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Functionalization of Polyurethanes by Incorporation of Alkyne Side-Groups to Oligodiols and Subsequent Thiol-yne Post-modification

Malgorzata Basko[a], Melania Bednarek[a], Le-Thu T. Nguyen[b,c], Przemyslaw Kubisa[a], Filip Du Prez[b,*]

[a] Center of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-362 Lodz, Poland

[b] Department of Organic Chemistry, Polymer Chemistry Research Group, Ghent University, Krijgslaan 281 S4-bis, B-9000 Ghent, Belgium

[c] Faculty of Materials Technology, Ho Chi Minh City University of Technology, Vietnam National University, Ly Thuong Kiet 268, 10 District, Ho Chi Minh City, Vietnam

Abstract

A versatile and upscalable method for the synthesis of polyurethanes (PUs) bearing pendant functionalities at the hard-soft segment interface from easily accessible commercial oligodiols is described. Reactive alkyne groups were introduced to polytetrahydrofuran (PTHF), poly(ε-caprolactone) (PCL) and polydimethylsiloxane (PDMS) diols by cationic ring-opening polymerization of glycidyl propargyl ether using these oligodiols as macroinitiators. The resulting oligodiols, with alkyne side groups located at both chain ends, were subsequently reacted with 1,4-butanediol and hexamethylene diisocyanate for the synthesis of PUs, containing several pendant alkyne groups between the soft and hard segments. The functionalized PUs based on different soft segments (PTHF, PCL or PDMS) have been further modified via metal-free thiol-yne chemistry. Proper reaction conditions were found for quantitative radical thiol-yne coupling reactions with benzyl mercaptan and thioglycerol.

Keywords: cationic ring-opening polymerization, functionalization, thiol-yne coupling chemistry, polyurethanes

Introduction

Polyurethanes (PUs) remain an essential class of synthetic polymers widely used in industry as adhesives, coatings, foams, packaging materials and biomedical aids. Such extensive application of PUs is possible as a result of the rational design of polymer properties tailored to exert distinct functions. As PUs are mostly prepared by step-growth polymerization between diisocyanates and diols or polyols, proper combination of these components determines the unique and on-demand properties of final products.

However, for many high-tech applications, PU materials should bear functionalities enabling tuning final material properties. The functionalization of PUs can be accomplished, either by introducing functional groups into oligodiols with further step-growth polymerization or afterwards on the end product. The former approach is preferred because incorporation of functional groups into low or medium molecular weight components (oligodiol, diisocyanate or chain extender) is experimentally more feasible. In practice, this is achieved by a variety of methods including the synthesis of polyols with functional groups that can be used as modification sites for further post-functionalization.[1-3]

Polyols are often obtained by ring-opening polymerization of cyclic ethers and esters. A convenient synthetic approach, as it has been demonstrated earlier, is a metal-free strategy based on the Activated Monomer (AM) mechanism.[4] In this mechanism, a hydroxyl group acts as initiator and a protic acid as catalyst. The heterocyclic monomer is activated in the presence of the catalyst by the formation of a protonated species that reacts with the hydroxyl group, leading to ring opening of the cyclic monomer. Thus, polymerization involves consecutive additions of protonated monomer molecules to the growing macromolecules fitted with hydroxyl groups at their chain ends. Such an AM polymerization offers several powerful synthetic possibilities. Indeed, when a diol is used as an initiator, a telechelic polymer terminated with hydroxyl groups is obtained. The use of a heterocyclic monomer containing a functional group leads to introduction of the pendant functional group into the polymer chain.

During the last decades, highly efficient “click” chemistry methodologies have been increasingly used for post-functionalization of polymers.[5] The “click” philosophy is based on the concept of modularity and orthogonality: building blocks for a final target can be made individually and subsequently assembled leading to complex polymer architectures.[6-8] One of the most popular click reaction applied in a wide range of research fields is the Huisgen 1,3-dipolar addition of azides and alkynes.[9-12] However, this kind of “click” reaction is in most cases performed in the presence of a copper catalyst, which may be a limitation for several

applications. Therefore, highly efficient reactive systems that do not contain any metal catalyst are often desired. In this respect, light-mediated thiol–ene[13,14] and thiol-yne[15-21] radical reactions have become widely used as they effectively combine some classical benefits of coupling reactions with the advantages of a photoinitiated process resulting in a powerful method for chemical synthesis and tailorable material fabrication.

In a previous contribution,[22] we have presented a synthetic route for preparation of functionalized PUs containing pendant alkynes distributed in the soft segments. This was achieved by the synthesis of alkyne-functionalized PTHF diol by cationic copolymerization of THF with glycidyl propargyl ether (GPE), proceeding according to the AM mechanism. As it is the polyol that imparts softness and flexibility to the PU, this strategy provides pendant functionalities in the soft segment. Finally, these alkyne side groups have been used as modification sites for further functionalization by a copper-catalyzed Huisgen cycloaddition. However, this approach is limited to oligodiols made from monomers that undergo copolymerization with GPE, and thus could only be applied to the synthesis of PTHF containing polyurethanes. Also, the subsequent modification was conducted by a metal catalyzed process.

For all these reasons, we have been interested in the development of a more versatile strategy that includes diversification of the soft segment nature in order to broaden the possibility of tailoring PU properties, for example for coating applications. Additionally, we focused on the introduction of functional groups strictly located between soft and hard segments of PUs and subsequent post-modification via the metal-free thiol-yne coupling reaction. Besides previously reported PUs with functional groups located in either hard[1,2] or soft[22] segments, the synthesis herein expands the library of PU materials with pendant functionalities at desired locations. Although not within the scope of this study, we believe that the possibility to localize the functional groups may influence thermal and physical properties of the obtained structures.

For this purpose, we propose herein a versatile and straightforward synthetic methodology in which commercially available polydiols such as poly(tetrahydrofuran) (PTHF), poly(caprolactone) (PCL) and poly(dimethylsiloxane) (PDMS) are modified by incorporating alkyne side groups to both chain ends with preservation of terminal hydroxyl groups. The availability of a wide range of commercial bulk polydiols allows facile tailoring of the physical and chemical properties toward specific applications. The modification of the polydiols, the synthesis of functionalized PUs from the resulting modified polydiols and

subsequent post-modification of the PUs by thiol-yne chemistry is the subject of this contribution.

