Thiol-yne Reaction of Alkyne-derivatized Fatty Acids: Thiol-Reactive Linear Polyurethane

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ABSTRACT: A thiol-reactive linear polyurethane was synthesized from a vinyl-sulphide-containing diol and a commercial diisocyanate. The diol was obtained from 10-undecynol, an alkyne-derivatized fatty compound, using hydrothiolation as a key reaction step. 10-Undecynol was prepared by reduction of 10-undecinoic acid methyl ester, which was prepared by successive bromation, dehydrobromination of the corresponding alkenic fatty acid. Solution and surface polymer modification with a fluorescent thiol was successful.

KEYWORDS: Vegetable oils, click chemistry, polyurethanes, renewable resources

1 INTRODUCTION

Polyurethanes (PUs) are a versatile class of polymers used in practically all the fields of polymer applications [1]. PUs which can be perfectly tailored by the right choice of diisocyanates, diols or polyols and catalyst, have become one of the most dynamic groups of polymers, exhibiting versatile properties suitable for use in the medical, construction, automotive, flooring and sports industries [2]. In ages of achieving greater awareness of sustainable development, PU technology is progressively moving towards environmentally friendly chemicals and processes. The general strategy being used to increase the sustainability of PUs consists of replacing the conventionally used petroleum-based monomers, i.e. isocyanates and polyols, with biobased starting products [3, 4]. Although the history of PU technology is strongly linked to renewable resources, plant oils, fatty acids and derivatives have recently attracted significant interest for the production of polyols and isocyanates leading to PUs partially or entirely from lipid feedstock.

Recently, much attention has been paid to the development of functional polymers, including PUs, as these materials would lead to new applications that can broaden the classical market. A broad palette of functional groups including hydroxyl, ester, and amino groups has been directly introduced into linear PUs by using a functional building block. Nevertheless, careful attention must always be paid to the inertness of the introduced functional groups during the PU synthesis. Thus, usually tedious protection/deprotection steps are required. On the other hand, functionalization strategies of PUs are moving to functional groups that may be involved in efficient chemical transformations exemplified by click chemistry reactions with high yields and with little or no byproduct [5]. The combination of PUs and click chemistry was explored by Fournier *et al* [6]. In this case, the most popular reaction of the chemical concept click chemistry, the highly efficient, regioselective and orthogonal copper(I) catalyzed alkyne-azide cycloaddition reaction, was used to functionalize alkyne-containing linear PU chains, as well as in films and foams, with a range of azide-containing molecules. Recently, efforts have been made in the application of suitable metal-free click reactions to the functionalization of linear PUs. A maleimide-containing diol was incorporated in different ratios into the PU backbone and subsequently coupled with several functional thiols, via the efficient metal-free thiol-maleimide coupling reaction. In this case, classical drawbacks associated with copper(I) catalyzed alkyne-azide cycloaddition reactions, such as undesired coloring and safety concerns with low molecular weight azides, are avoided [7].

Our group and others have widely applied thiol-ene coupling (TEC) and more recently thiol-yne

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coupling (TYC) to plant oils, fatty acids and derivatives, paying special attention to the preparation of biobased diols and polyols [8–19]. TEC and TYC have become outstanding synthetic tools, owing to their special features such as chemoselectivity, versatility, and the absence of any need for metal catalysts [20, 21]. The TYC, whose discovery dates back to the mid-1900s [22], serves to introduce two thiol fragments across a carbon-carbon triple bond. Notably, the thiol-yne reaction can be photoinitiated in the UV-visible range (254–470 nm) and proceeds at room temperature with high efficiency in the presence of oxygen/water. Recently, Lo Conte *et al*. demonstrated for small molecules [23], and later more complex and biologically relevant molecules [24], that the photoinduced hydrothiolation of the triple bonds can be carried out by the sequential addition of two different thiols. Thus, under suitable reaction conditions the vinyl sulphide intermediate formed by addition of a first thiol can be trapped by a second different thiol via a thiol-ene type coupling.

