Synthesis of glycerin carbonate-based intermediates using thiol-ene chemistry and isocyanate free polyhydroxyurethanes therefrom

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PAPER

Synthesis of glycerin carbonate-based intermediates using thiol–ene chemistry and isocyanate free polyhydroxyurethanes therefrom†

Sofia Benyahya,[a] Myriam Desroches,[a] Rémi Auvergne,*[a] Stéphane Carlotti,[b] Sylvain Caillol[a] and Bernard Boutevin[a]

A new synthesis of 4-[(prop-2-en-1-yloxy)methyl]-1,3-dioxolan-2-one (**AGC**) was performed by Williamson ether synthesis from 4-(hydroxymethyl)-1,3-dioxolan-2-one. Dicyclocarbonates were synthesized by UV thiol–ene coupling of allyl-cyclocarbonate with a 2,2′-oxydiethanethiol. This photochemical thiol–ene reaction was carried out under air, with neither solvent nor photoinitiator. The products, obtained with high yield, were characterized by ¹H NMR and FTIR analysis. The synthesized dicyclocarbonates were used without purification to synthesize polyhydroxyurethanes without isocyanate by step growth polyaddition with 1,10-diaminodecane. The synthesized polyhydroxyurethanes were characterized by ¹H NMR, FTIR, ATG and DSC analysis. These polyhydroxyurethanes exhibited glass transition temperatures from −31 °C to −14 °C, molecular weight from 7,000 g mol⁻¹ to 9000 g mol⁻¹ and degradation temperature for 5% of weight loss (T_d 5%) between 227 °C and 250 °C.

Introduction

Polyurethanes (PUs) are one of the most dynamic groups of polymers, exhibiting versatile properties suitable for use in practically all fields of polymer applications—foams, elastomers, thermoplastics, thermorigids, adhesives, coatings, sealants, fibers and so on. Generally, PUs are obtained from the reaction of an oligomeric polyol (low molar mass polymer with terminal hydroxyl groups) and a diisocyanate (or polyisocyanate). However, the use of diisocyanate should be avoided for several reasons. Isocyanate reactants are generally very harmful for human health, particularly for people exposed during polyurethane synthesis, and could entail adverse health effects such as asthma, dermatitis, conjunctivitis and acute poisoning.[1] Moreover, isocyanates are synthesized from phosgene which is a very toxic chemical that raises questions in industry. Therefore the synthesis of PUs from step growth polyaddition of dicyclocarbonates and diamines should be favored.[2,3] Thus, this old reaction is currently gaining a great deal of attention as a substitution route for the synthesis of PUs. This method is particularly interesting since no hazardous isocyanates are used. Moreover dicyclocarbonate reactants could be provided from renewable resources such as glycerin. This route allows polyhydroxyurethanes (PHUs) with hydrogen bonds to be obtained, presenting higher chemical and hydrolysis resistances.
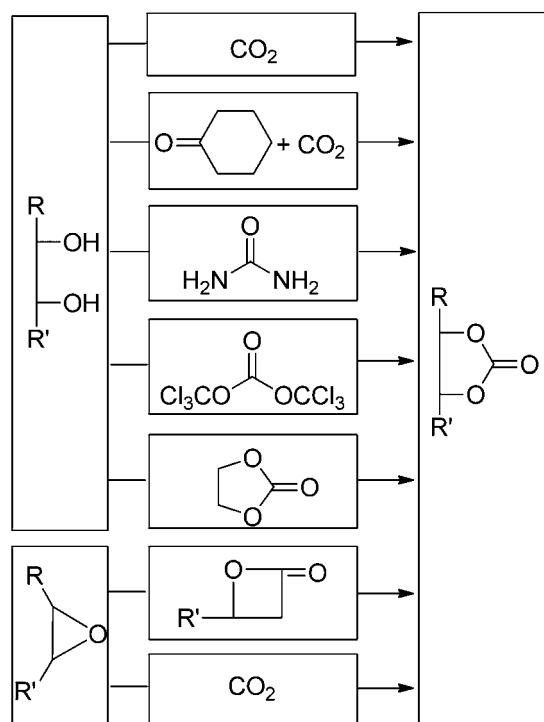
The synthesis of PHUs from step growth polyaddition of dicyclocarbonates and diamines was extensively reported in the literature, particularly by Endo.[4] Indeed, several cyclocarbonates were synthesized and some polyhydroxyurethanes were thereof characterized.[5–8]

