Foam-to-Elastomer Recycling of Polyurethane Materials through Incorporation of Dynamic Covalent TAD-Indole Linkages

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ABSTRACT Polyurethane (PU) foams are a large volume commodity product and as such pose a considerable recycling challenge for the polymer manufacturing industry. The incorporation of dynamic covalent bonds within a PU network chemistry is a possible strategy to improve the sustainable development of PU foams. Herein, we report the outcome of a research program aimed at the incorporation of thermoreversible triazolinedione (TAD)-indole linkages within an industrial standard PU foam formulation. A scalable synthesis of the required TAD-indole building blocks was developed, aiming at maximizing their physicochemical compatibility with standard polyol and isocyanate PU foam ingredients. A pilot scale synthesis of a TAD-based cross-linker was developed, affording more than 50 kg of an IPDI-derived bis-urazole building block. Propoxylation of the indole fragments proved to be a key technology enabling the kilogram scale production of TAD-indole based polyols. The innovative dynamic covalent polyols were successfully used to produce a range of flexible PU foams and elastomers in a solvent-free foam formulation. Owing to the thermoreversible nature of the TAD-indole linkers, the PU foams could be processed into PU elastomers through thermal compression molding, which could be further recycled up to seven times in the same manner. We studied the effect of network compositions on the foaming process and on the recycling efficiency. The thermal and mechanical properties of the materials have been studied with thermal analysis, tensile measurements, and rheology. This work demonstrates that TAD-indole chemistry is a viable strategy to improve polyurethane recycling, but also points out some critical aspects and obstacles related to the design of such dynamic covalent PU foams.

INTRODUCTION

Polyurethanes (PUs) are an important polymer class due to their high versatility and their large added value to modern economy. Polyurethanes can be found in many bulk applications as solid thermosets and elastic materials, but 67% of PU materials can be found in foam materials with an open cellular structure.[1] Most PU foams are thermosets and are further categorized into flexible and rigid foams.[1] The production of thermosetting PU foams is a refined and complicated process, as the open cell structure is formed at the same time as the covalent cross-links throughout the bulk of the material. Polyurethane foams are by necessity cured and structured at the same time in an intricate chemical process, the parameters of which have to be closely controlled. Once the PU network is formed, the foam derives a high dimensional stability and resistance to deformation as a result of its covalently cross-linked structure. This gives PU foams a long useful lifetime as matrasses, or as comfort foams in furniture or automotive applications (for flexible foams), or in insulation panels or packaging (for rigid foams). The characteristics that endear PU foams to their users (durability and dimensional stability) also present a considerable sustainability problem for end-of-life PU foams (matrasses, upholstery furniture, automotive and transport sector), as well as for the production of waste PU foam (trimmings). PU foams are indeed a quite problematic material waste stream. Within the EU, they make up a significant fraction of annual industrial and municipal waste volumes, adding up to almost 1 million tons in 2016.[2,3]

Within the context of the recycling of thermoset polymers, a couple of strategies are usually considered. Mechanical recycling of PU foams involves foam shredding and addition of binders, followed by thermal compression in order to reprocess PU foams into repurposed objects, often of inferior quality, such as mats.[4,5] On the other hand, chemical recycling involves a full chemolysis back to monomers, which is thermodynamically quite unfavourable (and thus energy intensive), but this can in theory be used to produce new PU products of any quality, thus avoiding the downgrading issue.[5,6] Simple ‘caloric’ recycling involves the incineration of PU foams, and is obviously a non-sustainable long-term strategy. In order to avoid land fill waste, a fourth option is at least in theory also possible, i.e., PU foams could be recycled by thermal reprocessing into high (or equal) quality PU products. This is in fact the currently most widely applied recycling strategy in the plastics industry (e.g., the repelleting of PET) but is usually considered unfeasible for thermosetting materials.[4]

Conversely, mechanical recycling has been considered as an interesting option since solvents or any chemical reagents are absent in the process. Although the industrially employed techniques for mechanical recycling typically result in downcycling, rather than recycling or upcycling, the thermo-mechanical reprocessing is seen to be a circular solution when dynamic covalent bonds are considered. Thus, thermo-mechanical recycling and thus reprocessing is accepted as a potential for the direct reuse of PU foam waste products.[7–10]

By the incorporation of dynamic covalent cross-links within a thermoset network, the chemical composition of the polymer network is less prohibitive towards thermal reprocessing and reshaping, while the durable structural characteristics of the material can be retained. The resulting materials are referred to as covalent adaptable networks (CANs), or as dynamic covalent polymers, and promise to bridge the gap between thermosets and thermoplastics.[11,12]

In the last decade, many suitable chemistries have been identified in academic research for a wide variety of polymer networks.[13–15] For PU materials,[16–27] and especially for PU foams,[8,28–36] the number of examples has been limited.