Experimental

Materials

Poly(tetrahydrofuran) (PTHF) diols (Aldrich, M_n = 650 and 1000), poly(caprolactone) (PCL) diols (Aldrich, M_n = 530 and 1250), and poly(dimethylsiloxane) (PDMS) diol (Gelest, M_n = 1000) were dried on a vacuum line at 40 ^oC under stirring. Glycidyl propargyl ether (GPE, Aldrich) was dried over molecular sieves and distilled under vacuum before use.

Hexamethylene diisocyanate (HDI, 98%, Aldrich), 1,4-butanediol (BDO, 99% Aldrich), dibutyltin dilaureate (95%, Fluka), ether complex of tetrafluoroboric acid ($HBF_4{\cdot}Et_2O$, 85%, Aldrich), benzyl mercaptan (Bz-SH, 99%, Aldrich), 3-mercapto-1,2-propanediol (Gly-SH, 90% aqueous solution, Acros Organics) and 2,2-dimethoxy-2-phenylacetophenone (DMPA, 99%, Aldrich) were used as received. Dichloromethane (POCh, Poland) was dried over CaH_2 and distilled. Ethyl acetate (EtOAc, HPLC grade, Aldrich) was distilled before use. Dimethylacetamide (99%, Aldrich) and diethyl ether (99.8%, Aldrich) were used as received.

Synthesis of Alkyne-Functionalized PTHF, PCL and PDMS oligodiols

A typical reaction procedure for the synthesis PCL diol functionalized with alkyne groups (Table 1, entry 5) is described: Commercial PCL diol with M_n = 530 (1.7 g, 6.4 mmol of –OH groups) was dissolved in 8.5 mL of dichloromethane in a round-bottom flask. To this solution 64 μL (0.47 mmol) of $HBF_4{\cdot}Et_2O$ was added. Then, a nitrogen flow was passed over the mixture and the flask was closed with a rubber septum. Then, 1 mL (1.04g, 9.3 mmol) of GPE was slowly introduced with a syringe during 7 h. The reaction mixture was kept at room temperature for 24 h, and, after that, the acid catalyst was neutralized with solid CaO. After filtration of CaO, the product was isolated by evaporation of solvent and was dried on vacuum line.

Synthesis of Alkyne Containing Polyurethanes

As an example, the synthesis of PU5 (see Table 3) is described. A round-bottom flask of 25 mL was charged with 0.30 g (35 mmol) of $(GPE)_1$-$(CL)_4$-$(GPE)_2$ with M_n equal to 870 Da, 31 μL (31mg, 35 mmol) of BDO, 110 μL (116 mg, 70 mmol) of HDI (molar ratio 0.5: 0.5 :1) and 2.5 mL of EtOAc. A nitrogen flow was passed over the reaction mixture and the flask was immersed in a preheated oil bath at 50 ^oC. Then, dibutyltin dilaureate (approximately 20 μL) was added, and the reaction mixture was stirred under nitrogen. Typically the experiment was

conducted for 5 h after which the precipitated fraction was separated by centrifugation. A fraction soluble in ethyl acetate was separated by solvent evaporation. Both fractions were analyzed by SEC and ^{1}H NMR.

Thiol-yne addition reaction of alkyne-functionalized PUs with thiols

As an example, the reaction of PU5 with M_n equal to 6060 Da (obtained from $(GPE)_1$-$(CL)_4$-$(GPE)_2$ diol) with benzyl mercaptan is described. 50 mg of PU5 was dissolved in 1.8 mL of DMA. To the solution, 8.5 mg of DMPA and 78 μL of benzyl mercaptan was added and the flask containing a stirring bar was closed with a rubber septum. The reaction mixture was degassed three times and was purged with nitrogen through a needle using vacuum/nitrogen line and the flask was exposed to UV irradiation (365 nm) for 40 minutes under magnetic stirring. After the reaction, the polymer was precipitated into cold diethyl ether and was washed three times with diethyl ether.

Measurements

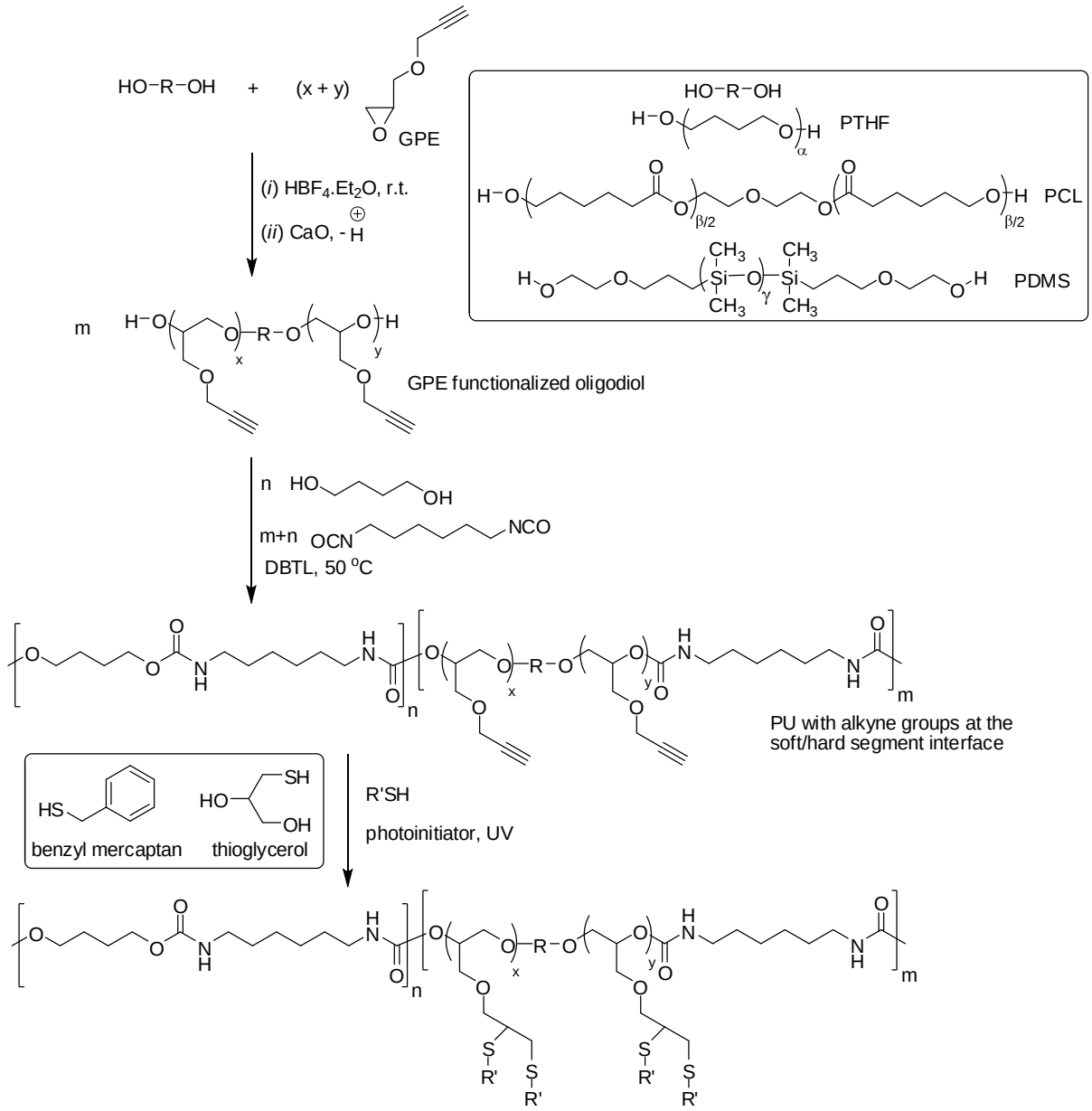
Molecular masses of PUs were measured on a SEC system using a Waters 610 Fluid pump, Waters 2414 RI Detector, Merck Hitachi column oven L-7300, Waters 717 Plus Autosampler and with set of columns PSS GRAM (10 μm 8,0x50mm, 30 A°, 10 μm 8,0x300 mm, 1000 A°, 10 μm 8,0x300 mm). *N*,*N*-dimethylacetamide (DMA) containing LiBr was used as eluent with a flow rate fixed at 1 mL min^{-1} and a temperature of 40 ^oC, with poly(methylmethacrylate) standards.