Several methods are used to synthesize five-membered cyclic carbonates (Scheme 1).[9–18] Most of these methods are based on epoxide or diol reactants. This is also the case of dicyclocarbonate syntheses (Scheme 2 (1–5)).[6,17,19–21] The production of methyl esters from vegetable oil leads to glycerin as a by-product. Thus, the use of glycerin carbonate (4-(hydroxymethyl)-1,3-dioxolan-2-one) presents a great interest for the synthesis of dicyclocarbonate. Generally, syntheses of PHUs from glycerin carbonate are based on esterification reactions from glycerin carbonate and dicarboxylic acid or derivatives (Scheme 2 (6)). In a previous study,[22] a five-membered dicyclocarbonate bis[(2-oxo-1,3-dioxolan-4-yl)methyl] benzene-1,4-dicarboxylate **DC_ter** was prepared by esterification of carboxylic acid groups of benzene-1,4-dicarboxylic acid with alcohol function of commercial 4-(hydroxymethyl)-1,3-dioxolan-2-one. This method was also reported by other authors for the synthesis of various polydicyclocarbonates, either symmetric or asymmetric.[8,23] Dicyclocarbonates synthesized present ester bonds on the carbon chain, thus the resulting materials are more sensitive to hydrolysis reaction.

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c1py00289a

Scheme 1 Various synthesis routes to obtain cyclic carbonates molecules.

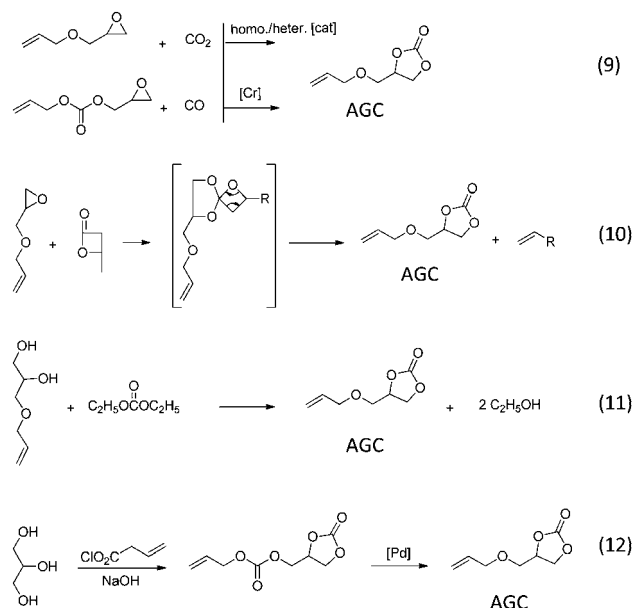**Scheme 2** Various dicyclocarbonate synthesis routes.

Furthermore, the synthesis of thioether five- and six-membered dicyclocarbonates by radical addition of ethane-1,2-dithiol with 4-(3-butenyl)-1,3-dioxolan-2-one(Scheme 2 (7))[14] or by reaction between 4-ethenyl-1,3-dioxolan-2-one (AC) and several thiols (Scheme 2 (8))[24] has been reported. These dicyclocarbonates allow polyhydroxyurethanes to be obtained without ester bonds. However, these monomers were not synthesized from glycerol derivatives and were very expensive.

Another cyclocarbonate monomer is reported in the literature, the 4-[(prop-2-en-1-yloxy)methyl]-1,3-dioxolan-2-one (**AGC**). **AGC** was obtained by different methods (Scheme 3) without the use of glycerin carbonate derivatives.

According to the literature, **AGC** molecule was generally synthesized by reaction between carbon dioxide and allyl glycidyl ether by homogeneous[25] or heterogeneous[26] catalysis (Scheme 3 (9)). Indeed, Schmidt reported the synthesis of 4-((allyloxy)methyl)-1,3-dioxolan-2-one by carbonylation of oxiran-2-ylmethyl prop-2-en-1-yl carbonate in the presence of chromium (III) octaethylpor-phyrinato tetracarbonylcobaltate [(OEP)-Cr(THF)$_2$][Co(CO)$_4$] (Scheme 3 (9)).[27] This carbonate was also synthesized from reaction between 4-methyloxetan-2-one and 2-[(prop-2-en-1-yloxy)methyl] oxirane with tetrabutylazanium bromide TBAB (Scheme 3 (10))[9] or by transcarbonatation between an allyl-diol and an organic carbonate (Scheme 3 (11)).[28] Finally, **AGC** was synthesized from reaction between propane-1,2,3-triol and 4-(chlorooxy)-4-oxobut-1-ene with palladium (Scheme 3 (12)).[29]

In the literature, thiol–ene coupling was initially reported on 4-(3-butenyl)-1,3-dioxolan-2-one thermally initiated with a radical initiator and in solvent. Purifications were needed and yields varied between 50 and 60%.[14] UV thiol–ene coupling with pho-toinitiator was also reported.[24] However, the use of a photo-initiator represents a drawback since residual fragments of photoinitiator remain in the polymer and could result in accel-erated ageing or yellowing of materials. In a previous study,[30]

Scheme 3 Different methods for 4-[(prop-2-en-1-yloxy)methyl]-1,3-dioxolan-2-one (AGC) synthesis.

UV thiol–ene coupling on vegetable oils without any photo-initiator has been described.