Interestingly, polyurethane (PU) materials are noted to exhibit dynamic behavior within their own structural network. Already around 70 years ago, Offenbach and Tobolsky reported a stress-relaxation character under specific temperature and pressure.[37,38] Besides incorporation of intrinsically reactive dynamic groups[16,21,33,39] numerous attempts to increase the internal dynamicity of PU-elastomers are reported.[20,23,40–42] Another chemorheological study[43,44] towards

PU materials containing free hydroxyl groups (polyhydroxyurethanes) contributed to the idea of recyclable PU materials. For example, Dicthel and Fortman studied a reprocessable PU-like material without the aid of an external chemical entry.[45,46] Since the materials were obtained starting from cyclic carbonates, the pioneering work contributed to non-isocyanate polyurethane (NIPU) foam literature.[30,32,35,47–50]

On the other hand, controlling the inherent dynamic behavior of urethane linkages represents a more direct and practical approach for large-scale recycling of these materials. In this context, the incorporation of Lewis acids to catalyze the exchange of urethane bonds into PU thermosets, resulting in rapid stress-relaxation and a dynamic covalent network, was studied.[20,41,42,46] Likewise, for PU-foams, Sheppard et al. developed a methodology, based on a technique referred to as "vitrimerization"[41], in which foams are treated with a solution of a tin-based catalyst (DBTDL) and reprocessed with twin-screw extrusion.[28,51] PU foam-to-foam recycling presents additional challenges that complicate the recycling process.[2,3,5,7,33,52,53] In this regard, Dichtel and coworkers recently reported the first conceptual demonstration of such a methodology on reprocessing PU foam-to-foam *via* extrusion after infusion of a blowing agent and a catalyst that promotes carbamate exchange.[34]

In this work, we report the outcome of an industrial development program aimed at developing flexible polyurethane foam formulations that can incorporate thermoreversible TAD-indole cross-links. The dynamic bond formation between TAD and indole moieties was previously identified as a promising dynamic covalent chemistry platform in polymer chemistry,[25,54–58] and has also been applied in thermosetting PU elastomers, showing improved elastomer-to-elastomer recycling by simple thermal compression molding. (Figure **1**)

In order to translate the technology to a PU foam context, the hurdle was to identify PU comonomers that (i) incorporate dynamic TAD-indole cross-links, (ii) are chemically and physically compatible with existing PU foam formulations, and (iii) are expected to offer versatility in order to produce PU foams with a wide range of properties. These latter two requirements proved quite challenging for the existing TAD-indole building blocks, which were largely solids and highly insoluble in typical PU foam ingredients.

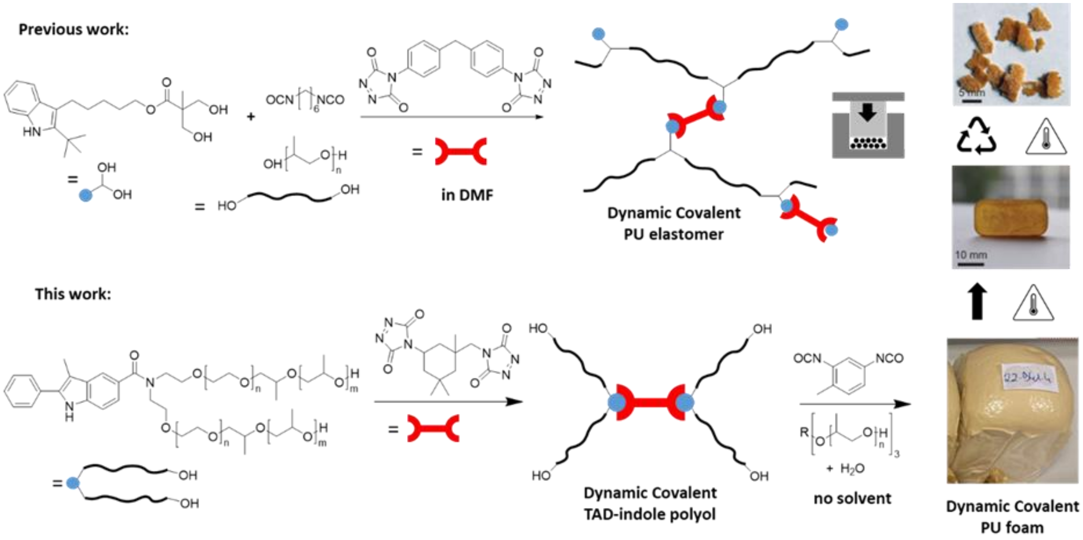


Figure 1. Graphical summary and outline. Previous work: TAD-indole based dynamic covalent chemistry within PU elastomer context, wherein linear indole-functional polyurethane chains are cross-linked with a bis-TAD cross-linker. This work: a practical strategy to incorporate the TAD-indole chemistry platform in PU foam formulations by design of a polyether-backbone polyol with an incorporated dynamic covalent TAD-indole moiety.