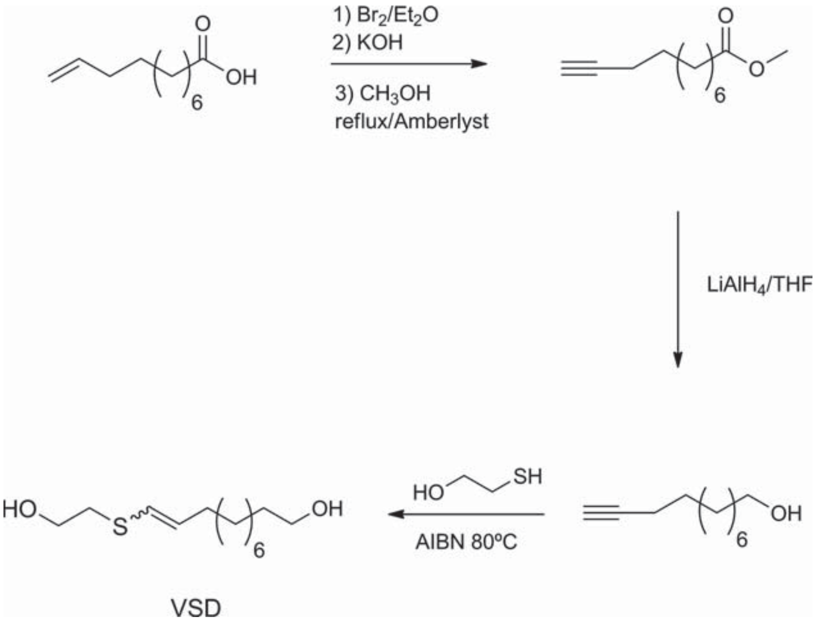
The aim of the present work was to synthesize and functionalize a thiol-reactive linear PU from renewable feedstock. To achieve this goal, a vinyl sulphide-containing diol (VSD, Scheme 1) has been synthesized from 10-undecynol, a 10-undecenoic acid derivative which is the major product of castor oil pyrolysis, and 2-mercaptoethanol. The further reaction of VSD and a commercial diisocyanate produced a linear PU bearing vinyl sulphide functionalities located on the main chain. Finally, the PU was functionalized with 7-mercapto-4-methylcoumarin (Cm-SH) as a fluorescent tag.

2 EXPERIMENTAL

2.1 Materials

The following chemicals were obtained from the sources indicated and were used as received: 10-undecenoic acid, trimethylorthoformate 98% (from Fluka), potassium hydroxide (90%, Scharlau), Amberlist 15, lithium aluminum hydride ($LiAlH_4$, 95%), 2,2-dimethoxy-2-phenylacetophenone (DMPA, 99%), 2,2′-azobis(2-methylpropionitrile) (AIBN, 99%), 2-mercaptoethanol (99%), tin(II) 2-ethylhexanoate, 4,4′-methylenebis(phenylisocyanate) (MDI), 7-mercapto-4-methylcoumarin (Cm-SH) and bromine (from Aldrich). Tetrahydrofuran (THF) was distilled from sodium immediately before use, N,N-dimethylformamide (DMF) was dried with CaH_2 for 24 h and freshly distilled before use. Other solvents were purified by standard procedures.

Synthesis of 10-undecynoic Acid. A 1000 mL, two-necked, round-bottom flask provided with a Teflon-coated magnetic bar and a pressure equalized dropping funnel was charged with 46 g (0.25 mol) of 10-undecenoic acid and 500 mL of diethyl ether. The flask was cooled in an ice/water bath, the solution was stirred magnetically, and 48 g (0.3 mol) of bromine was added during a period of 1 h. The mixture was allowed to warm up gradually to room temperature, and after



Scheme 1 Synthesis of VSD from 10-undecenoic acid using thiol-yne coupling as a key reaction step.

stirring overnight, the solvent and the excess of bromine was removed under reduced pressure. The brown liquid dibromo acid was transferred to a 2 L round-bottom flask containing 800 mL of n-propanol, and a solution of 120 g of potassium hydroxide in 140 mL of water was added. After heating at reflux temperature for 15 h, 1.5 L of water was added and the reaction mixture neutralized with HCl 2N. The product was extracted with several portions of diethyl ether, dried with anhydrous magnesium sulfate, and concentrated under reduced pressure. The residue was distilled under reduced pressure (0.85 mmHg) and the fraction at 122–134°C was collected. The product that solidified on cooling was recrystallized twice from hexane to obtain a white solid (yield 70%, mp 41–42°C).

