Results in Materials 15 (2022) 100294

Contents lists available at ScienceDirect

Results in Materials

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An efficient synthesis of bio-based Poly(urethane-acrylate) by SiO_2-Supported $CeCl_3{\cdot}7H_2O$–NaI as recyclable Catalyst

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ARTICLE INFO

Keywords:
Bio-based Poly(urethane-acrylates)
Catalysis
Chemical and thermal characterization
Catalyst recyclability
Non-toxicity

ABSTRACT

Poly(urethane-acrylates) (PUAs) are UV-curable resins used for biomedical applications, coatings, adhesives, and many others. Their syntheses usually involve the use of aromatic diisocyanates and polyols coming from fossil-based resources, in the presence of tin-based catalysts, which present a very well-known toxicity. In the last years the increase of environmental and economic issues related to the depletion of limited sources, the increase of greenhouse gas emissions, the release of toxic degradation compounds and the catalyst contamination has shifted the attention toward more sustainable solutions. In this study a low-impact, sustainable and efficient procedure for the synthesis of bio-based PUA promoted by solid supported $CeCl_3{\cdot}7H_2O$–NaI/SiO_2 was developed. This catalytic system provides the target compounds with good monomer conversion and molecular weights and allow the synthesis under heterogeneous conditions as main advantage, with the final recovery of the catalyst. We also confirmed its rapid separation, stability, and efficient recycling of the catalyst, obtaining comparable results over a seven reactions cycles. The goodness of the polymerization process under heterogeneous condition was confirmed by chemical and thermal characterizations.

1. Introduction

Green and sustainable catalytic reactions always find application in polymer synthesis, and particular attention is paid to 'precision polymerization' where the catalyst plays a key role [1]. In this context, rare earth-heterogeneous-catalyzed processes are widely applied to polymer synthesis [2], and cerium(III) salt based systems have found increasing application as eco-friendly catalysts for polymer synthesis innovation [3–5]. To our knowledge there are no data in the literature on the use of Ce(III) salts as catalysts in the preparation of polymers within the polyurethanes family. Conversely, Ce(IV) has found greater application, especially added as nano-cerium colloids to previously synthesized waterborne polyurethane dispersions [6]. Recently, CeO_2 has been used as a catalyst in the synthesis in situ of diisocyanate from diamine, CO_2 and methanol for a suitable preparation of polyurethane [7]. Given that, in the last few decades we were able to demonstrate how Ce(III) is an active species in the promotion of important reactions concerning new carbon-carbon and carbon-heteroatom bond formation [8], where instead Ce(IV) does not behave as catalyst [9]. Thus, we found useful to develop in this manuscript a new methodology for the synthesis of bio-based PUAs promoted by $CeCl_3{\cdot}7H_2O$–NaI supported on SiO_2.

The synthesis of polyurethanes (PUs) and poly (urethane-acrylates) (PUAs) is of great interest. In fact, they are a class of polymers with a wide-ranging application, such as automotive, thermal insulation, coatings, adhesives, construction, etc., due to their properties which can be adapted by varying the chemical composition, the molecular weight, and the ratio of the soft-to-hard segments [10–16].

Conventional PU materials are based on aromatic diisocyanates such as toluene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI), that release toxic and carcinogenic aromatic diamine products as a consequence of in vivo degradation [17,18]. Therefore, aliphatic and cycloaliphatic isocyanates, such as hexamethylene diisocyanate (HMDI) and isophorone diisocyanate (IPDI), result suitable for the synthesis of these polymeric derivatives [19], also due to their UV-resistance, finding

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https://doi.org/10.1016/j.rinma.2022.100294
Received 21 March 2022; Received in revised form 17 May 2022; Accepted 15 June 2022
Available online 20 June 2022

application in the field of transparent coatings [20]. Another important aspect is that being the PU industry strongly dependent on fossil-based materials, environmental and economic concerns have led to the growth of interest in starting materials coming from renewable resources such as, sorbitol, amino acids, furan derivatives, cellulose, lignin, vegetable oils and derivatives [21–23]. In fact, the use of sustainable materials avoids the depletion of limited resources, reducing greenhouse gas emissions and health related issues [24–27].

During the last few decades, UV-curing technology has attracted attention in the fields of drug delivery systems, coatings, and adhesives. This technology is environmentally friendly (less VOC emissions) with low energy consumption and fast curing conditions [28,29].

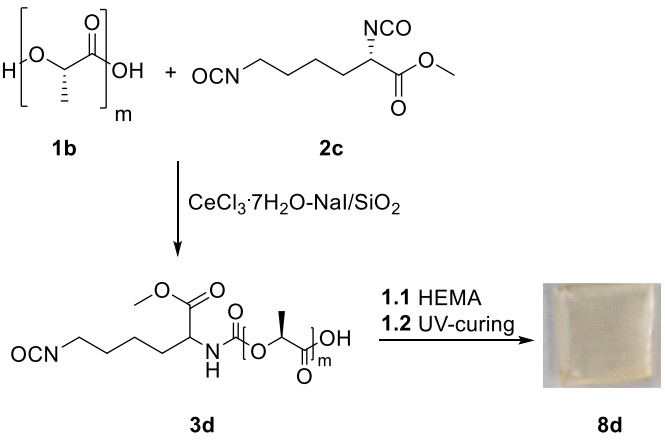
Among UV-curable resins, poly(urethane-acrylates) have been drawing growing interest thanks to their unique properties as excellent abrasion and chemical resistance, adhesion to substrates, light stability, water resistance and weatherability, as well as mechanical properties which are highly desirable for industrial applications [30–32].