As the use of solvent is not a sustainable option to produce large volumes of PU foams, several generations of innovative TAD-indole based polyols were synthesized and assayed in foam formulation trials. A key technology proved to be propoxylation of the indole building blocks. This process gave access to dynamic covalent building blocks having the same range of molecular weight and functionality as typical polyols used in industrial PU formulations. We also developed a pilot scale synthesis (50 kg) of a bis-TAD cross-linker, establishing the industrial viability of the TAD-technology. With these 'foam compatible' TAD-indole comonomers in hand, several PU foams have been prepared and the effect of the incorporation of the dynamic crosslinks has been assayed.

EXPERIMENTAL SECTION

Full experimental details, data and procedures can be found in the supporting information.

Synthesis of indole polyol building blocks. Tailorable indole polyols with varying chain lengths and monomer composition were synthesized *via* an amide coupling between an indole carboxylic acid and a bis-propoxylated secondary amine.

Preparation and scale-up of secondary amine functional polyols. The starting materials for secondary amine-functional polyols were prepared through propoxylation or ethoxylation starting from benzylamine as a bifunctional nucleophile. Afterwards, a free secondary amine was obtained when these polyols were debenzylated through hydrogenation with Pd/C and H_2(g) on large/semi-industrial scale (Figure **2**).

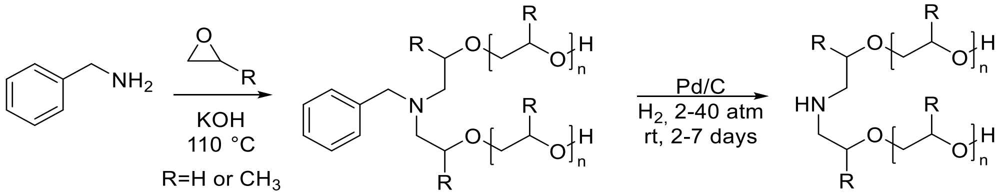


Figure 2. Generic scheme for secondary amine-functional polyol synthesis starting from benzylamine.

The propoxylation of benzylamine to a polyether diol with an OH-number of 246.8 mg KOH/g is described in detail in the supplementary information. Briefly, in a 2 L reactor, 353 g (3.29 mol, 1.0 eq.) benzylamine is reacted with 1146.8 g (19.75 mol, 6.0 eq.) propylene oxide in the presence of potassium hydroxide as catalyst at 110 °C under inert atmosphere, yielding the desired polyol **2** (Figure S-1). For polyol 4 and 4L the alkoxylation process was started with a small amount of ethylene oxide, before the polymerization was continued by adding propylene oxide. In the course of scale-up, polyol 4L was delivered in a larger quantity (Table S-1).

Although both batches are separately mentioned, both of them (polyol 4 and 4L) are considered as interchangeable polyols due to close properties. In Table S-1, OH-number (measured *via* titration), the corresponding average molecular weight (calculated), the estimated average number of repeating units of ethylene oxide (EO) and propylene oxide (PO) in each chain (Figure **3**), and the total obtained amount of material are shown.

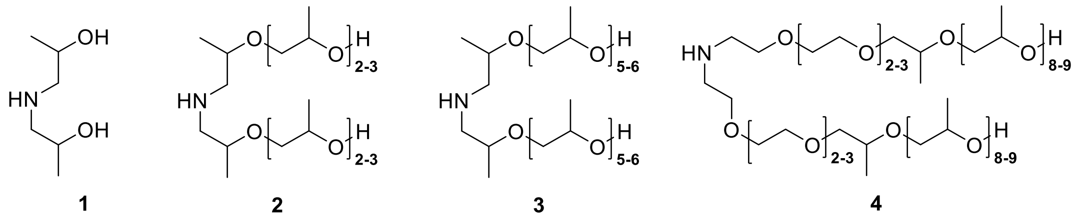


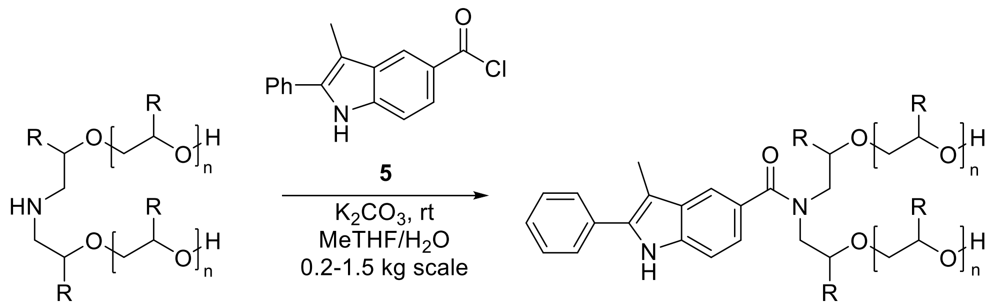
Figure 3. Structural representation of diisopropanolamine (1) and benzylamine-derived hydrogenolyzed polyols (2-4).