^{1}H NMR spectra of modified oligodiols were recorded in $CDCl_3$ on Bruker AC200 (200 MHz) and spectra of polyurethanes were recorded in DMSO using Bruker Avance 300 spectrometer.

MALDI TOF analysis was performed using a Voyager Elite apparatus in linear mode using dithranol as a matrix and NaI as cationating agent. Nitrogen laser desorption at a wavelength equal to 337 nm was applied.

Results and discussion

The general idea of the straightforward and upscalable synthesis of functionalized polyurethanes presented in this work is depicted in Scheme 1.



Scheme 1. The synthesis of PUs with alkyne pendant groups located at the hard-soft segment interface and subsequent functionalization via thiol-yne reactions.

The introduction of alkyne groups to the oligodiol chain ends with preservation of the alcohol groups was done by the addition of a glycidyl propargyl ether unit (proceeded by earlier activation of GPE by protic acid i.e. $HBF_4 \cdot Et_2O$) in the presence of the polymeric diol.

Three commercial oligodiols, i.e. PTHF, PCL and PDMS (chemical structures shown in Scheme 1), with varying M_n (Table 1), were used as macroinitiators for cationic polymerization of GPE. In all cases, GPE was slowly introduced to the system containing macroinitiator and $HBF_4 \cdot Et_2O$ as catalyst. An addition of the protonated GPE to the terminal hydroxyl groups leads to the modified polydiol containing a desired number of repeating units of GPE, located strictly at the polymer chain ends. The characteristics of the obtained oligodiols is presented in Table 1.

Table 1. Characterization of alkyne-functionalized oligodiols

Starting oligodiol		Alkyne-functionalized oligodiol				
Structure[1)]	M_n ($g \cdot mol^{-1}$) [2)]	Entry	Structure, x+y [3)]	$M_{n,theor}$ [4)]	THF (CL, DMS)/ GPE theor.	THF (CL, DMS)/ GPE ^{1}H NMR[5)]
HO-$(THF)_9$-OH	650	1 2	HO-$(GPE)_x$-$(THF)_9$-$(GPE)_y$-OH, 2 HO-$(GPE)_x$-$(THF)_9$-$(GPE)_y$-OH, 4	870 1090	4.5 2.25	4.0 2.2
HO-$(THF)_{14}$-OH	1000	3	HO-$(GPE)_x$-$(THF)_{14}$-$(GPE)_y$-OH, 4	1450	3.5	3.4
HO-$(CL)_4$-OH	530	4 5	HO-$(GPE)_x$-$(CL)_4$-$(GPE)_y$-OH, 2 HO-$(GPE)_x$-$(CL)_4$-$(GPE)_y$-OH, 3	750 870	2 1.5	2.2 1.3
HO-$(CL)_{10}$-OH	1250	6 7	HO-$(GPE)_x$-$(CL)_{10}$-$(GPE)_y$-OH, 2 HO-$(GPE)_x$-$(CL)_{10}$-$(GPE)_y$-OH, 4	1470 1700	5 2.5	5.5 3
HO-DMS_{10}-OH	1000	8 9	HO-$(GPE)_x$-$(DMS)_{10}$-$(GPE)_y$-OH, 2 HO-$(GPE)_x$-$(DMS)_{10}$-$(GPE)_y$-OH, 4	1220 1450	5 2.5	5.5 2.3

[1)] Additional unit corresponding to initiator used in the synthesis of the commercial diol present in oligodiol is not shown.

[2)] M_n as given by the supplier .

[3)] Theoretical structures of obtained oligodiols were calculated on the basis of M_n provided by the supplier and the added amount of GPE (for complete GPE conversion).

[4)] M_n theoretical = M_n (oligodiol) + M_n (GPE) · (x + y).

[5)] The ratio of THF (CL, DMS) to GPE units was found on the basis of ^{1}H NMR analysis.

The functionalized oligodiols were characterized by ^{1}H NMR and MALDI TOF analysis because M_n determined by SEC with polystyrene calibration differed considerably from theoretical values. Thus, taking into consideration on one hand the M_n values of available oligodiols, applied as macroinitiators, and on the other hand the [GPE] / [THF] ([CL], [DMS]) ratios determined from ^{1}H NMR spectra, M_n values of the obtained products were calculated.

Figure 1 presents ^{1}H NMR spectra of GPE-functionalized oligodiols based on PTHF, PCL and PDMS diols. In the spectra, all expected signals corresponding to both types of

monomer units are present. By comparing the intensity of signals corresponding to methylene protons in the vicinity of the alkyne group (signal d) or alkyne methine proton (f) with that of any separate signal corresponding to THF, CL or DMS unit, the total number of attached GPE units per oligodiol chain could be calculated as shown in Table 1. It should be noted that analysis of ^{1}H NMR spectra does not allow determination of the number of GPE units at each chain end, which raises the question whether GPE units are attached at both ends.