Therefore, in this study, the 4-[(prop-2-en-1-yloxy)methyl]-1,3-dioxolan-2-one AGC has been synthesized by a new, easy and inexpensive method, based on the use of the Williamson reaction. Synthesized AGC and commercial AC have been used to synthesize bis-AGC and bis-AC from thiol ene addition (click chemistry), and bis-AGC and bis-AC were polymerized with 1,10-diaminedecane (DA10) to obtain polyhydroxyurethane materials.

Results and discussion

Two different cyclocarbonates, 4-ethenyl-1,3-dioxolan-2-one AC and 4-[(prop-2-en-1-yloxy)methyl]-1,3-dioxolan-2-one AGC, were used for the synthesis of dicyclocarbonates bis-AC and bis-AGC by thiol–ene coupling. AC cyclocarbonate is a commercial chemical, whereas the AGC cyclocarbonate was synthesized by Williamson ether reaction. As AC cyclocarbonate is a commercial product, its characterization is not reported here. The AGC cyclocarbonate synthesis is reported herein.

Synthesis of dicyclocarbonates: bis-AGC and bis-AC

Bis-AGC and bis-AC were synthesized by reaction between a dithiol and AGC or AC, respectively. This reaction was carried out by UV thiol–ene coupling without a photoinitiator (Scheme 4).

This reaction was realized without any solvent, with a thiol/double bonds ratio of 1/1 and an irradiation between 250 and 450 nm, at 10 W cm^{-2}. Firstly, dicyclocarbonate bis-AC was synthesized in one step by UV thiol–ene coupling of 2,2′-oxydiethanethiol on commercial cyclocarbonate AC in 2 hours. The ^{1}H NMR spectrum of the product allows clear identification of the expected product (Fig. 1).

Addition of thiol was confirmed by the disappearance of signals corresponding to the vinylic protons at 5.43 ppm (CH=CH$_2$) and 5.88 ppm (CH=CH$_2$), and by the appearance of signals corresponding to the thioether protons between 2.65 ppm and 2.78 ppm (CH$_2$–S, signal d, d′) and between 1.94 ppm and 2.08 ppm (CH$_2$–CH$_2$–S, signal c, c′) (Fig. 1). These signals corresponding to protons in α and β positions of sulfur appeared as a multiplet dedoubled due to the vicinity of the asymmetric carbon b. The product of thiol addition on the more substituted carbon is not observed in this spectrum, which confirms the selectivity of thiol–ene coupling.

The UV thiol–ene coupling was then successfully used for the synthesis of dicyclocarbonate AGC and was carried out in 5

hours. This lower reactivity of this reaction is in agreement with allylic ether reactivity. As observed previously, ^{1}H NMR analysis confirmed thiol addition (Fig. 2). Indeed, the disappearance of signals corresponding to the protons of double bonds at 5.26 ppm (CH=CH$_2$) and at 5.85 ppm (CH=CH$_2$) and the appearance of signals corresponding to the protons of thioether in the α position of sulfur at 3.58 ppm (CH$_2$–S, signal f; Fig. 2) and in the β position at 1.81 ppm (CH$_2$–CH$_2$–S, signal e; Fig. 2) were observed.

In this case, thiol–ene coupling for the synthesis of dicyclocarbonates fits perfectly with the Sharpless principles of "click chemistry"[31] stoichiometry of reactant 1/1, no solvent, no catalyst, high yield and no by-product.

Polyhydroxyurethanes synthesis

Then, step growth polyaddition of synthesized building blocks bis-AC and bis-AGC with commercial decane-1,10-diamine DA10 was carried out and yielded respectively PHU-bis-AC and PHU-bis-AGC polyhydroxyurethanes (Scheme 5). Scheme 5 presents idealized structures (isomer primary–secondary alcohol); most isomers such as primary–primary alcohol, primary–secondary alcohol and secondary–secondary alcohol were obtained.

Both synthesized PHUs were characterized by ^{1}H and ^{13}C NMR spectrometry and by FTIR analysis. The ^{1}H NMR spectrum of synthesized PHU-bis-AGC is reported in Fig. 3.

This spectrum confirms the formation of the carbamate group with the signal of the proton on nitrogen at 8 ppm.[32] The shifts of characteristic signals of carbonate function (aa', b, cc' in Fig. 2) in a, b, c and x, y, z (Fig. 3) are observed. These signals represent the different isomers of cyclocarbonate ring opening. Indeed, ring opening of the cyclocarbonate function by the primary amine function is not regioselective and leads to three PHU isomers, with primary and secondary alcohols.[4–8,33] The percent of primary and secondary alcohols was determined thanks to y and b proton integration according to eqn (1):

$$R_{\text{OHp}} = \frac{I_y}{I_y + I_b} \times 100 \qquad (1)$$

where R_{OHp}, I_y and I_b stand for primary alcohol percent, y proton integration and b proton integration, respectively.