^{1}H NMR (CDCl$_3$,TMS, δ, ppm): 1.24-1.33 (m, 8H, -CH$_2$-), 1.44 (m, 2H, , -CH2-CH$_2$-C≡CH), 1.55 (m, 2H, -CH2-CH$_2$-COOH), 1.88 (s, 1H, -C≡CH), 2.11 (m, 2H, -CH$_2$-C≡CH), 2.23 (t, 2H, -CH$_2$-COOH), 11.81 (s, 1H, -COOH).

^{13}C NMR (CDCl$_3$, δ, ppm): 180.67 (s), 84.89 (s), 68.31 (d), 34.27 (t), 29.30 (t), 29.19(t), 29.01(t), 28.65(t), 28.50(t), 24.79 (t), 18.55 (t).

Synthesis of methyl 10-undecynoate. A 500 mL round-bottom flask was charged with 54.7 g (0.3 mol) of 10-undecynoic acid, 200 mL of methanol, 17 mL (15.9 g, 0.15 mol) of trimethyl orthoformate, and 2 g of Amberlist 15. The mixture was heated at reflux temperature for 4 h, resin was filtered, and 200 mL of ether was added. The solution was washed twice with water and dried with anhydrous magnesium sulfate, and the ether was removed under reduced pressure. Methyl 10-undecynoate was purified by fractionated distillation (4 mmHg, 96–98°C) (yield 87%).

^{1}H NMR (CDCl$_3$,TMS, δ, ppm): 1.24-1.33 (m, 8 H, -CH$_2$-), 1.44 (m, 2 H, -CH2-CH$_2$-C≡CH), 1.55 (m, 2 H, -CH2-CH$_2$-COOCH$_3$), 1.88 (t, 1 H, -C≡CH), 2.15 (m, 2 H, -CH$_2$-C≡CH), 2.28 (t, 2 H, -CH$_2$-COOCH$_3$), 3.65 (s, 3 H, -COOCH$_3$).

^{13}C RMN (CDCl$_3$,TMS, δ, ppm): 18.49 (t), 25.02 (t), 29.30 (t), 29.19(t), 29.01(t), 28.65(t), 28.50(t) , 34.18 (t), 51.57 (q), 68.26 (d), 84.78 (s), 174.38 (s).

Synthesis of 10-undecynol. A 250-mL, two-necked, round-bottom flask equipped with a teflon-coated magnetic bar and a pressure-equalized dropping funnel was charged with LiAlH4 (0.3 g, 7.8 mmol) and anhydrous THF (15 mL) under argon. Methyl 10-undecynoate (1.9 g, 5.3 mmol) dissolved in 10 mL of anhydrous THF was added slowly with stirring for 1 h. Anhydrous THF (2 × 10 mL) was added as the viscosity increased. After 30 min, excess LiAlH$_4$ was decomposed by the addition of 25 mL of ethyl acetate dropwise, then a saturated 10% H$_2$SO$_4$ aqueous solution (50 mL) was added, the phases were separated, and the aqueous layer was extracted with ethyl acetate. The combined organic phase was washed with a saturated aqueous NaCl solution, dried over anhydrous magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The product was purified by vacuum distillation (140–142°C, 0.85 mm Hg), to afford pure diol in 89% yield.

^{1}H NMR [CDCl$_3$, TMS, δ, (ppm)]: 3.62 (t, 2H, -CH$_2$-OH), 2.15 (t, 2H, -CH2-C≡CH), 1.91 (s, 1H, -C≡CH), 1.58 (m, 2H, -CH$_2$-CH$_2$-OH), 1.53-1.26 (m, 12H, -CH2-).

^{13}C NMR [CDCl$_3$, TMS, δ, (ppm)]: 85.12 (s), 69.12 (d), 65.22 (t), 34.22 (t), 29.76 (t), 29.66 (t), 29.32 (t), 29.11 (t), 28.75 (t), 26.13 (t), 19.13 (t).

2.2 General Procedures for the 2-Mercaptoethanol Monoaddition to 10-Undecynol Under Thermal and Photoinduced Conditions

2.2.1 *Thermal Initiation*

10-Undecynol and 2-mercaptoethanol were introduced in different molar ratios (see Table 1) into a round-bottom flask with magnetic stirrer. The radical initiator, AIBN, was added in the proportion of 5 or 10% mol init./mol C≡C with the amount of toluene necessary to dissolve the thermoinitiator, and stirred at 80°C for 15 min.