In a stainless-steel pressure reactor, 50 g of polyol 2 was transferred with 5% (w/w) of Pd/C (10%) without any solvent. The reaction mixture was stirred 48 h at room temperature under 40-45 atm hydrogen atmosphere. The progress of the reaction was monitored by TLC analysis. Upon completion of the hydrogenolysis of the benzyl group, the reaction mixture was diluted with 100 mL of isopropanol, and then filtered over a pad of celite to remove the Pd/C catalyst. Solvent evaporation in vacuo afforded the desired product (amine polyol **2**) as a colorless liquid in quantitative yield (Figure S-2). Polyol 3 could be hydrogenolyzed using the same procedure as for polyol 2.

The hydrogenolysis of polyol 4 was performed in a large stainless-steel pressure reactor (150-200 g per batch). The reaction was observed to be completed in 72 h at room temperature at 40-45 atm of hydrogen pressure. The work-up was most efficient by diluting the reaction mixture with distilled water (3:1 v/v). Filtration over laboratory filter paper was an effective way to remove the palladium on carbon catalyst. Then, the obtained aqueous solution was saturated with sodium chloride and amine polyol **4** was isolated *via* back-extraction with 2-methyltetrahydrofuran as a slightly yellow liquid (Figure S-4). This reaction was repeated 3-4 times with a consistent yield. After combining the material, an overall yield of 60% was obtained. Attempts at filtration of the amine polyol **4** over celite were ineffective, as this gave catalyst leaching.

For the polyol 4L, a specialized equipment (Parr Shaker Hydrogenation Apparatus) was used to process 800 g of the polyol in one batch (see supporting information).

Synthesis and coupling of the indole carboxylic acid to the bis-polyol amine



1-4 (R = CH_3 or H)
2 (n = 2-3, R = CH_3): complete reaction
3 (n = 5-6, R = CH_3): slow but complete reaction
3' (n = 17, R = CH_3): no reaction
4 (R = H: n = 2-3; R = CH_3: n = 8-9): complete reaction

6.1-6.4 (n= 1 to ~13)
6.2 (>95%)
6.3 (>95%)
6.4 (>95%)

Figure 4. Generic synthetic scheme of the indole-functionalized polyols *via* coupling of indole carboxylic chloride to either diisopropanol amine or one of the propoxylated amine chains.

Synthesis of the indole acid chloride 5. Propiophenone and 4-hydrazinobenzoic acid were mixed in equimolar ratios in glacial acetic acid (10 mL per gram of propiophenone) with 1.0 molar equivalent of sulfuric acid. The resulting mixture was stirred and heated to reflux (120-125 °C) for 1-2 h. Next, the reaction mixture was concentrated *via* distillation of acetic acid, and the product was precipitated from the mixture by addition of water and collected *via* filtration. This afforded the expected indole carboxylic acid in 79% isolated yield and 99.9% purity (Figure S-5). The indole carboxylic acid from the previous step was then dissolved in toluene (for 19 g starting material 120 mL of toluene) in a 250 mL round bottom flask and treated with 1.1 molar equivalents of thionyl chloride. Afterwards, the mixture was heated for a maximum of 3 h at 70 °C until a dark green mixture was obtained. Heating for longer times results in a dark purple mixture indicating anhydride formation visualized on TLC (8:2 pentane/EtOAc) and LCMS analysis. After 3 h of stirring the mixture was cooled to room temperature and the excess of thionyl chloride was removed under a small vacuum (30 min in a 40 °C water bath briefly stirred at vacuum). The obtained acid chloride **5** was used in the next step (Figure **4**) without further purification.

Amide coupling of indole acid chloride and 1. The crude acid chloride **5** obtained above was not isolated, but directly used in the next step (Figure **7**). First, 1.0 molar equivalent of diisopropanol amine (**1**) was dissolved in 2-methyltetrahydrofuran (100 mL per 5 g). Subsequently, 100 mL of a saturated aqueous solution of potassium carbonate was added to the same reaction flask and vigorously stirred at room temperature to achieve the typical Schotten-Baumann conditions. Finally, a solution of the acid chloride in toluene (as obtained in step 2) was added slowly in a dropwise fashion to this biphasic mixture and the resulting mixture was stirred for 3 h at room temperature. The organic layer was collected, and the solvent was removed in vacuo and overnight in a vacuum oven at 40 °C and indole diol **6.1** was obtained as a brown amorphous solid (Figure S-6), as a mixture of mono and double addition in a 99:1 ratio based on a LCMS analysis.