The ratio of primary and secondary alcohols was 25/75, which is in agreement with Endo studies.[34]
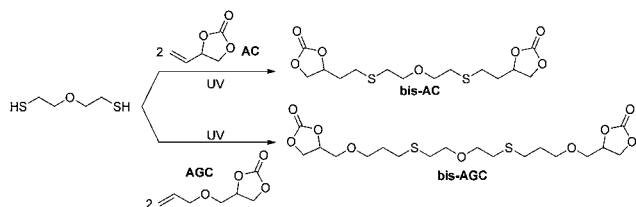
The FTIR spectrum (Fig. 4) confirms formation of PHU-bis-AGC polyhydroxyurethane with the three characteristic bands of the carbamate function: N–H bond stretching vibration, hydrogen bonded C=O stretching and N–H bond deformation are respectively observed at 3078 cm^{-1}, 1686 cm^{-1} and 1530 cm^{-1}.

The large absorption band of the hydroxyl group OH at 3326 cm^{-1} also appeared.

On the PHU-bis-AGC FTIR spectrum, the absence of the absorption band of C=O carbonyl of the carbonate group at 1785 cm^{-1} reveals a total conversion of initial bis-AGC.

Table 1 summarizes the main characteristics of both synthesized PHUs, Mn (SEC), T_g (DSC) and T_d 5% (TGA). The corresponding figures are given in the ESI†.

As expected, the carbon chain length of dicyclocarbonate influences the T_g value of polymer obtained. Thus, the AGC monomer presents two methyl groups and one ether bond in the

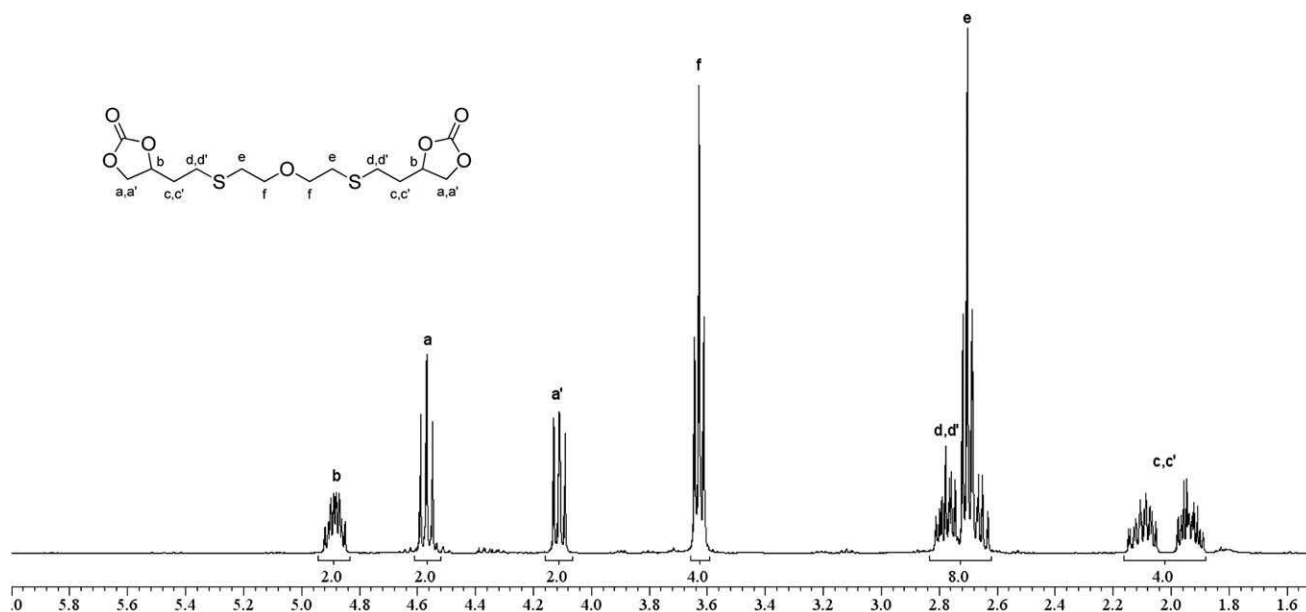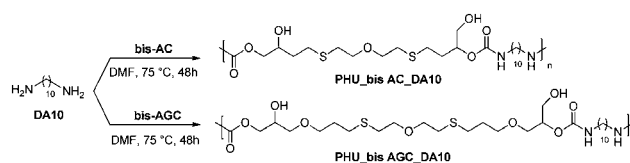Scheme 4 Synthesis of dicyclocarbonate by thiol–ene coupling (ratio thiol/double bond of 1/1, irradiated at 10 W cm^{-2}).

Fig. 1 ^{1}H NMR spectrum of commercial cyclocarbonate (AC) after thiol–ene coupling (ratio thiol/double bond of 1/1, irradiated 2 hours at 10 W cm^{-2}).

chain, leading to a more flexible chain than the AC monomer. This assumption was confirmed by T_g values −31 °C and −14 °C for **PHU-bis-AGC** and **PHU-bis-AC**, respectively (see the ESI, Fig. S1†).