PUA is generally obtained by the reaction of a polyol **1** with a diisocyanate **2** in the presence of a catalyst, and using a stoichiometric excess of diisocyanate, the resulting urethane oligomer chains **3** are NCO-terminated (Scheme 1). Afterwards, the isocyanate end-groups react with hydroxyl functional acrylic monomers of 2-hydroxyethyl methacrylate (HEMA) (**4**) to obtain a urethane acrylate oligomer (UAO) **5**, with unsaturation at the end of the polymer backbone. The last step is the radical polymerization by UV radiation of vinyl group of end-capped acrylates, in the presence of benzophenone as well-known type II photo-initiator (**6**) and methyl diethanolamine (**7**) as co-initiator, to obtain PUA **8** [33,34].

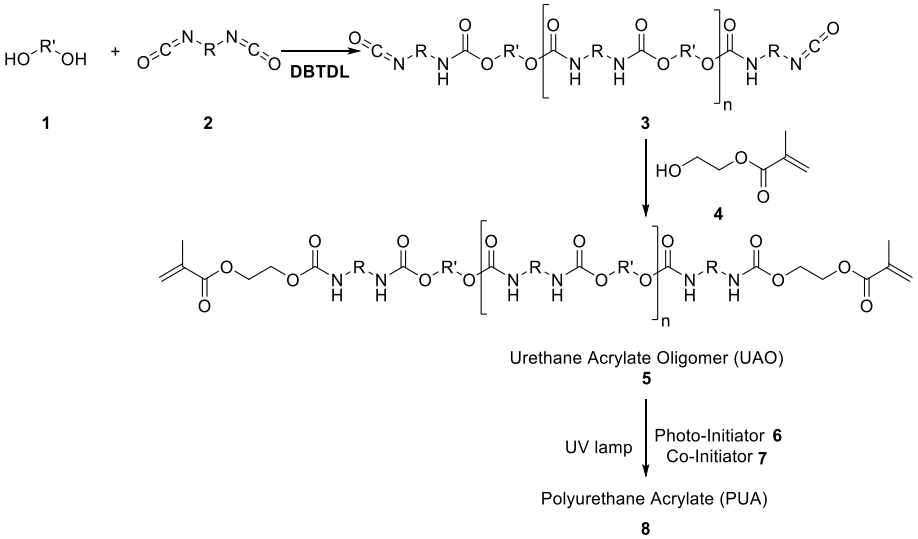
The most employed catalysts during this synthesis are tin-based compounds [35], one of the most used is the dibutyltin dilaurate (DBTDL), but its homogenous nature means that complete removal of the catalyst from the polymer matrix is not feasible. Furthermore, many studies have been shown the potential toxicity of tin, and this aspect limits its use in the synthesis of polymers involved in biomedical application [36]. Nowadays, the challenge is to reduce the metal content in the final product. For this purpose, the replacement of homogenous catalysts with heterogeneous ones represents a potential solution. This feature allows to recover and reuse the catalyst, reducing the metal content and wastes produced [37,38]. Herein, we studied a new and eco-compatible cerium(III) salt-solid supported catalyst with a remarkable activity in PUA synthesis. We developed an efficient polymerization process promoted by an inexpensive, non-toxic silica supported cerium trichloride heptahydrate-sodium iodide system ($CeCl_3{\cdot}7H_2O$–NaI/SiO_2) [39,40]. Furthermore, we synthesized a fully bio-based poly(urethane-acrylate) (Scheme 2), starting from renewable poly(L-lactic acid) (PLLA) and L-lysine diisocyanate, comparing its final chemical and thermal properties to those coming from fossil based materials, prepared with the same approach. The very soft reaction conditions does not allow the oligomers alteration with the subsequent formation of polyamide derivatives [41]. The development of this PUA encloses the bio-based economy principles, allow the generation of PUA suitable for biomedical appications and drug delivery systems, due to the very low toxicity of $CeCl_3{\cdot}7H_2O$–NaI/silica catalyst.

2. Material and methods

Materials. All reagents such as dibutyltin dilaurate (DBTDL), Ce$(OAc)_3$, $CeCl_3{\cdot}7H_2O$, NaI, CuI, KI, SiO_2, Al_2O_3, Isophorone diisocyanate (IPDI), Hexamethylene diisocyanate (HDI), L-Lysine, PEG400, L-Lactic Acid, Isosorbide, 2-hydroxyethyl methacrylate (HEMA), benzophenone and N-methyldiethanolamine were all purchased from Merck. As first treatment, both diols and diisocyanate were dried at 50 °C under vacuum for 24 h, in order to remove residual water. In the case of air and moisture sensitive reactions, the glassware was oven dried at 100 °C for more than 2 h prior to use, when the reactions were performed under nitrogen atmosphere. L-lysine methyl ester diisocyanate was synthetized according to reference of Nowick *et al.* [42] $CeCl_3{\cdot}7H_2O$–NaI/SiO_2 was prepared according to Bartoli *et al.* procedure [43].