In the spectra of GPE-functionalized oliogodiols, signals of HO-CH(R)- groups of terminal HO-GPE units may be identified (signals denoted as a', Figure 1). Although these signals partially overlap with others for several samples, integration of signal a' is still possible. From the M_n values of oligodiols and the intensity of the ^{1}H NMR signal, corresponding to repeating units of starting oligodiol (assuming that each oligodiol chain has two GPE end groups), the intensity of the terminal HO-CH(R)- groups (a') signal can be estimated and is compared to that obtained from the spectra (Table 2).

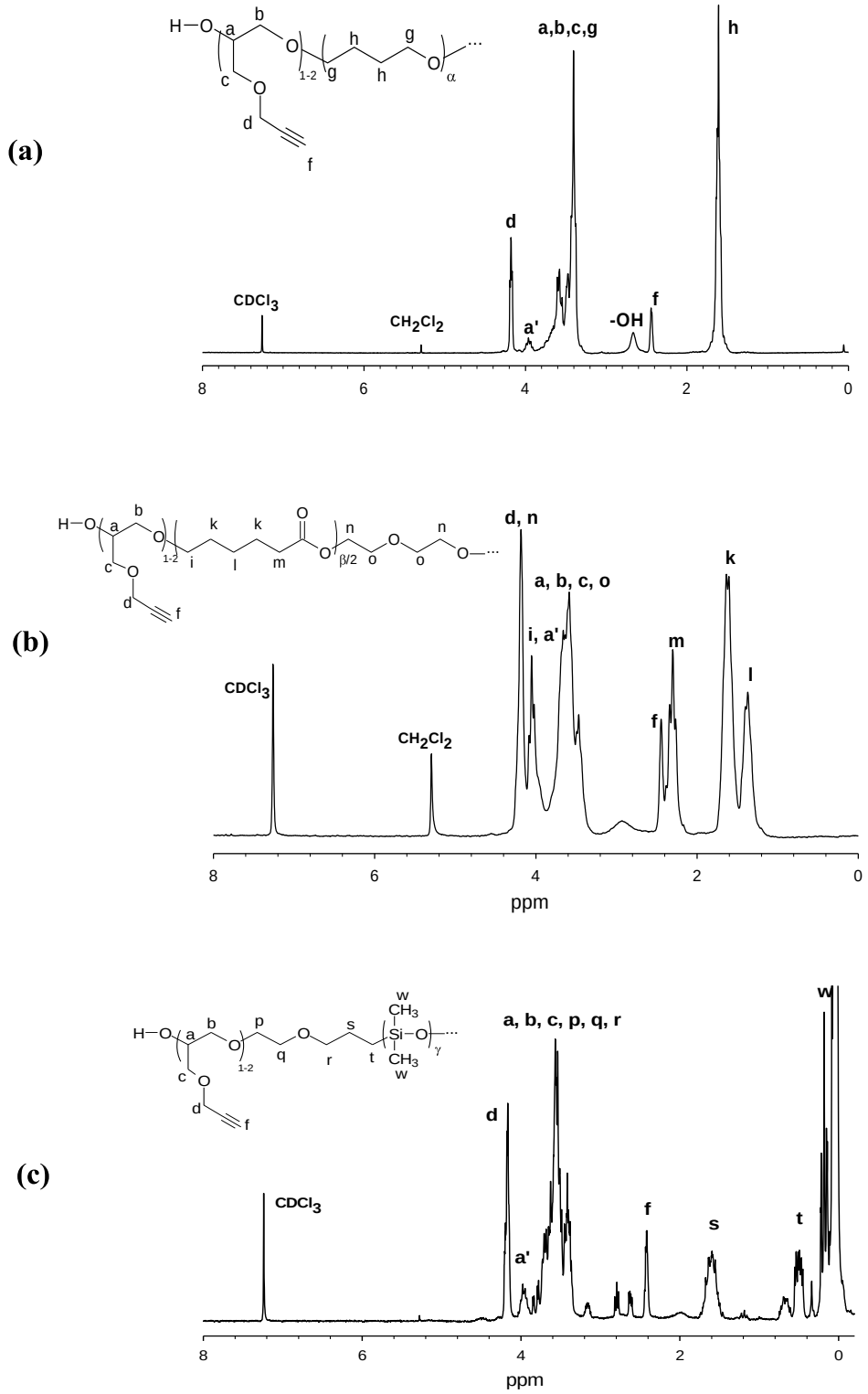


Figure 1. ^{1}H NMR spectra in $CDCl_3$ of GPE-functionalized oligodiols based on PTHF (a), PCL (b) and PDMS (c).

Table 2. Comparison of observed and calculated intensities of the signals corresponding to HO-CH(R)- groups from the terminal GPE unit.

