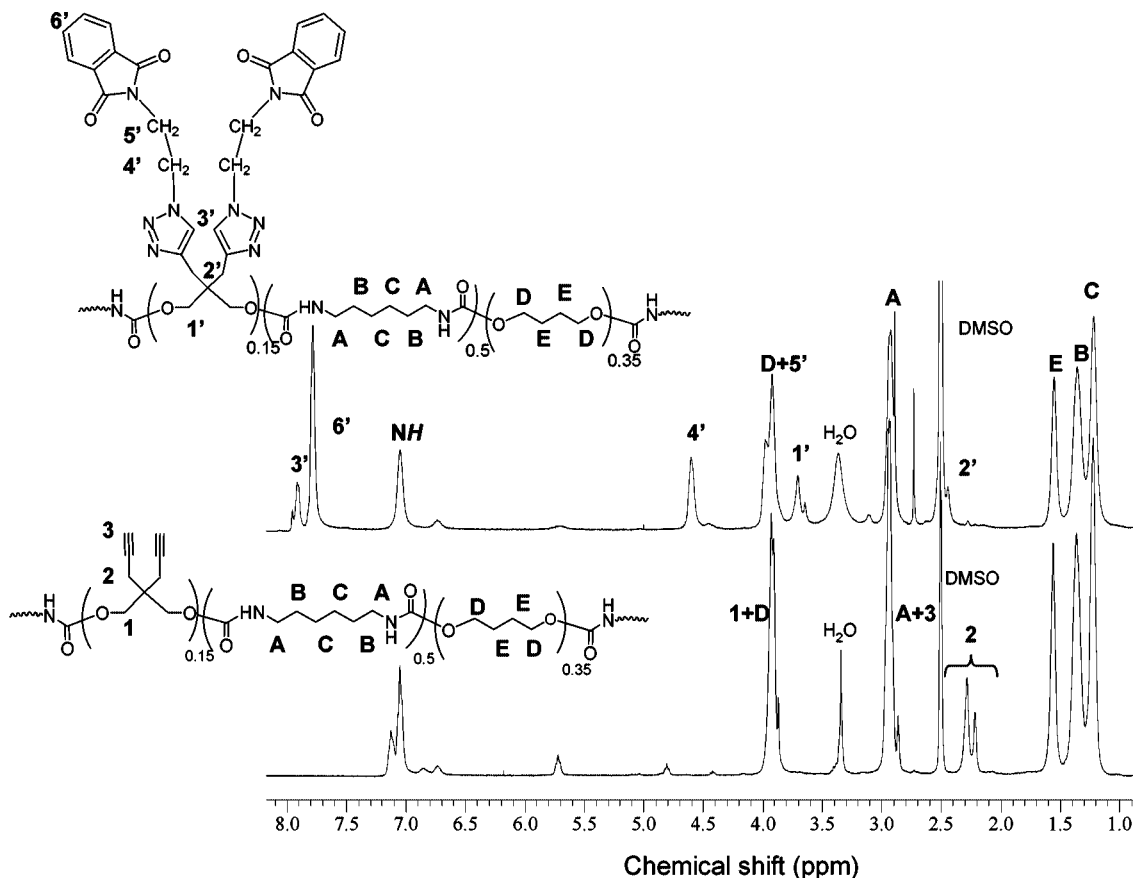
PU sample	azide compound	catalyst <sup>b</sup>	$M_n^c$ (g/mol)	yield <sup>d</sup> (%)	char yield <sup>e</sup> (%)
PU-DPPD-50	BzN <sub>3</sub>	CuBr/PMDETA	9140	>99	12.0
	PHT-N <sub>3</sub>	CuBr/PMDETA	6250	>99	17.0
PU-DPPD-15	BzN <sub>3</sub>	CuBr/PMDETA	16900	>99	7.0
	PHT-N <sub>3</sub>	CuBr/PMDETA	10200	>99	12.4
	TDFO-N <sub>3</sub>	CuBr/PMDETA	13400	<i>f</i>	17.2

<sup>a</sup> Starting materials: PU-DPPD-50:  $M_n$  = 4800 g/mol, PDI = 2.66. PU-DPPD-15:  $M_n$  = 8300 g/mol, PDI = 2.01. Reaction conditions: PU (1 equiv), azide (2 equiv), time = overnight. <sup>b</sup> CuBr/PMDETA: 0.1 equiv each, DMF, 60 °C. <sup>c</sup> Determined by GPC calibrated with PMMA standards. <sup>d</sup> Determined by  $^1\text{H}$  NMR in  $\text{DMSO}-d_6$ . <sup>e</sup> Determined by TGA analyses. Heating ramp: 20 °C/min under air from 25 to 800 °C. <sup>f</sup> The final material not soluble in NMR solvent.