Scheme 2. Our approach to the synthesis of fully bio-based PUA.



Scheme 1. General PUA synthetic procedure with DBTDL.

Instruments. Compounds were characterized by FT-IR ATR analysis, performed with a PerkinElmer FT-IR spectrometer Spectrum Two UATR, equipped with ZnSe crystal. The measurements were performed in a 400-4000 cm^{-1} range at a 2 cm^{-1} resolution, 4 scans and processed by a PerkinElmer data manager (Spectrum). The molecular weights of polymer matrix were evaluated by gel permeation chromatography. The measurements were carried out with an Agilent 1260 Infinity II Multi Detector Suite (MDS) device. In this device, there was an Agilent 1260 Infinity Quaternary Pump (G7111B), containing a 4-channel vacuum degasser to pump the eluent into the system. The auto sampler was G7129A and the thermostatic column compartment G7116A. The used device consisted of three different detectors (G7800A): a dual light scattering detector (measuring in the angles of 15° and 90°), an RI detector, and a VS-detector. The THF mobile phase contained 250 ppm of BHT (butylated hydroxytoluene) and the flow rate was fixed at 1.0 ml/min. In the measurements and data analysis, an Agilent GPC/SEC Software, was used. GPC system was equipped with two columns in series (PLgel MIXED-C and PLgel MIXED-D) and before the columns there was also a guard column (Agilent GPC/SEC Guard Column). The standards used in the measurements for column calibration were PSs with different Mp values in the range of 580–283800 g/mol. The chemical nature of poly(urethane-acrylate) was determined by nuclear magnetic resonance. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury 400 (400 MHz or 100 MHz respectively). Chemical shifts are quoted in ppm and are referenced to residual protons in the deuterated solvent as the internal standard such as $CDCl_3$ (7.26 ppm for ^{1}H and 77.0 ppm for ^{13}C) or dimethyl sulfoxide-d6 (DMSO-d_6, 2.50 ppm for ^{1}H and 39.5 ppm for ^{13}C). Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Thermogravimetric analysis (TGA) was performed to evaluate their thermal stability. TGA was carried out using a Netzsch STA 2500 Regulus thermal analyzer, equipped with Al_2O_3 crucibles. 10 mg of samples were heated from room temperature to 900 °C, under nitrogen atmosphere with a heating rate of 10 °C/min. The thermal behaviour was also determined by differential scanning calorimetry (DSC). Samples (8–9 mg in an aluminum concave pan with pierced lid) were analyzed in a DSC 250 TA, according to the following thermal program: heating from −90 °C to 100 °C (2 min hold), cooling to – 90 °C (2 min hold) and heating to 100 °C, all steps at 10 °C/min. Microscopic morphology of polymer samples was evaluated by an high-resolution scanning electron microscope with field emission gun (FE-SEM, Sigma Family, Zeiss, Oberkochen, Germany) operated at 15 keV, equipped with an energy-dispersive X-ray spectroscopy system (Quantax 200, EDS, Bruker) that enables elemental analysis. Samples were deposited on aluminium stabs using self-adhesive carbon conductive tabs and sputtered with a thin film of chromium (5 nm) by the sputter coater Quorum QT150 (Quorum, Laughton, UK). UV-Lamp used for the curing step is the VL-215.G-2.15 W with a characteristic wavelenght at 254 nm, filter size 495 × 120 mm and power[W]: 2 × 15.

2.1. Methods and experimental procedures

Experimental procedure for the synthesis of compounds **3a-f**. In a 25 ml two-necked round bottom flask, 500 mg of polyol was reacted with diisocyanate (1.5 equivalents) at 70 °C in the presence of $CeCl_3{\cdot}7H_2O$–NaI/SiO_2 (0.3 wt%) for 2 h, under nitrogen atmosphere. Then, the catalyst was filtered off, washed with fresh CH_2Cl_2 (1 ml) and the products **3a-f** were isolated after solvent evaporation under vacuum.

Experimental procedure for the synthesis of compounds **8a-f**. The NCO-terminated urethane pre-polymers (**3a-f**) obtained were cooled down to 50 °C and then end-capped with HEMA (2.5 mmol, 2 equivalents), by adding it dropwise to the reaction mixture. The synthesis of UAO was performed at 50 °C for 4 h and the products were isolated after solvent evaporation under vacuum. Afterwards, benzophenone (1.5 wt %) with methyl diethanolamine (1.5 wt%) were added to **5a-f** [34]. The reaction mixture was deposed in a small glass plate and was exposed to the UV-lamp for 10 min to obtain PUAs (**8a-f**).