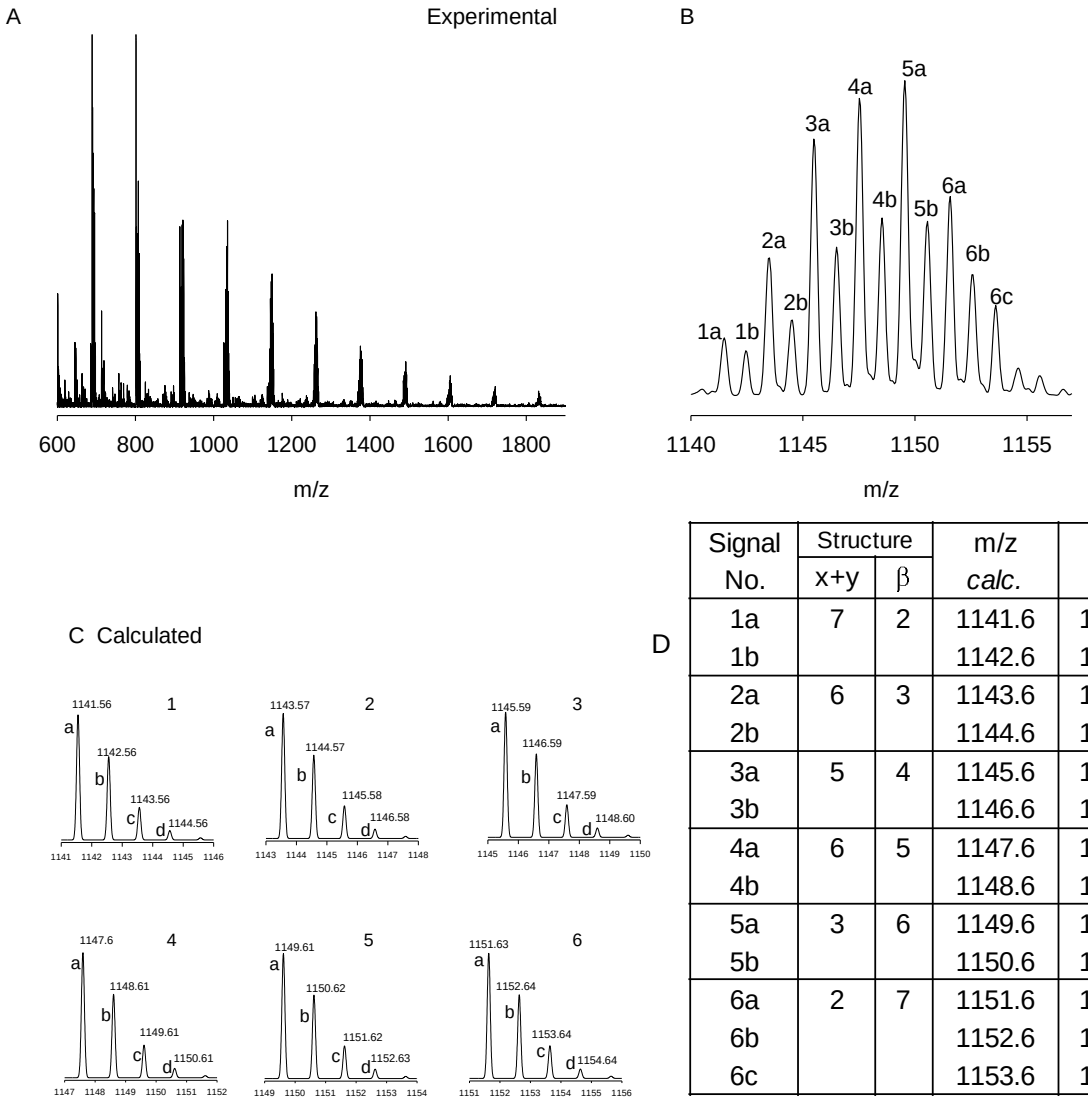
Entry[1)]	Oligodiol structure, x+y	Intensity ratio of observed to calculated terminal GPE (a') signal
3	HO-(GPE)$_x$-(THF)$_{14}$-(GPE)$_y$-OH, 4	1.21
5	HO-(GPE)$_x$-(CL)$_4$-(GPE)$_y$-OH, 3	1.00
8	HO-(GPE)$_x$-(DMS)$_{10}$-(GPE)$_y$-OH, 2	0.56
9	HO-(GPE)$_x$-(DMS)$_{10}$-(GPE)$_y$-OH, 4	1.26

[1)] Entries correspond to those in Table 1.

An observed-to-calculated intensity ratio of signal a' equal to 1 confirms the structure of oligodiols with both GPE end groups. As shown in Table 2 for Entry 8 containing average only 2 GPE units per chain, the ratio is 0.56, suggesting that a significant fraction of the oligomer chains is fitted with 2 GPE units at one end while the other hydroxyl end group originates from the starting diol. Nevertheless, for the other samples, the integration ratio is relatively close to 1. Thus, the incorporation of more than 2 GPE units per oligodiol chain (Entries 3, 5, 9, Table 2) is essential for incorporating alkyne groups at both chain ends.

The opening of the GPE ring occurs by breaking the O-CH(R) bond with the formation of a terminal secondary hydroxyl group.[23] The primary hydroxyl group present in the starting oligodiols (see Scheme 1 for the structures of oligodiols) is much more reactive than the secondary hydroxyl group formed upon addition of GPE unit towards protonated GPE. Therefore, protonated GPE reacts preferentially with primary hydroxyl groups of oligodiols and only after consumption of these groups, the reaction with secondary hydroxyl groups occurs.

MALDI TOF spectra confirm the expected structure of all products. The spectra are rather complex because of the distribution, both in chain length of the starting oligodiol and in the number of attached GPE units. The MALDI TOF spectrum of GPE-functionalized PCL (Entry 5 in Table 1) shown in Figure 2 will be discussed here in more detail, while those of other products are given in the Supplementary Material.



D

Signal No.	Structure x+y	Structure β	m/z *calc.*	m/z *exp.*
1a	7	2	1141.6	1141.5
1b			1142.6	1142.3
2a	6	3	1143.6	1143.5
2b			1144.6	1144.5
3a	5	4	1145.6	1145.5
3b			1146.6	1146.5
4a	6	5	1147.6	1147.5
4b			1148.6	1148.5
5a	3	6	1149.6	1149.6
5b			1150.6	1150.5
6a	2	7	1151.6	1151.6
6b			1152.6	1152.3
6c			1153.6	1153.6

Figure 2. A) MALDI TOF spectrum of GPE-functionalized PCL diol (Entry 5 in Table 1) registered with dithranol as matrix and NaI as cationating agent; B) Expanded fragment of the spectrum; C) Calculated isotope distributions for macromolecules with structure HO-$(GPE)_x$-$(CL)_\beta$ -$(GPE)_y$-OH, Na^+; D) A comparison of calculated and observed m/z values. Calculated m/z values take into account an additional unit present in the commercial PCL diol as indicated by the supplier (see Scheme 1).

The average composition of this product corresponds to 4 CL units and 3 GPE units in one macromolecule. The spectrum consists of series of signals separated by either 112 or114 m/z units. The molar mass of a CL unit is 114.14 Da while that of a GPE unit is 112.13 Da. An expansion of the spectrum reveals the complex nature of each signal, and an example is given in Figure 2B. At least 13 individual signals separated by 1 m/z unit can be identified.

This complex pattern results from the similarity of the molar masses of CL and GPE units as well as from the isotope distribution. Calculations of molar masses indicate that in the region shown in spectrum B (m/z = 1140-1155), the signals of six individual macromolecules containing varying numbers of CL and GPE units appear, as shown in the Table of Figure 2. Additional signals observed are ascribed to the isotope distribution in those six species, as demonstrated by simulated spectra that take the isotope distribution into consideration. In the observed spectrum, signals c and d with much lower intensity overlap with signals a and b of the next species. Similarly, analysis of MALDI TOF spectra of the other modified oligodiols based on PTHF and PDMS (see Supplementary Material) also confirms the expected structure of the obtained products.