an exception, PU-PBM-50-TDFO (PU-PBM-50 after the “click” reaction with TDFO- $\text{N}_3$ ) has a slightly lower molecular mass ( $M_n$  = 7800 g/mol, Table 3) than the starting material. This can be attributed to the change of hydrodynamic volume of the obtained macromolecules, which have quite hydrophobic side-chains.

To further prove the concept of functionalized polyurethanes, “click” reactions were also performed with the other series of materials, i.e. PU-DPPD, having two alkyne functions per DPPD unit. Their reactivity toward BzN<sub>3</sub> and PHT-N<sub>3</sub> were studied using CuBr/PMDETA as catalyst system. Table 4 summarizes the results obtained during the “click” reactions with PU-DPPD-50 and PU-DPPD-15.

The “click” reaction between BzN<sub>3</sub> and PU-DPPD was executed with the experimental conditions described in Table 4. The reaction with BzN<sub>3</sub> led to quantitative yields with both PU-DPPD-50 and PU-DPPD-15 and an increase of the molecular weight was observed in both cases by GPC. These materials PU-DPPD were also allowed to react with PHT-N<sub>3</sub>. As mentioned in Table 4, quantitative yields were observed by  $^1\text{H}$  NMR in  $\text{DMSO}-d_6$  leading to materials bearing phthalimide groups on the side-chains of the polyurethanes. In Figure 9, the overlay of  $^1\text{H}$  NMR spectrum corresponding to starting PU-DPPD-15 and PU-DPPD-15-PHT is represented.



**Figure 9.**  $^1\text{H}$  NMR spectra (300 MHz,  $\text{DMSO}-d_6$ ) of the starting polymer PU-DPPD-15 (lower spectrum) and PU-DPPD-15-PHT (upper spectrum).

New peaks appear at 7.7–7.8 and 4.6 ppm ( $6'$  and  $4'$ , upper spectrum) corresponding, respectively, to the grafted phthalimide group onto the PU and to the methylene protons close to the triazole ring. Second, a peak also appears at 7.9 ppm ( $3'$ , upper spectrum) proving the formation of the triazole ring. Moreover, the protons corresponding to the two  $\text{CH}_2$  groups at 2.2–2.4 ppm near the terminal alkyne functions (2, lower spectrum) have been completely shifted to 2.4 ppm (upper spectrum) proving the success of the “click” reaction. Finally, the measured integrations fit very well when taking into account the molar composition of the PU. Relating to the TGA measurements (Table 4), it appears that the final char yields of all “clicked” PUs are again quite higher than the starting material.

Additionally, the cycloaddition reaction between TDFO- $\text{N}_3$  and PU-DPPD-15 was undertaken (Table 4) in order to synthesize highly hydrophobic materials. It was observed that the material PU-DPPD-15-TDFO was insoluble in DMSO, making the  $^1\text{H}$  NMR analysis not feasible. Nevertheless, from TGA measurements, a high char yield was obtained (i.e., 17.2%, Table 4), which may indicate the presence of fluorinated grafted side-chain along the PU backbone.

## Conclusions

PUs bearing alkyne functions as pendant groups have been synthesized by incorporating an alkyne diol (PBM and DPPD) during their elaboration. This resulted in PUs with a variable amount of “clickable” functions. Moreover, it has been proved by TGA measurements that such PUs have a high thermal stability and that the final char yield is proportional to the alkyne content in the material. In a second step of the research, the Huisgen 1,3-dipolar cycloaddition was employed by reacting these alkyne functionalized materials with several azide com-

pounds in the presence of a copper catalyst. After the success of the “click” reaction with  $\text{BzN}_3$ , amine and fluorinated compounds have been attached to the PUs. In almost all cases, a quantitative yield was obtained as observed by  $^1\text{H}$  NMR, leading to PUs with new functionalities in the side-chain of the backbone. We are currently studying the use of PU based on polyols, the kinetics of the “click” chemistry reaction and the surface properties of the corresponding PU coatings. This concept of universal functionalized PU is believed to afford new classes of PU materials with easily adaptable physical properties by making use of readily accessible azide compounds.

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