3. Results and discussion

Catalyst screening and synthesis of NCO-terminated urethane pre-polymer. Following our previous studies on the development of efficient and sustainable lactic acid polymerization [4], and synthesis of biomass-based PUA composite [5] we disclose a low-impact procedure for the synthesis of poly(urethane-acrylate). Several cerium-based catalysts were tested for the urethane oligomer (**3a**) formation (Table 1), starting from polyethylene glycol (PEG 400, **1a**) and isophorone diisocyanate (IPDI, **2a**). From the screening, $CeCl_3{\cdot}7H_2O$ combined with NaI (Table 1, CAT5), leads to the formation of **3a** with a molecular weight Mw = 1700 Da and monomer conversion of 94% comparable to those achieved with dibutyltin dilaurate, DBTDL, (Table 1, CAT2). This catalytic system based on cerium is a more active Lewis acid promoter, where the oligomeric structure of cerium(III) trichloride is broken by iodide ion to give more reactive monomeric structure [43], has also been confirmed by the XPS analysis performed in our previous studies [4]. Furthermore, the LD_{50} value of $CeCl_3{\cdot}7H_2O$ (2800 mg/kg) is sixteen times higher than DBTDL (175 mg/kg) and thanks to its non-toxicity, low cost and easy handling make this system an important alternative to obtain PUA, reducing the impact of the chemical process from both an economic and safety point of view. To further investigate the eco-friendly catalytic system, other iodine sources were tested (Table 1, CAT7-8), in combination with $CeCl_3{\cdot}7H_2O$. The highest molecular weight was reached with sodium iodide (Table 1, CAT 5) as it is able to form a complex with a very strong Lewis acid character. Furthermore, to minimize costs and environmental impact, we performed the synthesis of **3a** under heterogeneous conditions (Table 1, CAT9-10), to recover and recycle the catalyst once the reaction is over. The best performing systems resulted in $CeCl_3{\cdot}7H_2O$–NaI/SiO_2 where a molecular weight of 1800 Da (Table 1, CAT9) was obtained.

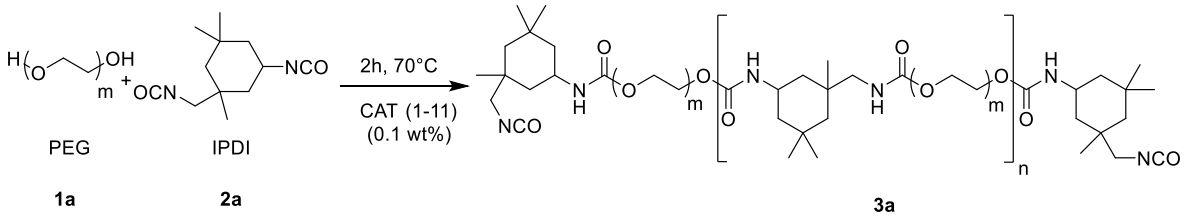
After selecting the best catalytic system, optimization of the reaction conditions was performed (Table 2). The highest molecular weight was obtained after 2 h at 70 °C with 0.1 wt% of $CeCl_3{\cdot}7H_2O$–NaI/SiO_2 and 1.5 equivalents of IPDI (Table 2, RC3). Afterwards, a kinetic study (Figure S2†) was performed and after 2 h the highest Mw = 1800 Da was obtained.

After this catalysts screening (Table 1), and following the good results obtained with solid supported $CeCl_3{\cdot}7H_2O$–NaI/SiO_2 catalytic system (Table 1, CAT9), we moved to the optimization of reaction conditions as follow (Table 2).

Catalyst recyclability. Additional tests were performed to determine the catalyst recyclability. $CeCl_3{\cdot}7H_2O$–NaI supported on SiO_2 can be filtered, washed, dried under vacuum, and reused for seven cycles without noting any appreciable decrease in activity (Fig. 1). Stability and composition of this recycled catalyst was determined by SEM-EDX and FTIR analysis. The results obtained proved that the elements detected in the fresh catalyst were still present after the seventh recycling (Fig. 2) and no differences are found in the FTIR spectra (Fig. 3). In particular, the peaks at 1080 and 800 cm^{-1} corresponding to different modes of O–Si–O or Si–O–Si vibrations, were again observed in the recycled catalyst.

Synthesis of bio-based poly(urethane-acrylates). To demonstrate the efficiency of the optimized catalytic procedure, we studied the reactivity of a plethora of polyols with different diisocyanate derivatives. We focused the attention on the synthesis of bio-based NCO-terminated urethane pre-polymer (Table 3). With the aim of replacing PEG 400 (**1a**), it was first performed the reaction between isophorone diisocyanate (**2a**) and different bio-based diols **1b** and **1c**. Oligo (*L*-lactic acid) (OLLA) (**1b**), with M_W of 400 Da and isosorbide (**1c**) led to the formation of compounds **3c** and **3e**, respectively, with a molecular weight of 1300 Da (Table 3). These data are comparable with those obtained with fossil-based polyols (compound **3a**). Pursuing the idea of synthesizing a fully bio-based NCO-terminated urethane pre-polymer, both OLLA and isosorbide were reacted with *L*-lysine diisocyanate (**2c**). The latter proved to be less reactive than IPDI towards this reaction

Table 1
Screening of catalysts and properties of **3a**.