2.2.2 *Photoinduced Initiation*

10-Undecynol and 2-mercaptoethanol were introduced in different ratios (see Table 1) into a round-bottom flask with magnetic stirrer. After the addition of DMPA (0.5 or 3.6% mol init./mol C≡C) with the amount of toluene necessary to dissolve the photoinitiator, the flask was placed onto a magnetic stirrer equipped with two 9W UV lamps (365nm) and stirred at room temperature for 15 min.

2.3 Diol and Polyurethane Preparation

2.3.1 *Synthesis of Vinyl Sulphide-containing Diol (VSD)*

In a 25-mL flask, 5.0 g (29.7 mmol) of 10-undecynol reacted with 2.44 g (31.19 mmol) of 2-mercaptoethanol. The radical initiator, AIBN, was added in the proportion of 10% mol init./mol C≡C. The amount of toluene necessary to dissolve the thermoinitiator was added (0.06 ml). The reaction was carried out at room temperature, without deoxygenation, by heating at 80°C. After 15 min the monoaddition reaction was confirmed by ^{1}H NMR by the appearance at 5.59–5.87 ppm of the hydrogens corresponding to the double bond signals between. The product was purified by column chromatography using hexane:ethyl acetate, 3:7, as eluent, to afford pure diol as viscous oil, in a 98% yield.

Table 1 Reaction conditions for the monoaddition of 2-mercaptoethanol to 10-undecynol.

Radical Initiator	Molar Ratio Alkyne : Thiol : Initiator	Unreacted Alkyne (%)	Monoaddition product (%)	Diaddition product (%)
–	1 : 1 : 0	100	–	–
–	1 : 2 : 0	80	3	17
DMPA	1 : 0.25 : 0.005	60	19	21
DMPA	1 : 0.5 : 0.005	47	26	25
DMPA	1 : 0.25 : 0.036	58	19	23
DMPA	1 : 0.5 : 0.036	38	30	32
DMPA	1 : 1 : 0.036	26	27	47
AIBN	1 : 1 : 0.05	32	38	30
AIBN	1 : 1 : 0.1	7	65	28
AIBN	1 : 1.05 : 0.1	2	80	18
AIBN	1 : 1.1 : 0.1	3	60	37
AIBN	1 : 1.15 : 0.1	3	51	46

^{1}H NMR [CDCl$_3$, TMS, δ, (ppm)]: 5.83-5.87 (m,-S-CH=CH-,2H,c,c`), 5.59-5.76 (dm, -S-CH=CH-,2H,d,d`), 3.73 (t, HO-CH2-CH$_2$-S-,4H,a,a`), 3.62 (t, -CH$_2$-OH,4H), 2.82 (m, HO-CH$_2$-CH2-S-,4H,b,b`) 2.10 (dq, -S-CH=CH-CH2-, 4H,e,e`), 1.58 (m,-CH$_2$-CH$_2$-OH,2H), 1.39- 1.26 (m,-CH2-, 12H).
^{13}C NMR [CDCl$_3$, TMS, δ, (ppm)]: 134,02 (d), 131,92 (d), 123,51 (d) 121,51 (d), 63,12 (t) 61,32 (t), 60,57 (t), 37,12 (t), 36,03 (t) 34.22 (t), 33,11 (t), 32,72 (t), 29.62 (t), 29.30 (t), 29.11 (t), 28.95 (t), 28.81 (t), 25,6 (t).
ESI-HMRS m/z calcd (M+Na)+: 199.0763, found: 199.1342.

2.3.2 *Synthesis of Polyurethane (PU)*

A dry 50 mL round-bottom flask was charged with 6 mL of DMF, 4.06 mmol of diol (UDEM-diol), 4 mmol of MDI, and 2%, w/w (with respect to MDI) of tin (II) 2-ethylhexanoate. The flask was immersed into a 50°C preheated silicone oil bath with magnetic stirring. The reaction was continued for 12 h, and the PU was isolated as white solid by precipitation into diethyl ether. Purification of PU was carried out by dissolving the polymer in the minimum volume of chloroform or THF and reprecipitation into diethyl ether. The pure polymer was dried under vacuum and stored in a desiccator until needed. Films were solution cast from DMF and dried at 50°C for 1 day and then in a vacuum oven until constant weight.