The molecular weight values obtained were similar, 7000 and 9000 g mol^{-1}, with polydispersity indices (PI) of 1.5 and 3.2 for

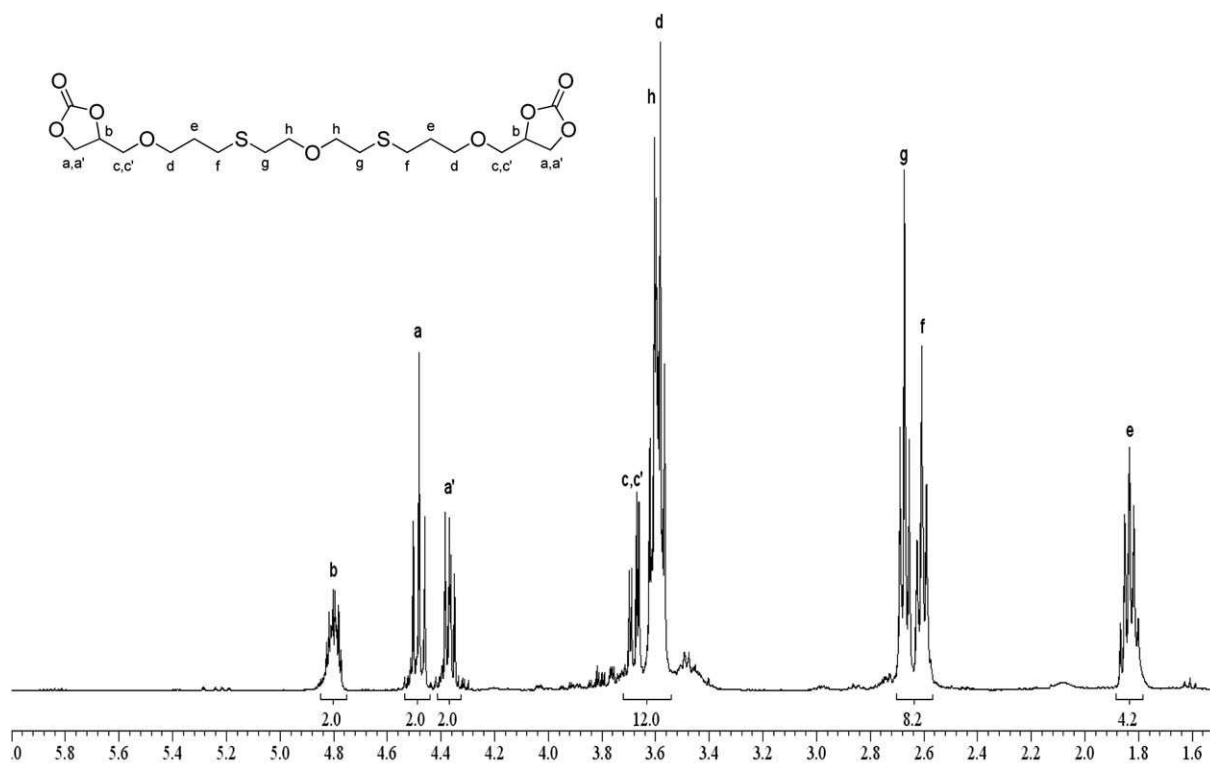**Scheme 5** Step growth polyaddition of DA10 and AC or AGC.