	Catalyst type	Mn[a] (g/mol)	Mw[a] (g/mol)	Monomer Conv.[b] (%)
CAT**1**	–	600	700	60
CAT**2**	DBTDL	1500	1900	96
CAT**3**	$Ce(OAc)_3$	1000	1400	86
CAT**4**	$CeCl_3{\cdot}7H_2O$	1000	1300	89
CAT**5**	$CeCl_3{\cdot}7H_2O$–NaI	1100	1700	94
CAT**6**	$CeCl_3$–NaI	900	1300	91
CAT**7**	$CeCl_3{\cdot}7H_2O$–CuI	900	1200	93
CAT**8**	$CeCl_3{\cdot}7H_2O$-KI	900	1300	87
CAT**9**[c]	$CeCl_3{\cdot}7H_2O$–NaI/SiO_2	1200	1800	95
CAT**10**[c]	$CeCl_3{\cdot}7H_2O$–NaI/Al_2O_3	800	1100	90

[a] Molecular weight has been determined by GPC analysis (detector RI, refractive index).
[b] Percentage of monomer conversion has been established by GPC peak area analysis (Fig. S1†) [44].
[c] Solid Supported Catalyst (SSCs).

Table 2
Optimization of the reaction conditions (RC) of **3a**.

	CAT9 (wt%)	IPDI (eq.)	Temp. (°C)	Mn[a] (g/mol)	Mw[a] (g/mol)	Monomer Conv.[b] (%)	Residual -NCO[c] (%)
RC**1**	0.1	2.0	70	600	800	78	4.5
RC**2**	0.1	1.0	70	1000	1500	98	2.8
RC**3**	0.1	1.5	70	1200	1800	95	4.3
RC**4**	0.2	1.5	70	1000	1600	93	4.2
RC**5**	0.3	1.5	70	1200	1700	92	4.0
RC**6**	0.4	1.5	70	1100	1600	92	4.1
RC**7**	0.1	1.5	80	1100	1600	95	4.2
RC**8**	0.1	1.5	60	900	1400	96	4.0

[a] Molecular weight has been determined by GPC analysis (detector RI, refractive index).
[b] Percentage monomer conversion has been established by GPC peak area analysis.
[c] The residual –NCO was determined by tritation with DIN EN ISO 14896 following the reported method.

and the pre-polymers **3d** and **3f** were obtained with a molecular weight of 1000–1100 Da (Table 3).

Furthermore, for the synthesis of **3d** we developed a one-pot process that involves a first transformation of L-Lactic Acid (LLA) to **1b** OLLA with a M_W of 400 Da, followed by reaction with L-lysine diisocyanate (**2c**). For compound **3d** it is useful to specify the reaction progress with a free carboxylic group which can then react with HEMA, to form an ester functionality, in order to ensure the curing process (Scheme 3). However, all pre-polymers obtained were further involved in the reaction with 2-hydroxyethyl methacrylate (HEMA, **4**) in order to obtain urethane acrylate oligomers (UAO, **5a-f**) and the molecular weights achieved are comparable to those of compounds **3a-f** (Table 3). Finally, the photo-polymerization of **5a-f** in the presence of benzophenone (**6**) as photo-initiator and N-methyl diethanolamine (**7**) as co-initiator was performed. The final PUAs (**8a-f**) were chemically characterized, and the thermal properties were determined. To demonstrate the scalability of our protocol, we investigated the synthesis of **8a** on a 5 g scale. The molecular weights (M_w) achieved for compound **3a** and **5a** were 1900 Da and 2000 Da, respectively.

Chemical and thermal characterization of compounds 3, 5 and 8. The urethane pre-polymers, **3**, were characterized by FT-IR and NMR

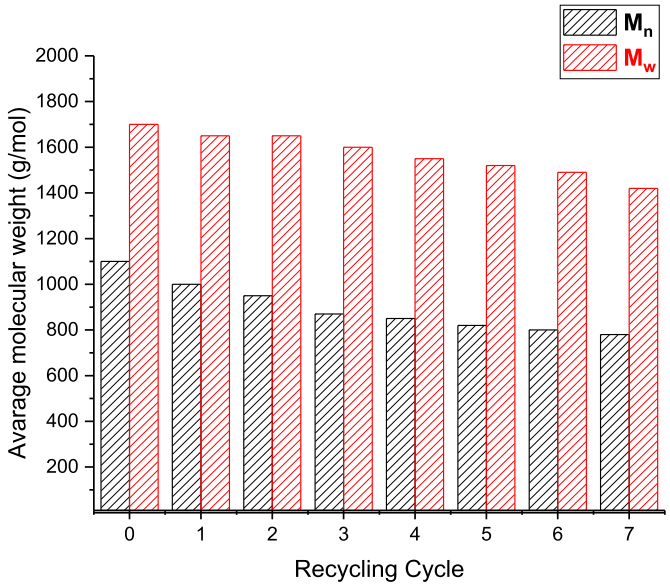


Fig. 1. Catalyst recyclability screening up to seven cycles.

analysis, to confirm their formation. The FT-IR spectrum (Fig. 4) shows that the peak relative to NCO stretching (2254 cm^{-1}) decreases while the peak at 1715 cm^{-1}, characteristic of the carbonyl group of the urethane bond increases, as the reaction proceeds. Furthermore, the broad peak at 3500 cm^{-1}, relative to the hydroxyl groups present in the polyol decreases and it is replaced by a narrow peak at 3200 cm^{-1} relative to the stretching of –NHR functionalities of the urethane group.