Then, PTHF, PCL and PDMS diols with several alkyne groups at both ends were used for the synthesis of polyurethanes, according to the standard procedure earlier described by us.[22] In summary, the alkyne-functionalized oligodiols and butanediol as chain extender were reacted with hexamethyldiisocyanate in the presence of dibutyltin dilaureate as catalyst. Using different proportions of oligodiol to butanediol, PUs containing different fractions of soft and hard segments and with different contents of pendant alkyne groups were obtained. The characterization of the synthesized polyurethanes is presented in Table 3.

Table 3. Polyurethanes obtained with functionalized oligodiols; ethyl acetate (EtOAc) as solvent, dibutyltin dilaurate as catalyst, 50 ^{o}C

PU	Modified oligodiol, x+y	Feedstock oligodiol/BDO/ HDI (molar ratio)	Product: EtOAc insoluble fraction		Product: EtOAc soluble fraction	
			wt.%[1])	Mn (GPC) [2)]	wt.%[1)]	Mn (GPC) [2)]
PU1	$(GPE)_1$-$(THF)_9$-$(GPE)_1$, 2	2 / 3 / 5	42	14840	55	4220
PU2	$(GPE)_2$-$(THF)_9$-$(GPE)_2$, 4	2 / 3 / 5	42	11140	53	4170
PU3	$(GPE)_2$-$(THF)_{14}$-$(GPE)_2$, 4	2 / 3 / 5	25	8880	75	5080
PU4	$(GPE)_1$-$(CL)_4$-$(GPE)_1$, 2	1 / 4 / 5	77	8430	23	-
PU5	$(GPE)_1$-$(CL)_4$-$(GPE)_2$, 3	2.5 / 2.5 / 5	64	6060	36	3750
PU6	$(GPE)_1$-$(CL)_{10}$-$(GPE)_1$, 2	2.5 / 2.5 / 5	34	5130	66	4030
PU7	$(GPE)_2$-$(CL)_{10}$-$(GPE)_2$, 4	1 / 4 / 5	49	9740	51	7510

PU8	$(GPE)_1$-$(DMS)_{10}$-$(GPE)_1$, 2	1 / 4 / 5	70	4400	25	-
PU9	$(GPE)_2$-$(DMS)_{10}$-$(GPE)_2$, 4	1 / 4 / 5	48	6300	49	2780
PU10	$(GPE)_2$-$(DMS)_{10}$-$(GPE)_2$, 4	2 / 3 / 5	41	3770	58	-

[1)] The sum of wt.% of both fractions is not always equal to 100% because of the loss during workup.

[2)] M_n determined using calibration with poly(methyl methacrylate) standards

During the polymerization, PU products partly precipitated from the reaction medium as observed earlier.[22] Thus, two fractions were obtained – a precipitated fraction and one that is soluble in ethyl acetate (EtAc). Only insoluble fractions, corresponding to higher molecular weights were subjected to further functionalization. Nevertheless, the yields and molecular weights of precipitated fractions were not high, facilitating polymer analysis, as the synthesis process was intentionally conducted in EtAc in which PUs have limited solubility.

Polyurethanes with pendant alkyne groups were used for the UV-initiated thiol-yne reaction with model thiols (see Scheme 1). Thus, 2.1 to 5 equivalents of benzyl mercaptan with respect to one alkyne group was used in the coupling reactions with PTHF and PCL based PUs while thioglycerol was used in the coupling reactions with PCL and PDMS based PUs. Representative ^{1}H NMR spectra of a PCL-based PU before and after thiol-yne reaction with excess of benzyl mercaptan (Entry 2, Table 4) are shown in Figure 3; spectra for other thiol-yne reactions are shown in Supplementary Material.