2.4 PU Modification in Solution

In a 25 mL flask 0.1 g (0.2 mmol) of PU reacted with 0.08 g (0,4 mmol) of Cm-SH. The radical initiator, DMPA, was added in the proportion 10% mol init./mol C=C. The amount of THF necessary to dissolve the PU was added (2 ml). The reaction was carried out at room temperature, without deoxygenation, by irradiation with two 9 W UV-lamps (λ=365 nm). The completion of the reaction was confirmed after 2 h by ^{1}H NMR by the complete disappearance of the vinyl sulphide signals that appear in the region of 5.5–6 ppm. The resulting PU was precipitated in toluene and dried under vacuum (yield 98%). The emission spectra of the Cm-SH, PU and PU-Cm solution were measured with excitation wavelength of 358 nm. Samples of 5 mg were dissolved in 1ml of DMF for fluorescence spectroscopy measurements.

2.5 PU Surface Modification

Six PU samples (0.7 × 0.7 × 0.02 cm^3) reacted with Cm-SH (molar ratio PU/ Cm-SH 1/2) in a 25 mL flask. The radical initiator, DMPA, was added in the proportion 10% mol init./mol C=C. The amount of acetonitrile necessary to dissolve the Cm-SH was added (4 ml). The reaction was carried out at room temperature, without deoxygenation, by irradiation with two 9 W UV-lamps (λ = 365 nm). The thiol-ene addition of Cm-SH on PU surface was followed by fluorescence at different times (30 min, 1, 2, 4, 8 and 24 h). The emission spectra of the PU films were measured with excitation wavelength of 358 nm. The resulting PU films were extensively washed with acetonitrile to remove the residual unreacted Cm-SH on the surface at different times.

2.6 Instrumentation

The FTIR espectra were recorded on a JASCO 680 FTIR spectrophotometer with a resolution of 2 cm^{-1} in the absorbance mode. An attenuated total reflection

(ATR) accessory with thermal control and a diamond crystal (Golden Gate heated single–reflection diamond ATR, Specac. Teknokroma) was used to determine FTIR spectra. ^{1}H 400 MHz and ^{13}C (100.5 MHz) NMR spectra were obtained using a Varian Gemini 400 spectrometer with Fourier transform, DMSO as solvent and TMS as internal standards. ESI MS were run on an Agilent 1100 Series LC/MSD instrument. Size exclusion chromatography (SEC) analysis was carried out with an Agilent 1200 series system equipped with an Agilent 1100 series refractive-index detector. THF was used as an eluent at a flow rate of 1.0 mL/min. The calibration curves for SEC analysis were obtained with polystyrene standards. Calorimetric studies were carried out on a Mettler DSC821e and DSC822e thermal analyzer using N_2 as a purge gas (20 ml/min) at scanning rate of 10°C/min. Mechanical properties were measured using a dynamic mechanical thermal analysis (DMTA) apparatus (TA DMA 2928) in the controlled force-tension film mode. The tensile essays were performed on rectangular films (5 × 2 × 0,2 mm^3) measuring the strain while applying a ramp of 3 N/min at 35°C. A preload force of 0.01 N and a soak time of 5 min. were used. The spectrofluorimetric data were acquired on an Aminco-Bowman Series 2 Luminescence spectrometer (SLM Aminco, Rochester, NY, USA) equipped with a 150W continuous xenon lamp and a PMT detector.