The ^{13}C NMR spectrum also confirms the formation of the pre-polymers. Basically, isophorone diisocyanate has a primary (Figure S3†, peak b) at 122.2 ppm and a secondary isocyanate group (Figure S3†, peak a) at 123.5 ppm. After the reaction with PEG 400, only the peak at 123.5 ppm disappears (Figure S4†, B), suggesting that under these reaction conditions, the secondary NCO group is more reactive than the primary one. In fact, the latter is shielded by the β-situated methyl substituents, the cyclohexane ring, and its neighboring methyl group, as reported by Hatada *et al.* [45] Therefore, the secondary NCO is

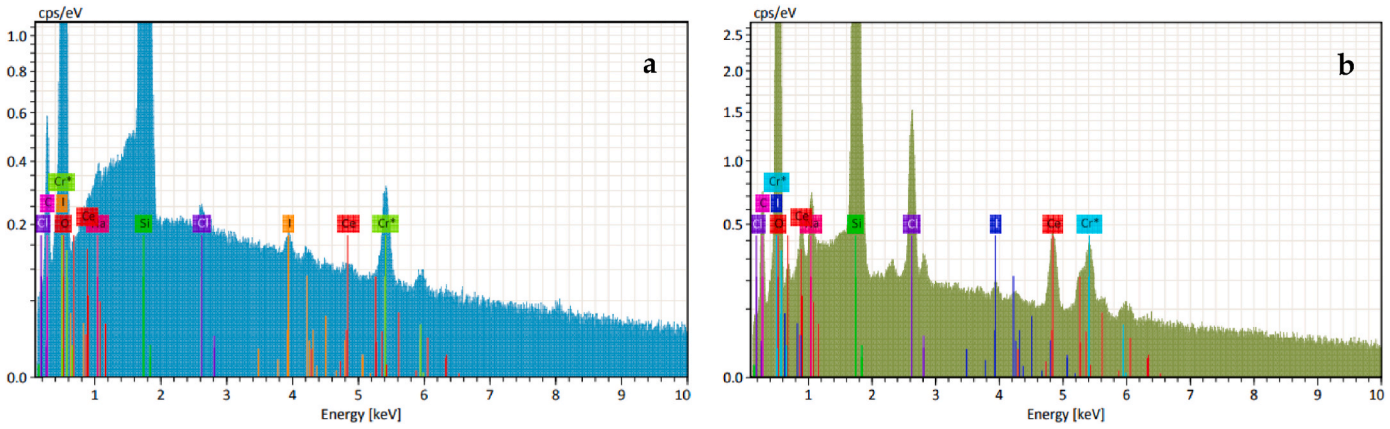


Fig. 2. SEM-EDX analysis of fresh catalyst (a) and recycled catalyst (b).

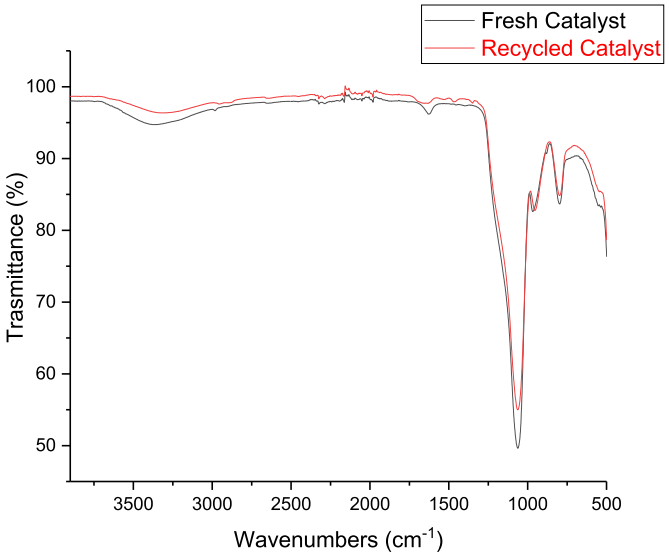


Fig. 3. FTIR spectra of fresh catalyst and recycled catalyst.

more available to react with the hydroxyl groups of polyols to form a urethane bond, confirmed by the signal at 155.56 ppm (Figure S4†, B). The formation of **5** was monitored by FT-IR analysis (Fig. 5). The disappearance of isocyanate peak at 2254 cm^{-1} after 4 h confirms the formation of urethane acrylate oligomer, due to the reaction between NCO groups with HEMA. The PUA formation was confirmed by FT-IR and was further characterized by TGA, DSC and SEM analysis. From the FT-IR spectrum (Figure S11†) the characteristic peaks of acrylate double bond (1634 cm^{-1} and 814 cm^{-1}) are not observed. This means that the carbon-carbon double bonds are involved in the formation of new chemical bonds by photo-polymerization.

TGA analysis of UV-cured films show two weight losses (Fig. 6) [5]. The first decomposition step occurs in the temperature range of 120 °C-350 °C and it is due to the thermal degradation of the hard segments, which involves the breakage of urethane linkage. The second stage, instead, is due to the degradation of soft segments. The latter has a higher thermal stability and begins to decompose in the temperature range of 350 °C-470 °C. On the other hand, the initial mass loss up to 120 °C was ascribed to moisture evaporation. The weight loss and T_{onset} (onset degradation temperature) in the two degradation steps remain unaffected when PUA was synthesized from renewable resources (Table 4).