Fig. 2 ^{1}H NMR spectrum of synthesized cyclocarbonate (AGC) after thiol–ene coupling (ratio thiol/double bond of 1/1, irradiated 5 hours at 10 W cm^{-2}).
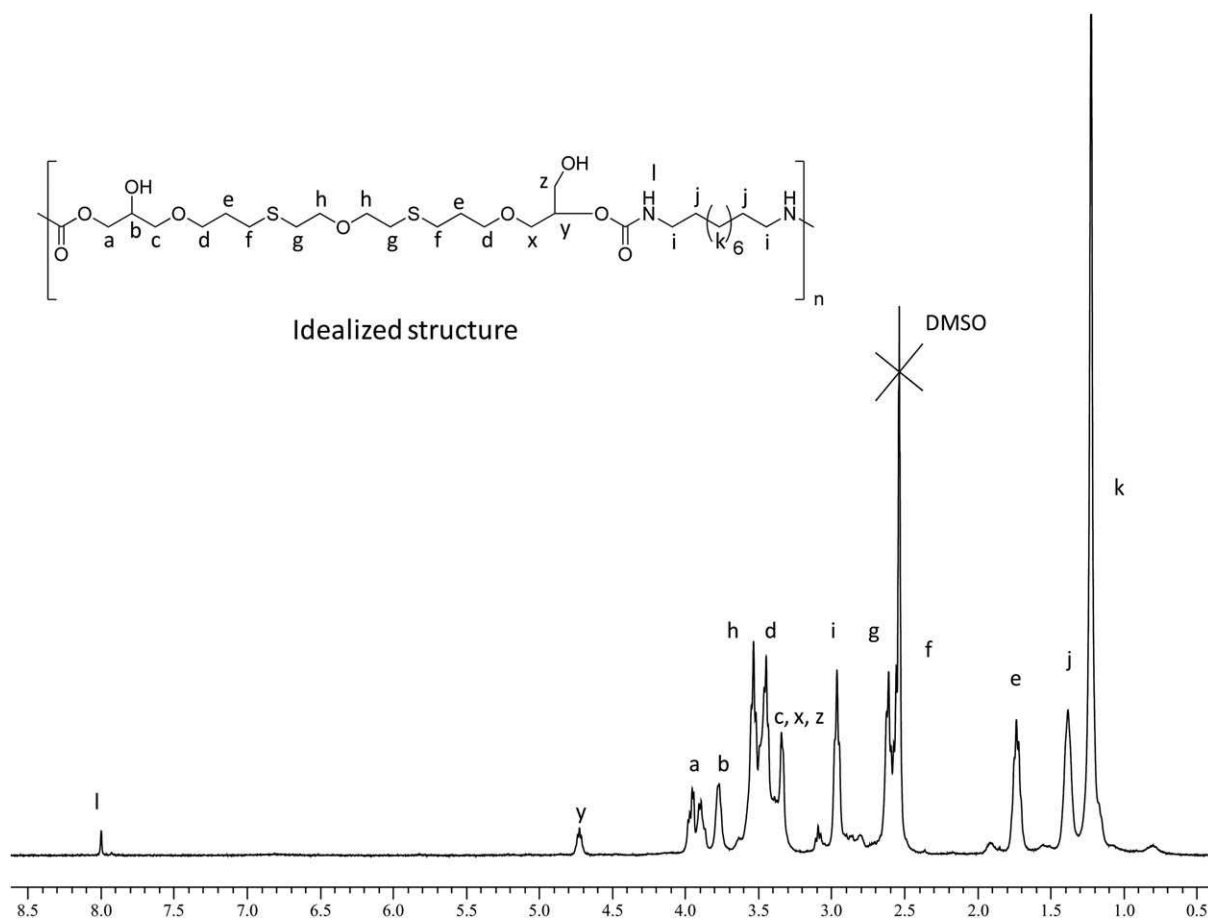
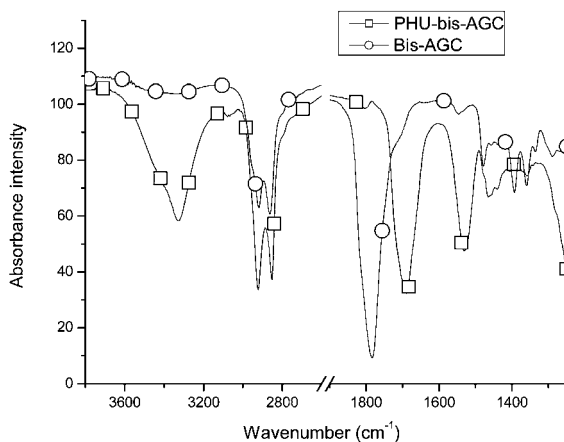**Fig. 3** 1H RMN spectrum (400 MHz, DMSO-d6) of PHU-bis-AGC.

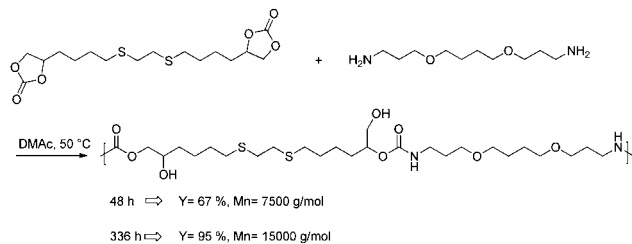**Fig. 4** Infrared spectra of bis-AGC and PHU-bis-AGC.

Table 1 Results of glass transition temperatures, degradation temperatures and molecular weights of synthesized PHUs

PHU	$T_g/°C$	T_d 5%/°C	$M_n{}^a$/g mol^{-1}	PI
PHU-bis-AC	−14	227	7000	1.5
PHU-bis-AGC	−31	249	9000	3.2

^{a} SEC DMF, calibrated using PMMA standards.