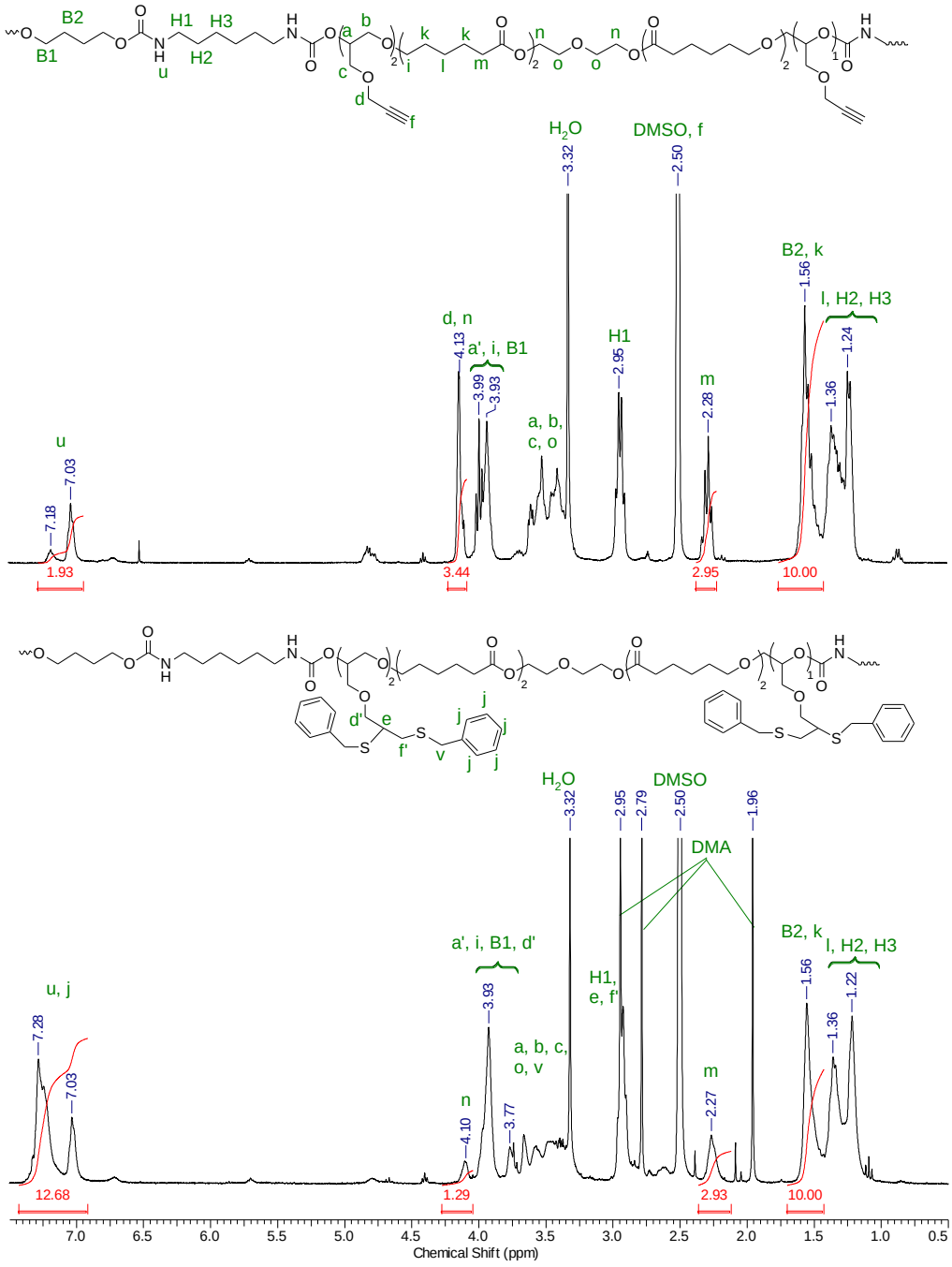


Figure 3. ^{1}H NMR spectra of a PCL-based PU (Entry 2, Table 4) in DMSO-d_6 before (a) and after (b) thiol-yne reaction with 5 equivalents of benzyl mercaptan.

The occurrence of thiol-yne reactions on the PUs was evidenced by the disappearance of the ^{1}H NMR signal of the propargyl methylene protons (signal d, Figure 3) around 4.1-4.2 ppm, along with the appearance of new signals corresponding to the coupled thiol molecules, i.e. signals of phenyl group of benzyl mercaptan at 7.2-7.5 ppm (in the case of thiol-yne reaction with benzyl mercaptan) or thioglycerol methylene groups at 4.3-4.9 ppm (see Supplementary Material). By comparing the signal intensities before and after the coupling

reaction, using a separate signal corresponding to the polymer backbone as the reference, both the conversion of alkyne groups and the number of attached thiol molecules per alkyne group could be determined. For all reactions performed, the ^{1}H NMR results indicated the occurrence of double addition of thiol molecules to the reacted alkyne groups. The absence of a monothiol adduct and thus the absence of double bonds in the final products after the coupling reaction is in accordance with earlier observations on thiol-yne reactions.[17-21] It was found earlier that the addition of the first thiol to the alkyne is the rate-limiting step, which is followed by the fast second thiol addition to the intermediate thiol-alkene.[15,16]

The conditions and corresponding degree of functionalization by thiol-yne reactions are summarized in Table 4.

Table 4. Conditions and functionalization degree of thiol-yne reactions on PUs

Entry	PU[1)]	Structure of diol, x+y	M_n of PU[2)] g.mol^{-1}	Thiol	[-SH] / [alkyne] in feed	mol% of DMPA [3)]	Functionalization degree [4)], %
1	PU3	$(GPE)_x$-$(THF)_{14}$-$(GPE)_y$, 4	8800	Bz-SH	2.2	10	66
2	PU5	$(GPE)_x$-$(CL)_4$-$(GPE)_y$, 3	6060	Bz-SH	5	25	~100
3	PU5	$(GPE)_x$-$(CL)_4$-$(GPE)_y$, 3	6060	Gly-SH	10	25	~100
4	PU10	$(GPE)_x$-$(DMS)_{10}$-$(GPE)_y$, 4	3770	Gly-SH	10	5	58
5	PU9	$(GPE)_x$-$(DMS)_{10}$-$(GPE)_y$, 4	6300	Gly-SH	10	10	70
6	PU9	$(GPE)_x$-$(DMS)_{10}$-$(GPE)_y$, 4	6300	Gly-SH	10	25	~100

[1)] PU numbers correspond to numbers in Table 3.
[2)] as determined by SEC
[3)] mol% with respect to alkyne groups
[4)] Functionalization degree corresponds to the number of alkyne groups undergoing thiol-yne double addition reaction with the thiol.

The results presented in Table 4 show that the conversion of alkyne groups depended strongly on the applied conditions of the thiol-yne reaction, particularly the photoinitiator concentration. For instance, a higher functionalization degree was observed with increasing photoinitiator content between 5 and 25 mol% with respect to alkyne groups (Entries 4-6, Table 4). Hence, a sufficient amount of photoinitiator is necessary to achieve a high functionalization degree, as also noted earlier.[3,24,25] Besides, as side reactions such as disulfide

bond formation or thiyl radical combination are inevitable in thiol-yne reactions,[2,3] the use of an excess amount of thiol was employed to obtain full conversion. Good agreement between conversion of alkyne groups and the amount of attached thiol was observed, which indicates that two thiol molecules reacted with one alkyne group.

The success of the thiol-yne coupling reactions proved that alkyne groups introduced at the PUs soft-hard segment interface remained reactive after the PU synthesis.

Conclusions

In the preceding paper we reported on the synthesis of functionalized oligodiols by cationic copolymerization of tetrahydrofuran with glycidyl propargyl ether (GPE). Using this procedure, oligodiols containing propargyl side groups distributed along the oligodiol chain were prepared, and were further used for the synthesis of alkyne-functionalized PUs. However, this approach is limited to oligodiols obtained from monomers that can be copolymerized with GPE. Besides, the content of alkyne groups depends on copolymerization reactivity ratios, and hence cannot be adjusted. In this manuscript, we demonstrate the feasibility of a much more versatile approach based on an Activated Monomer (AM) oligomerization of GPE using commercially available oligodiols as macroinitiators. In the presence of a cationic catalyst, protonated GPE reacts with the terminal hydroxyl group of oligodiol and one or a few GPE units are attached to both chain ends. Using this approach, any oligodiol, such as PTHF, PCL and PDMS oligodiols as demonstrated here, can be functionalized with a few alkyne side-groups while both hydroxyl chain ends are preserved. Although the terminal hydroxyl groups are secondary ones, such modified oligodiols reacted efficiently with diisocyanates forming polyurethanes bearing alkyne groups, which were fully post-modified with model thiols via thiol-yne chemistry. The alkyne groups are fully preserved during polyurethane synthesis and their quantitative conversion in reactions with thiols may be achieved. In summary, this procedure allowed for the synthesis of polyurethanes, with soft blocks of different nature and with controllable number of attached side functional groups, making this a promising synthetic platform for coating applications for example.