3 RESULTS AND DISCUSSION

A vinyl sulphide-containing diol (VSD, Scheme 1) was obtained from 10-undecynol, an alkyne-derivatized fatty compound, using hydrothiolation as a key reaction step. 10-Undecynol was prepared by reduction of 10-undecinoic acid methyl ester, which was prepared by successive bromation, dehydrobromination of the corresponding alkenic fatty acid. Reaction conditions were optimized to allow only one equivalent of 2-mercaptoethanol to add to the alkyne-fatty alcohol. Thus, coupling between the two components was carried out using different alkyne/thiol molar ratios under thermal and photoinitiated conditions as summarized in Table 1. Reactions performed under the thermal conditions (80°C) were carried out using AIBN as a radical initiator, whereas photoinduced reactions were carried out at room temperature under UV irradiation (365 nm) using DMPA as a photoinitiator. All reactions were performed for 15 min. The highest amount of VSD was obtained using 10% mol AIBN as a thermal initiator and a slight excess of thiol. Lower amounts of initiator lead to a significant % of unreacted alkyne. VSD was isolated by column chromatography as a mixture of *E* and *Z* isomers. Figure 1 shows the ^{1}H NMR spectrum of the isolated product with all the assignments. The presence of the vinyl thioether intermediate was confirmed by the presence of two sets of signals between 5.5–6.0 ppm corresponding to the *E* and Z C-C double bond protons. Signals b/b′ and e/e′ also appeared, split into two signals due to the presence of both isomers. The unequivocal assignments could be carried out using 2-D NMR gHSQC experiments. Thus, it could be proved that whereas ^{1}H NMR spectrum shows protons d/d′ more shielded than c/c′, the corresponding carbons showed inverse trend in ^{13}C NMR spectrum.

VSD was combined with MDI to produce a vinyl sulphide-containing linear PU. Figure 2 shows the ^{1}H NMR spectrum of the synthesized PU. The resonance of C-C double bond protons appears at around 6 ppm proving that the functionalized diol has been incorporated into the polymer without any side reaction. SEC and solubility data are summarized in Table 2. Molecular weight

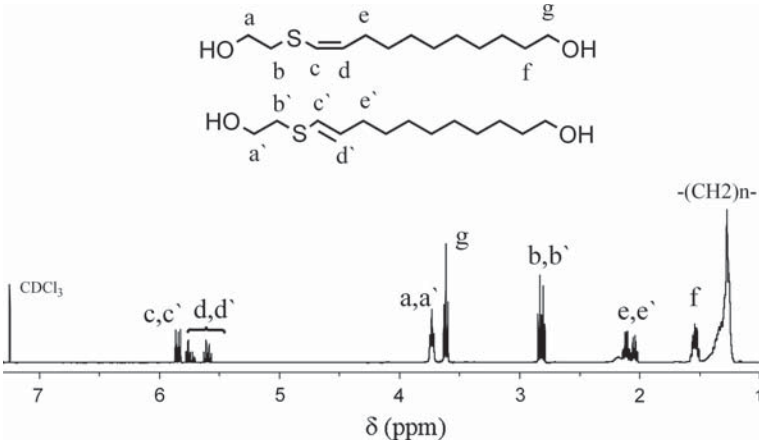


Figure 1 ^{1}H NMR spectrum of VSD.

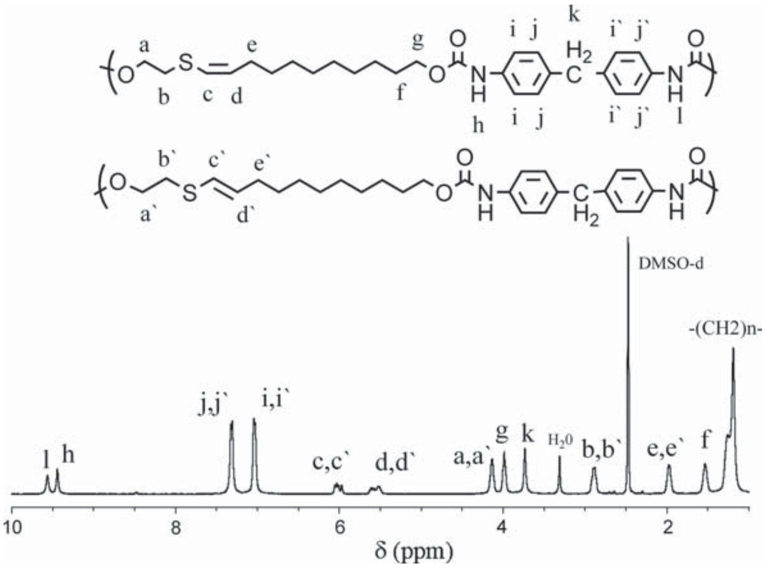


Figure 2 ^{1}H NMR spectrum of vinyl sulphide-containing PU.

Table 2 Polycondensation results and some properties of PU.