Amide coupling of indole acid chloride and 2-4. The indole polyol **6.2** (avg. molecular weight=595 g/mol) was synthesized from amine polyol **2** using the previously optimized Schotten-Baumann conditions. In a 1 L round bottom flask, 1.0 molar equivalent of amine polyol **2** (avg. molecular weight=365 g/mol) was dissolved in 2-methyltetrahydrofuran (200 mL per 10 g of amine polyol). Then, a saturated solution of potassium carbonate was added to generate a biphasic system. The saturation of the solution was needed, as it prevents the solubility of the amide in the water phase. The resulting mixture was vigorously stirred at room temperature, and the mixture of the indole acid chloride **5** in toluene (1.0 molar equivalent, as obtained in previous step) was slowly added (dropwise) to the biphasic system. After complete addition of the acid chloride solution, the biphasic reaction mixture was stirred overnight at room temperature to ensure complete consumption of the acid chloride. Afterwards, the organic layer was separated, and the solvent was removed under reduced pressure. The remaining solvent was removed in a vacuum oven at 40 °C. In the end, the indole polyol **6.2** was obtained (50 g, starting from 31 g of amine polyol **2**) as a brown/orange viscous liquid as confirmed *via* NMR and LCMS analysis (Figure S-8 and S-9). The same procedure was repeated with amine polyols **3** and **4**, affording indole polyols **6.3** and **6.4**, respectively. The indole polyol **6.4** (Figure S-13) was scaled up to afford 588 gram (from polyol **4**) and 1500 gram (from polyol **4L**), which were sufficient volumes to conduct foaming trials.

Synthesis of IPDI-derived bis-urazole cross-linker precursor

Semicarbazide synthesis from IPDI. A total of 2.0 molar equivalents of ethyl carbazate was first dissolved in 2-methyltetrahydrofuran (~250 mL for 50 g of ethyl carbazate) and then stirred under an inert atmosphere at room temperature and 1.0 molar equivalent of isophorone diisocyanate (i.e., IPDI) was added to the stirring mixture in a dropwise fashion. Following the complete addition, the resulting mixture was stirred for 2 h at room temperature and afterwards heated to 60 °C for 1 h, during which the reaction progress was monitored by GC analysis. At completion (after 1 h at 60 °C), the solvent was evaporated under reduced pressure and substituted by methanol to obtain the corresponding semicarbazide as a methanolic solution that was used in the next step without any further purification.

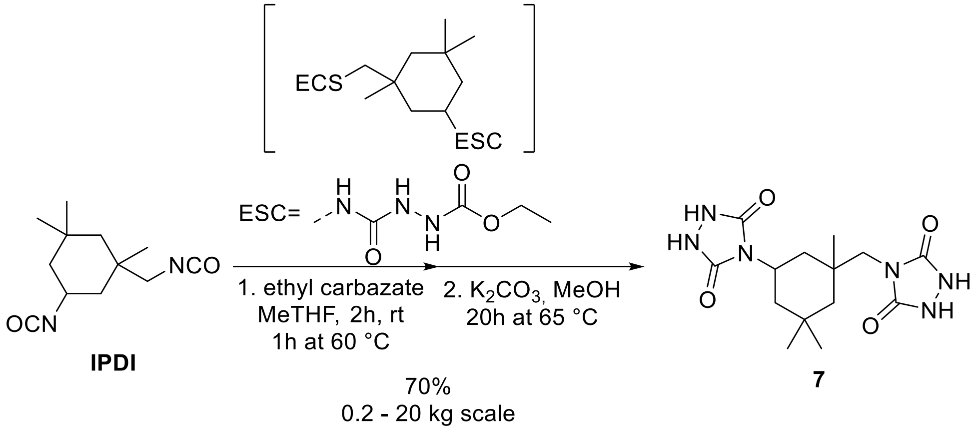


Figure 5. Synthesis of the bis-urazole starting from isophorone diisocyanate *via* bis-ethylsemicarbazide (ESC) intermediate.

Synthesis of the IPDI-derived bis-urazole 7. To a total of 1.0 molar equivalent of the semicarbazide obtained above (assuming 100% theoretical yield) as methanolic solution (~400 mL per 100 g semicarbazide), 4.7 molar equivalents of anhydrous potassium carbonate was added. The resulting mixture was stirred and heated to reflux for 20 h. After this heating period, the obtained reaction mixture was filtered warm at 50 °C, and the filter cake was washed twice with methanol. The resulting filtrate was then cooled to room temperature before being acidified to pH=7 by addition of hydrochloric acid (37%), followed by filtration of the precipitated potassium chloride salts and evaporation of solvent in vacuo under solvent exchange with water. The precipitated urazole was filtered and washed with water, followed by drying under reduced pressure overnight yielding the desired urazole in 70% accumulated yield as a mixture of cis and trans isomers (80:20 ratio), reflecting the isomeric ratio of the original IPDI starting material. A single crystallization from water-methanol yielded an isomerically pure IPDI-bis-urazole in 68% yield (100:0 diastereomer ratio).