PHU-bis-AC and **PHU-bis-AGC**, respectively. These values are low but still comparable to those reported in the literature. The SEC chromatogram is presented in the ESI, Fig. S2†. Indeed, Endo *et al.* reported the step growth polyaddition of 4,4′-[ethane-1,2-diylbis(sulfanediylbutane-4,1-diyl)]bis(1,3-dioxolan-2-one) in DMAc at 50 °C in 48 h. This reaction led to a PHU with a yield of 67% and a molecular weight of 7500 g mol^{-1}. After 14 days of reaction under the same conditions, a conversion of 95% is reached with a molecular weight of 15 000 g mol^{-1} (Scheme 6).[14]

Finally, concerning thermal degradation measured by ATG, synthesized **PHU-bis-AGC** and **PHU-bis-AC** exhibit a degradation temperature (T_d 5%) of 249 °C and 227 °C, for 5% of weight loss, respectively. These values confirm the stability of these

Scheme 6 Step growth polyaddition of 1,2-bis[4-(1,3-dioxolan-2-one-4-yl)-butylthio]ethane with 3,3′-[butane-1,4-diylbis(oxy)]dipropan-1-amine.[11]

polymers above 200 °C, as other PUs. The thermal degradation of PHU polymers proceeds in three steps: the first step, between 250 and 350 °C (for PHU-bis-AC) and between 250 and 380 °C (for PHU-bis-AGC) for a weight loss corresponding to 75%; a second degradation step until 480 °C with a weight loss of 10%; and the last step until 580 °C for total degradation (see the ESI, Fig. S3†).

Concerning **PHU-bis-AC**, thermal degradation under air or nitrogen conditions for 5% of degradation occurred at 227 °C and 225 °C, respectively. We did not observe any difference during thermal degradation under air or nitrogen conditions until 350 °C. Between 350 °C and 450 °C, a difference of 10% was observed, oxidation phenomena under air explain this difference. After 450 °C, the polymer reaches total degradation at 580 °C (see the ESI, Fig. S4†).

Experiment section

Materials

Sodium hydride (95%), 1,10-diaminodecane (DA10) (95%), 3-bromo-1-propene (99%), sodium iodide (99.99%), 2,2′-oxy-diethanethiol, 4-ethenyl-1,3-dioxolan-2-one (99%) were purchased from Sigma Aldrich and used as received. 4-(Hydroxy-methyl)-1,3-dioxolan-2-one (JEFFSOL®) was supplied by Huntsman (Saint-Mihiel, France). Sodium chloride, magnesium sulfate, tertrahydrofuran (THF) and N,N-dimethylmethanamide (DMF) were purchased from SDS Carlo Erba (Val de Reuil, France). Before use, THF and DMF were dried according to current methods, then distilled and stored under argon atmosphere. Deuterated solvents (CDCl$_3$ and DMSO) were purchased from Eurisotop (Saint-Aubin, France).

Analytical techniques

All nuclear magnetic resonance (^{1}H, ^{13}C NMR) measurements were recorded on a Bruker AC-400 MHz spectrometer at room temperature in deuterated chloroform (CDCl$_3$) or dimethylsulf-oxide (DMSO). The chemical shifts were reported in parts per million relative to tetramethylsilane.

IR spectra were recorded with a Nicolet 210 FT-IR spectrometer. Size exclusion chromatography (SEC) was performed on a Varian ProStar Model 210 equipped with an RI refractive index detector. Two PLgel 5 μm MIXED-C 600 mm were used at 70 °C with a 0.8 mL·min^{-1} flow rate of DMF, calibrated using PMMA standards. Differential scanning calorimetry (DSC) analyses were performed under inert atmosphere with a calorimeter DSC1 from Mettler Toledo. The polymer was weighted in an aluminium pan and consecutively placed in the measurement heating cell. An empty pan was used as reference. All the samples were heated under inert atmosphere from −120 to 100 °C at a heating rate of 20 °C min^{-1}.

Three runs were recorded and the glass transition temperature (T_g) values were measured during the second run and confirmed by a third run. T_gs were calculated at the inflexion point of the heat capacity jump.

Thermogravimetric analyses (TGA) were performed using a TGA Q50 W/MFC apparatus of TA Instruments under air flow (25 ml min^{-1}) from room temperature to 580 °C at a heating

rate of 20 °C min^{-1}. The analysis consisted of registering the weight loss of the sample as a function of temperature.

Synthesis

Synthesis of 4-[(prop-2-en-1-yloxy)methyl]-1,3-dioxolan-2-one (AGC). Sodium hydride NaH (60% in oil, 2.43 g, 102 mmol) was added to a solution of 4-(hydroxymethyl)-1,3-dioxolan-2-one (10 g, 85 mmol) in THF (90 ml) at 0 °C under Ar. The reaction mixture was stirred for 10 min at 0 °C followed by an addition of 3-bromoprop-1-ene (15.37 g, 127 mmol) and NaI (1.26 g, 8.47 mmol). The resulting mixture was stirred for 24 h at 23 °C before being filtered and washed with saturated aqueous NaCl, dried over MgSO$_4$, and concentrated under reduced pressure. The product was obtained as yellow oil (10.98 g, 82%) and characterized by ^{1}H and ^{13}C NMR spectrometry.

RMN ^{1}H/CDCl$_3$ d$_6$: δ (ppm) = 5.86–5.75 (1H, m, CH$_2$= CH–), 5.24–5.14 (2H, dd, CH$_2$=CH–), 4.83–4.77 (1H, m, CH$_2$–CH–O–), 4.49–4.45 (2H, m, O–CH–CH$_2$), 4.37–4.32 (2H, d, = CH–CH$_2$–O), 3.67–3.54 (2H, m, CH$_2$–O–CH$_2$).