			SEC			Solubility[a]			
T (°C)	t (h)	Yield (%)	M_n (g/mol)	M_w (g/mol)	M_w/M_n	H_2O	DMSO	$CHCl_3$	THF
50	12	99	66,100	140,120	2.1	–	+	+	+

[a] Solubility at 25 °C: + soluble, – insoluble.

of 66.1 kDa was obtained using polystyrene standards as a reference, and synthesized PU was soluble in all tested solvents excepting water. Thermal and mechanical properties were studied by DSC, TGA, and DMTA (Table 3). PU showed a glass transition temperature (T_g) at 65°C and a melting process at 132°C. Thermal stability was analyzed under nitrogen atmosphere and a 5% weight loss was observed at around 300°C as expected for PU-type polymer. Concerning mechanical properties, PU showed a typical behavior of semicrystalline polymer presenting strain-induced crystallization after the yield point of cristalline domains [25]. Tensile strength and elongation at break were evaluated using the stress-strain curve shown in Figure 3.

PUs containing vinyl sulphide groups in the main chain are expected to be highly thiol reative. Vinyl sulphide-containing PU modification was studied using a 7-mercapto-4-methylcoumarin (Cm-SH) as a fluorescent probe using DMPA as a photoinitiator in THF solution. The success of the polymer modification was assessed by ^{1}H NMR analysis. Figure 4 shows how after irradiation at 365 nm for 2 h, signals corresponding to the C-C double bonds completely disappeared

Table 3 Thermal and mechanical properties of PU.

DSC			TGA (°C)		Mechanical Properties	
T_g (°C)	T_{m1} (°C)	ΔH_1 (J/g)	$T_{5\%}$	T_{max}	σ_{max} (MPa)	ε_{max} (%)
65	132	24	298	351/470	27	400

and new signals corresponding to coumarin moieties appeared. SEC analysis could not be carried out due to the limited solubility of this polymer in THF. Nevertheless, the incorporation of coumarin moiety to PU could also be confirmed by fluorescence spectroscopy. Figure 5a shows the emission spectrum of Cm-SH solution after excitation at 358 nm. The emission band presents a maximum at 400 nm. When emission fluorescence spectrum of the modified PU was recorded in the same experimental conditions, a new emission band appears at 531 nm and the maximum of the initial band is shifted to 412 nm, which is indicative that the emission of coumarin is produced in a different

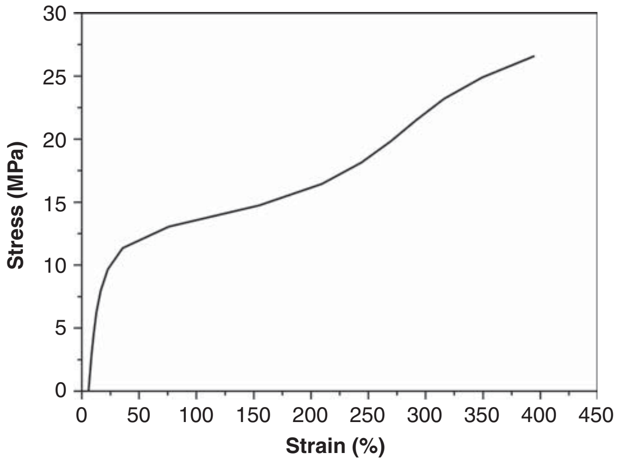


Figure 3 Stress-strain curve of the vinyl sulphide-containing PU.

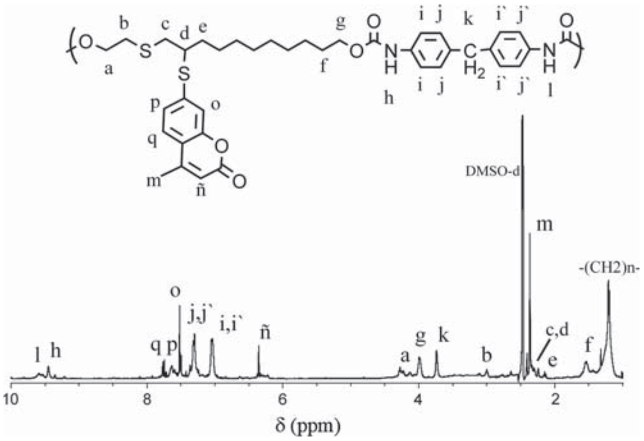


Figure 4 ^{1}H NMR spectrum of the Cm-modified PU.

chemical environment (Figure 5b). Considering that initial PU shows a lower emission band at 460 nm it is possible to conclude that coumarin moiety is linked to PU main chain.