This synthesis (Figure **5**) was repeated twice at pilot scale (20 kg of ethyl carbazate + 20 kg IPDI), each affording 25-30 kg of the bis-urazole **7**, which was isolated in different batches of different isomeric purity.

Oxidation and coupling of IPDI-derived bis-TAD cross-linker with indole polyols

The syntheses of dynamic covalent TAD-indole tetraol **9.1** and TAD-indole polyols **9.2-9.4** were completed through oxidation of the bis-urazole **7** into the bis-TAD cross-linker **8.** The IPDI-bis-TAD (**8**) is hydrolytically not stable and has limited shelf life at room temperature in unpurified (crude) form. Thus, oxidation starting from the IPDI-bis-urazole (**7**) is best performed just prior to or in tandem with the coupling to indoles.

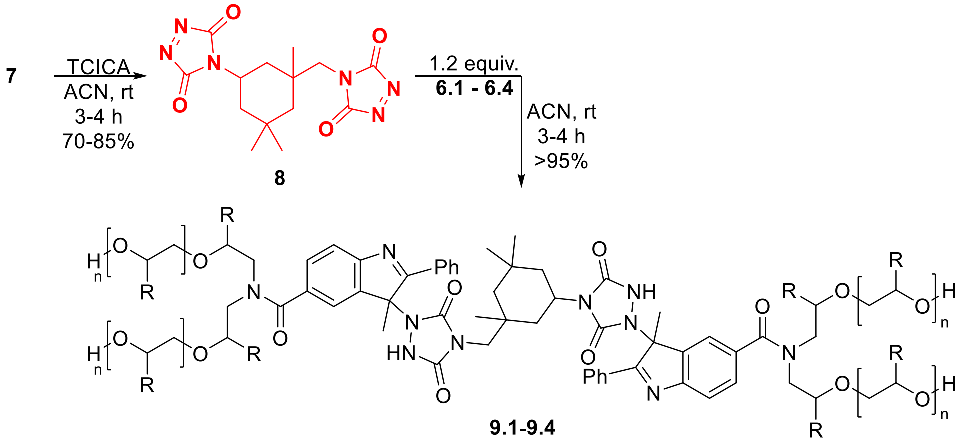


Figure 6. Oxidation of bis-urazole **7** and subsequent TAD-indole cross-linking with the indole diols.

Oxidation of bis-urazole 7 to bis-TAD cross-linker 8. In a round bottom flask, 1.0 molar equivalent of IPDI-bis-urazole and 0.66 molar equivalent of trichloroisocyanuric acid were mixed with acetonitrile (10 ml per 1 g of reactant) at room temperature with vigorous stirring. As the oxidant started dissolving in the solvent, the distinct red color of IPDI-bis-TAD appears. The reaction mixture remains a suspension throughout the duration of the oxidation. The insoluble urazole is transformed into soluble bis-TAD, but the oxidant and especially its reduced form remain highly insoluble. The reaction mixture was vigorously stirred 3-4 h at room temperature. The resulting red and heterogeneous solution was filtered over a fritted glass funnel and washed with minimal amount of acetonitrile until no more red color could be observed in the filter cake. Then, solvent was removed under vacuum and the residue was dried overnight at room temperature with the help of a vacuum pump while the flask was covered with aluminium foil and kept from ambient light. The IPDI-bis-TAD was then collected as a bright red solid with 70-80% yield depending on the scale of operation. As hydrochloric acid is a by-product of oxidation, care needs to be taken when removing the volatiles from the filtrate.

TAD-indole coupling of indole diol 6.1 and indole polyols 6.2-6.4 with cross-linker 8. In a round bottom flask, 2.4 (2 x 1.2) molar equivalent of the indole diol **6.1** was dissolved and diluted with acetonitrile while IPDI-bis-TAD was redissolved with a similar volume of solvent. When the solutions were combined in reaction flask with a vigorous stirring, the progress was followed with disappearance of the red color from IPDI-bis-TAD. When the red color was not recognizable anymore, the solvent was removed under vacuum, and it was further dried under at 50-60 °C for multiple nights in a vacuum oven. The desired product **9.1-9.4** was either collected as a brown solid or liquid with a quantitative yield (Figure S-7, S-10, S-12, S-14 and S-15). The tetraol **9.1** and polyol **9.2** were both solids. The polyol **9.3** was a highly viscous liquid, and the polyol **9.4** was free running liquid (Figure **8**), comparable to (and fully miscible with) normal PU foam polyol ingredients.