RMN ^{13}C/CDCl$_3$ d$_6$: δ (ppm) = 155.4 (O–CO–O), 115.45 (CH$_2$=CH–), 132.8 (CH$_2$=CH–), 75.77 (CH$_2$–O–CH$_2$), 72 (O–CH–CH$_2$), 71.8 (=CH–CH$_2$–O), 61.7 (O–CH–CH$_2$).

Bis AG and bis AGC syntheses by thiol–ene coupling. Photochemical thiol–ene reaction was performed in quartz reactors of 20 mL equipped with an Ultracure 100SS plus/Novacure lamp (unfiltered radiation between 250 and 450 nm) and a magnetic stirrer under air. After cyclocarbonate (2.50 g) and 2,2′-oxy-diethanethiol (1.52 g for 4-ethenyl-1,3-dioxolan-2-one AC and 1.11 g for the synthesized AGC) introduction, the homogeneous reaction mixture was irradiated for several hours at 10 W cm^{-2}. During reaction, the photochemical beam was stopped every hour to remove aliquots. The conversion of double bonds was monitored by ^{1}H NMR spectrometry (vinyl proton signals at 5.4 and 5.9 ppm). No purification was carried out. The product was obtained as a viscous liquid.

RMN ^{1}H of Bis AG/CDCl$_3$ d$_6$: δ (ppm) = 4.90 (1H, m), 4.57 (1H, t), 4.12 (1H, t), 3.62 (2H, t), 2.77 (2H, m), 2.70 (2H, t), 1.95–2.10 (2H, m).

RMN ^{13}C of Bis AG/CDCl$_3$ d$_6$: δ (ppm) = 155.0 (O–CO–O), 75.8 (O–CH–CH$_2$), 70.9 (O–CH$_2$–CH$_2$–S), 69.4 (CO–O–CH$_2$–CH), 34.1 (O–CH$_2$–CH$_2$–S), 32.0 (CH–CH$_2$–CH$_2$–S), 27.8 (CH–CH$_2$–CH$_2$–S).

RMN ^{1}H of Bis AGC/CDCl$_3$ d$_6$: δ (ppm) = 4.80 (1H, m), 4.50 (1H, t), 4.38 (1H, t) 3.70 (2H, m), 3.60 (2H, t), 3.58 (2H, t), 2.68 (2H, t), 2.60 (2H, t), 1.82 (2H, m).

RMN ^{13}C of Bis AGC/CDCl$_3$ d$_6$: δ (ppm) = 154.6 (O–CO–O), 74.6 (O–CH–CH$_2$), 70.0 (O–CH$_2$–CH$_2$–S), 69.7 (CO–O–CH–CH$_2$–O), 69.4 (CO–O–CH$_2$–CH), 65.5 (O–CH$_2$–CH$_2$–CH$_2$–S), 31.1 (O–CH$_2$–CH$_2$–S), 29.0 (O–CH$_2$–CH$_2$–CH$_2$–S), 28.5 (O–CH$_2$–CH$_2$–CH$_2$–S).

Polyhydroxyurethane (PHU-bis-AC and PHU-bis-AGC) syntheses

Step growth polyaddition of dicyclocarbonates bis-AC and bis-AGC was realized with DA10 under stirring in distilled DMF and under argon atmosphere at 75 °C during 48 h. At the end of

reaction, DMF is evaporated and PHU-bis-AC and PHU-bis-AGC polymers were precipitated in methanol. After drying, PHUs were quantitatively obtained.

Both synthesized PHUs were characterized by ^{1}H NMR spectrometry and by FTIR analysis. Only ^{1}H NMR and FTIR spectra of bis-AGC dicyclocarbonate and PHU-bis-AGC corresponding polyhydroxyurethane are reported.

Conclusion

A new one-step synthesis of 4-[(prop-2-en-1-yloxy)methyl]-1,3-dioxolan-2-one **AGC**, from 4-(hydroxymethyl)-1,3-dioxolan-2-one (glycerol derivatives), has been reported. This route is particularly interesting since it is an inexpensive, one-step synthesis from biobased glycerin carbonate. Then precursors of PHU have been synthesized by thiol–ene coupling of dithiol with AGC and AC. This "click-chemistry" reaction is particularly advantageous since it requires neither solvent nor photoinitiator and is quantitative in stoichiometric conditions. Finally, polyhydroxyurethanes have been synthesized by step growth polyaddition reaction of bis-AC and bis-AGC with 1,10-diaminedecane. This reaction, carried out without isocyanates, is a less hazardous synthesis. The synthesized polyhydroxyurethanes contain neither hydrolysis sensitive ester bonds nor UV sensitive aromatic groups and exhibit low T_g, therefore they could profitably be used in exterior coatings.

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