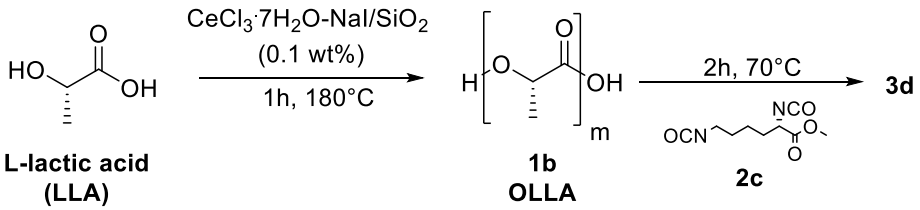
The glass transition temperature (Tg) of the cured samples **8a-f** (Table 4), were analyzed by DSC. DSC curves showed a characteristic thermal behaviour of poly(urethane-acrylates). In fact, only compound **8e**, exhibited a positive Tg of 68 °C, due to the cyclic structure of both starting materials, isosorbide and IPDI (DSC graphs, Figures S22-27†).

SEM images (Fig. 7) show that the surface of bio-based and fossil-based poly(urethane-acrylates) is smooth and homogeneous in which no crack or phase separation are observed, confirming the goodness of polymerization process.

Table 3
Synthesis of compounds **8a-f**.

Compound 1	Compound 2	Compound 3	Mn[a] (g/mol)	Mw[a] (g/mol)	Compound **5**	Mn[a] (g/mol)	Mw[a] (g/mol)	Compound 8
1a[b]	**2a**	**3a**	1200	1800	**5a**	1400	1900	**8a**
	2b	**3b**	2000	3400	**5b**	2100	3600	**8b**
1b	**2a**	**3c**	900	1300	**5c**	1000	1400	**8c**
	2c	**3d**	600	1000	**5d**	800	1100	**8d**
1c	**2a**	**3e**	800	1300	**5e**	1100	1500	**8e**
	2c	**3f**	700	1100	**5f**	900	1100	**8f**

[a] Molecular weight has been determined by GPC analysis (detector RI, refractive index).
[b] Reaction performed also on a 5 g scale with comparable results.



Scheme 3. One-pot synthesis of **3d**.

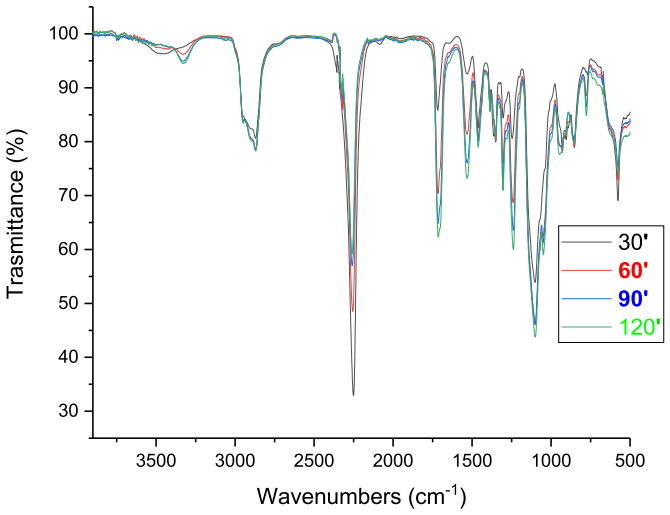


Fig. 4. FTIR spectra of **3a** at different reaction times (30′, 60′, 90′ and 120′).

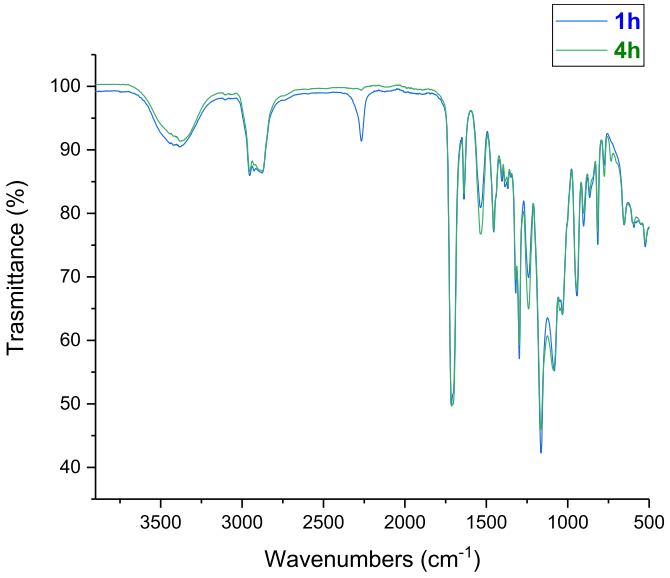


Fig. 5. FTIR spectra of **5a** (at 60′ and 240′).