Preparation of dynamic covalent polyurethane foams from 9.1-9.4

Foaming trials were not performed for **9.1**, as this was a highly insoluble solid. Polyol **9.2** was also a solid product and polyol **9.3** was the first non-solid TAD-indole based polyol. In terms of adaptation, solubilization in complementary polyols (PPG 725, 1000 and 2000) was considered. Polyols **9.2** and **9.3** were not readily soluble in PPG2000 or PEG725, so could be formulated into foams in that form, albeit with limited success. Good foaming was achieved with the longer chain polyol **9.4**, which was fully liquid and fully miscible with all foam ingredients to which it could be admixed in any desired ratio (Figure **8**). The shorter chain polyols **9.2** and **9.3** were either not miscible with the other foam ingredients, gave collapsing foams or resulted in much too rigid foams (Figure S-21) when used in higher amounts (*vide infra*).

Dissolution of the dynamic covalent polyols in PPG 725. The polyol **9.2** (containing free of indole polyol **6.2**), were added to PEG725 (58.3 wt% of the final mixture). This mixture was then put under magnetic stirring on a heating plate at 60-70 °C. After 2 h of stirring, everything was dissolved, affording a viscous and stable blend at room temperature which could be directly used together with other components for foaming trials. Polyol **9.3** was not considered for any foaming practice in favor of polyol **9.4**. For polyol **9.4**, this pretreatment was not required, direct inclusion to foaming formulations were achieved.

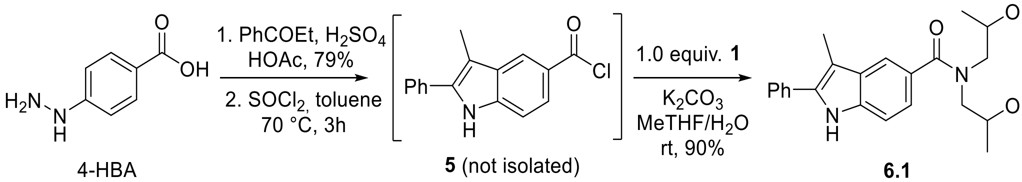
Preparation of polyurethane foams. The hydroxyl numbers (IOH) of the dynamic covalent polyols **9.2-9.4** were theoretically calculated starting from the IOH of starting polyols. This value was used to calculate the required amount of isocyanate needed in the formulation for a specific NCO index. All raw materials were used at room temperature (around 20 °C). Polyols, additives, catalysts, TAD-indole polyols (**9.2** in PPG 725 and **9.4**) and water were combined and mixed for 30 sec at 3000 rpm. Isocyanate(s) were then added, and the complete formulation was mixed for 10 more seconds at 3000 rpm. The complete reaction mixture was then poured into a mold where it was allowed to cure in about 2-3 min (reaction to full rise). The density, air permeability and reprocessing behavior of the produced foams was determined.

Thermal processing of dynamic covalent PU foams into dynamic covalent PU elastomers. Thermal reprocessability of the dynamic covalent PU foams was demonstrated by turning the foam into PU elastomers *via* compression molding. First, pieces of foam based on polyol **9.2** (prepared in PPG 725) were properly transferred into the mold (Figure S-45, left) and subjected to hot pressing. The temperature of the compression machine was set at 130 °C, and the compression pressure was increased to a constant pressure of 4 metric tons. After being hot-pressed for 30 min under constant pressure, the mold with the specimen was transferred to a cold plate and left to reach room temperature prior to opening and further testing of the reprocessed material. Secondly, the PU foams based on polyol **9.4** were prepared and reprocessed in Recticel Engineered Foams with a hot compression machine (Figure S-45, right). The temperature of the compression machine was set at 130 °C and the foam samples were reprocessed under 100 bar pressure for 10 min.

RESULTS AND DISCUSSION

Development and synthesis of covalent dynamic TAD-indole polyols

Polyurethane foams are typically prepared by cross-linking a polyol component (mostly a trifunctional macromonomer) with an excess of isocyanates and some water, which acts as a blowing agent (in situ generation of CO_2 reaction with isocyanates). By adding covalent dynamic polyols into such formulations, a number of dynamic cross-links can be installed in the polymer network (Figure **1**). In order to achieve this, suitable indole-functionalized comonomers are required, such as indole polyols, which can be dynamically cross-linked by bis-TAD reagents.



4-HBA

5 (not isolated)

6.1

Figure 7. Generic synthesis scheme of the indole-functional diol and synthetic basis for indole-functional polyols.