In view of these results, the surface modification of synthesized vinyl sulphide-containing PU was also investigated. The surface modification was also carried out using a Cm-SH [26]. Figure 6 shows the emission spectrum of the PU films at different reaction times. As the reaction proceeded, the intensity of the emission spectra (425 nm) increased, with sufficient sensitivity to monitor the thiol-ene addition of Cm-SH to vinyl sulfide groups present on PU surface. Nowadays this behavior may be exploited in biomedical applications since these fluorescence-sensitive polymers not only facilitate the delivery of therapeutic agents but also allow monitoring of the degradation profile of implants over time by fluorescence imaging [27].

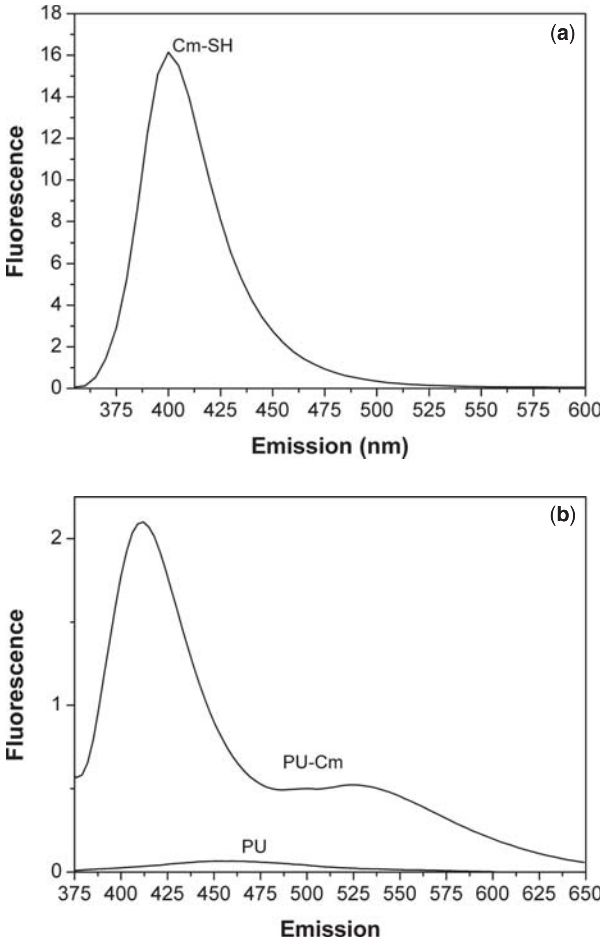


Figure 5 Fluorescence spectra of the **(a)** Cm-SH, **(b)** PU and PU-Cm in DMF solution with excitation (λ_{exc}) at 358 nm.

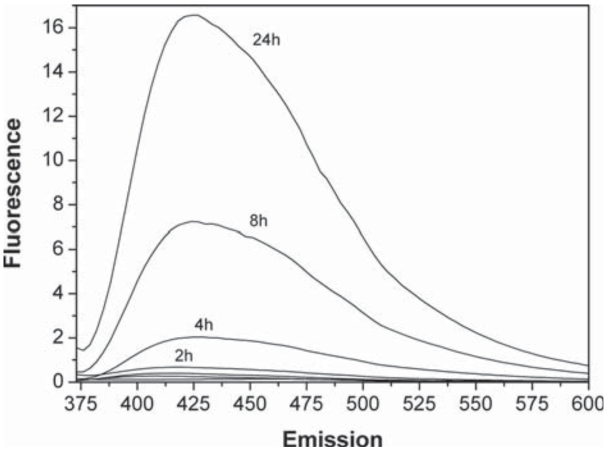


Figure 6 Fluorescence spectra of PU films during the surface modification with Cm-SH.

4 CONCLUSIONS

A thiol-reactive linear PU was synthesized from a vinyl-sulphide-containing diol and a commercial diisocyanate. The diol was obtained from 10-undecynol using hydrothiolation as a key reaction step. Solution and surface polymer modification with a fluorescent thiol was successful.

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