4. Conclusions

We disclosed an efficient and low impact procedure for the synthesis of fully bio-based poly(urethane-acrylate) promoted by $CeCl_3{\cdot}7H_2O$–NaI supported on SiO_2. This catalytic system can be recycled for seven times without a decrease in activity, obtaining a pre-polymer with a molecular weight of 1800 Da. Furthermore, we demonstrated the scalability of our approach, preserving the M_w and monomer conversion. PUA formation was confirmed by the chemical characterization and the final thermal properties were determined. DSC, TGA and SEM analysis proved that

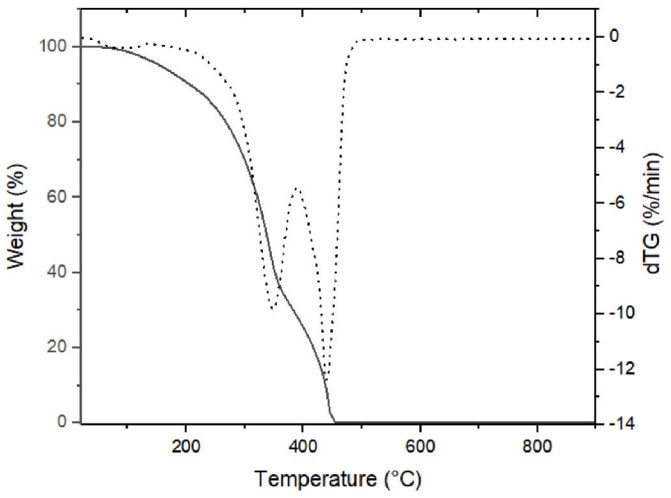


Fig. 6. TGA thermograms of **8a**, as example (TGA graphs, Figures S28-33†).

Table 4
Thermal properties of compounds **8a-f**.

Specimen	TGA Analysis		DSC Analysis
	T_{on}I °C (Weight loss %)[a]	T_{on}II °C (Weight loss %)[a]	T_g (°C)[b]
8a	310 (48)	431 (46)	−1
8b	315 (47)	432 (47)	−28
8c	298 (49)	430 (45)	−4
8d	310 (49)	430 (45)	−30
8e	297 (50)	433 (44)	68
8f	300 (48)	428 (46)	−42

[a] Determined by TGA analysis.
[b] Determined by DSC analysis.

bio- and fossil-based PUAs have similar chemical characteristics and behaviour. In this work, the use of a sustainable and recyclable catalyst together with aliphatic diisocyanates and polyols coming from renewable resources contribute to reduce greenhouse gas emissions, health issues and avoid the depletion of limited resources. Furthermore, we replaced the most used Tin based catalysts, which present a very well know toxicity, also recognized by the European Union (EU) [46] with a very no-toxic catalyst based on Cerium(III) salts, synthesizing this new fully bio derived polymer with a very promising future for biomedical applications and drug delivery systems.

Credit author statement

Genny Pastore: Investigation, Validation, Writing – original draft.; **Serena Gabrielli**: Supervision, Conceptualization, Methodology, Writing – original draft.; **Roberto Giacomantonio**: Investigation, Validation.; **Gabriele Lupidi**: Investigation, review & editing.; **Sabrina Capodaglio**: Investigation, Validation.; **Francesca Stella**: Investigation, Validation.; **Ezio Leone**: Investigation.; **Tommaso Compagniucci**: Investigation.; **Enrico Marcantoni**: Supervision, Conceptualization, Writing – original draft.

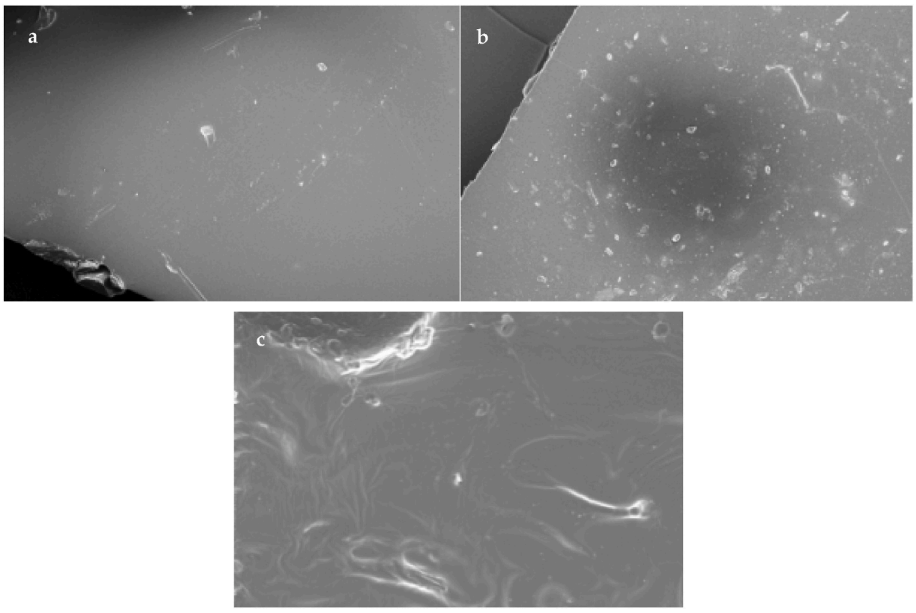


Fig. 7. SEM images of compounds: a) **8a**, b) **8c** and c) **8d**.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

The work was carried out under the framework of the University Research Project 'FAR2018: Fondo di Ateneo per la Ricerca' supported by the University of Camerino, Italy. The authors are thankful to Marche Applied Research Laboratory for Innovative Composites (MARLIC) of Marche Region for the post-doc fellowship to G. P., and thanks to iGuzzini Recanati and Elantas Europe Ascoli Piceno and Delta-Plados Plants for grating doctoral fellowships to R. G., T. C.and E. L., respectively.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.rinma.2022.100294.

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