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References

1. D. Fournier and F. Du Prez, *"Click" Chemistry as a Promising Tool for Side-Chain Functionalization of Polyurethanes*, Macromolecules, 2008, **41**, 4622-4630.
2. L. Billiet, O. Gok, A. P. Dove, A. Sanyal, L.-T. T. Nguyen and F. E. Du Prez, *Metal-Free Functionalization of Linear Polyurethanes by Thiol-Maleimide Coupling Reactions*, Macromolecules, 2011, **44**, 7874-7878.
3. L.-T. T. Nguyen, J. Devroede, K. Plasschaert, L. Jonckheere, N. Haucourt and F. E. Du Prez, *Providing polyurethane foams with functionality: a kinetic comparison of different "click" and coupling reaction pathways*, Polym. Chem., 2013, **4**, 1546-1556.
4. P. Kubisa and S. Penczek, *Cationic activated monomer polymerization of heterocyclic monomers*, Prog. Polym. Sci., 1999, **24**, 1409-1437.
5. H. C. Kolb, M. G. Finn and K. B. Sharpless, *Click Chemistry: Diverse Chemical Function from a Few Good Reactions*, Angew. Chem. Int. Ed., 2001, **40**, 2004-2021.
6. C. J. Hawker, V. V. Fokin, M. G. Finn and K. B. Sharpless, *Bringing Efficiency to Materials Synthesis: The Philosophy of Click Chemistry*, Aust. J. Chem., 2007, **60**, 381-383.
7. C. Barner-Kowollik, F. E. Du Prez, P. Espeel, C. J. Hawker, T. Junkers, H. Schlaad and W. Van Camp, *"Clicking" Polymers or Just Efficient Linking: What Is the Difference?*, Angew. Chem. Int. Ed., 2011, **50**, 60-62.
8. C. J. Hawker and K. L. Wooley, *The Convergence of Synthetic Organic and Polymer Chemistries*, Science, 2005, **309**, 1200-1205.
9. V. V. Rostovtsev, L. G. Green, V. V. Fokin and K. B. Sharpless, *A Stepwise Huisgen Cycloaddition Process: Copper(I)-Catalyzed Regioselective "Ligation" of Azides and Terminal Alkynes*, Angew. Chem. Int. Ed., 2002, **41**, 2596-2599.
10. J.-F. Lutz, *1,3-Dipolar Cycloadditions of Azides and Alkynes: A Universal Ligation Tool in Polymer and Materials Science*, Angew. Chem. Int. Ed., 2007, **46**, 1018-1025.
11. R. K. Iha, K. L. Wooley, A. M. Nystrom, D. J. Burke, M. J. Kade and C. J. Hawker, *Applications of Orthogonal "Click" Chemistries in the Synthesis of Functional Soft Materials*, Chem. Rev., 2009, **109**, 5620-5686.

12. L. Billiet, D. Fournier and F. Du Prez, *Step-growth polymerization and 'click' chemistry: The oldest polymers rejuvenated*, Polymer, 2009, **50**, 3877-3886.
13. C. E. Hoyle and C. N. Bowman, *Thiol–Ene Click Chemistry*, Angew. Chem. Int. Ed., 2010, **49**, 1540-1573.
14. A. B. Lowe, *Thiol-ene "click" reactions and recent applications in polymer and materials synthesis*, Polym. Chem., 2010, **1**, 17-36.
15. B. D. Fairbanks, E. A. Sims, K. S. Anseth and C. N. Bowman, *Reaction Rates and Mechanisms for Radical, Photoinitated Addition of Thiols to Alkynes, and Implications for Thiol−Yne Photopolymerizations and Click Reactions*, Macromolecules, 2010, **43**, 4113-4119.
16. B. D. Fairbanks, T. F. Scott, C. J. Kloxin, K. S. Anseth and C. N. Bowman, *Thiol−Yne Photopolymerizations: Novel Mechanism, Kinetics, and Step-Growth Formation of Highly Cross-Linked Networks*, Macromolecules, 2009, **42**, 211-217.
17. R. Hoogenboom, *Thiol–Yne Chemistry: A Powerful Tool for Creating Highly Functional Materials*, Angew. Chem. Int. Ed., 2010, **49**, 3415-3417.
18. R. M. Hensarling, V. A. Doughty, J. W. Chan and D. L. Patton, *"Clicking" Polymer Brushes with Thiol-yne Chemistry: Indoors and Out*, J. Am. Chem. Soc., 2009, **131**, 14673-14675.
19. M. Bednarek, *Coupling reaction with thiols as the efficient method of functionalization of ''clickable" polylactide*, React. Funct. Polym., 2013, **73**, 1130-1136.
20. V. T. Huynh, G. Chen, P. d. Souza and M. H. Stenzel, *Thiol–yne and Thiol–ene "Click" Chemistry as a Tool for a Variety of Platinum Drug Delivery Carriers, from Statistical Copolymers to Crosslinked Micelles*, Biomacromolecules, 2011, **12**, 1738-1751.
21. S. B. Rahane, R. M. Hensarling, B. J. Sparks, C. M. Stafford and D. L. Patton, *Synthesis of multifunctional polymer brush surfaces via sequential and orthogonal thiol-click reactions*, J. Mater. Chem., 2012, **22**, 932-943.
22. M. Basko, M. Bednarek, L. Billiet, P. Kubisa, E. Goethals and F. Du Prez, *Combining cationic ring-opening polymerization and click chemistry for the design of functionalized polyurethanes*, J. Polym. Sci., Part A: Polym. Chem., 2011, **49**, 1597-1604.
23. M. Bednarek, T. Biedron, P. Kubisa and S. Penczek, *Activated monomer polymerization of oxiranes. Micro-structure of polymers vs. kinetics and*

thermodynamics of propagation, Makromol. Chem. Macromol. Symp., 1991, **42-43**, 475-487.

24. P. Derboven, D. R. D'hooge, M. M. Stamenovic, P. Espeel, G. B. Marin, F. E. Du Prez and M.-F. Reyniers, *Kinetic Modeling of Radical Thiol–Ene Chemistry for Macromolecular Design: Importance of Side Reactions and Diffusional Limitations*, Macromolecules, 2013, **46**, 1732-1742.
25. S. P. S. Koo, M. M. Stamenović, R. A. Prasath, A. J. Inglis, F. E. Du Prez, C. Barner-Kowollik, W. Van Camp and T. Junkers, *Limitations of radical thiol-ene reactions for polymer–polymer conjugation*, J. Polym. Sci., Part A: Polym. Chem., 2010, **48**, 1699-1713.