The previously established syntheses of indole diol PU monomers required four synthetic operations.[25,54] As a first improvement, we designed a three-step synthesis in which only one intermediate separation was required (Figure 7). Commercially available 4-hydrazinobenzoic acid (4-HBA) was reacted with propiophenone in a classical Fischer indole synthesis. The resulting indole carboxylic acid was isolated in very pure form *via* precipitation and then transformed into its corresponding acid chloride **5** by treatment with thionyl chloride. Partial distillation of the reaction mixture removed volatiles, and then allowed direct coupling with commercially available amine diol **1** under classical biphasic Schotten-Bauman conditions, without isolation of the intermediate acid chloride. Amine diol **1** was chosen for the introduction of secondary alcohols onto the reactive indole moiety, as this is the same terminal functionality for most industrially applied polyols in PU synthesis. We expected that it should be incorporated at the same rate as standard polyol monomers. The resulting amide **6.1** was obtained in high yield and high purity from the organic layer after evaporation of solvents. This afforded a very scalable procedure that could easily be conducted on a 100-200 gram scale using standard laboratory equipment, using robust industrially scalable procedures.

In order to arrive at a suitable dynamic covalent TAD-indole polyol, cross-linking of the indole diol **6.1** with a bis-TAD reagent should afford a dynamic tetraol **9.1**. Bis-TAD cross-linkers can be prepared from any commercially available bis-isocyanate in three synthetic operations.[54–56] We selected isophorone diisocyanate (IPDI) as a starting material (Figure **5**). The synthetic transformation into a bis-TAD reagent has been reported before on small laboratory scale, and it is a relatively bench stable, solid and easily isolated bis-TAD reagent. Moreover, it was preferred in this project because aliphatic TAD reagents have a reversibility profile with an onset of dynamic covalent exchange at ~100 °C, while the more common aromatic TADs (derived from aromatic bis-isocyanates) already show a dynamic character at ~70 °C.[57,58] For longer term applications in structurally stable foams, the 70 °C threshold may be too low.

Although the synthesis of IPDI-based bis-TAD cross-linker **8** was already established on small scale,[55] the synthesis was adapted to enable large scale synthesis (Figures **5** and **6**). Urazoles are classically elaborated from isocyanates in two steps: addition of ethyl carbazate, and cyclization to urazole with expulsion of ethanol. The process development started from switching solvents from toluene to industrially friendly green solvent; 2-methyl-tetrahydrofuran in the first coupling step. The cyclization step was not performed in water as is most common, but in the industrially more handleable (lower boiling) solvent methanol. These improvements allowed a straightforward synthesis, easily performed in the lab on 200 gram batches. Moreover, using these improved conditions, a pilot scale synthesis was initiated to demonstrate the industrial viability of this interesting cross-linker, affording over 50 kg of the bis-TAD precursor **7** from two batches.

The final synthesis step towards the IPDI-bis-TAD cross-linker requires an oxidation of IPDI-bis-urazole. Initial trials in aqueous nitric acid provided the bis-TAD easily, as this spontaneously precipitated and could be filtered off. While no incidents occurred during these studies, safety studies conducted on the reaction mass showed a dangerous reaction profile prohibiting its scaling up. Also, the purity and shelf life of the obtained product was not fully reproducible. A safer alternative was found in the use of the much milder oxidant trichloroisocyanuric acid (TCICA),[59,60] which gave a scalable reaction mass. Interestingly, the isolated bis-TAD was of high purity and could be stored without problems for a few days at room temperature, whereas generic TAD reagents often have to be used directly after their synthesis.[56] Longer term stability studies were not conducted.

With a safe and scalable procedure in hand for both the bis-TAD and indole diol compounds, we next coupled the isolated cross-linker **8** with indole diol **6.1**. This is a click reaction[54,56–58] and proceeds simply by mixing the two compounds at room temperature in a suitable solvent. In this case, we elected acetonitrile. By varying the stoichiometry of **1** and **8**, the average polyol functionality can be varied between 2.0 (100% diol) to 4.0 (100% tetraol). We avoided stoichiometric ratios as common polyol functionality in PU foam industry is around 3.0. Moreover, an excess of free indoles is always required in a dynamic polymer network to ensure swift bond exchanges in the covalent adaptable polymer networks. Previous studied showed that a molar excess of about 20% of the indole reagents with respect to the TAD moieties is ideal.[25,54]

With the TAD-indole tetraol **9.1** in hand, we initiated PU elastomer synthesis experiments (see supporting information). These proceeded smoothly, giving similar results to our earlier developed TAD and indole PU comonomers.[25,54] However, the tetraol **9.1** was obtained as a solid, and was also not soluble in any liquid polyol PU monomer. Thus, PU networks had to be prepared in solvent (DMF). As this option is not available for PU foam synthesis, we needed to improve the physicochemical parameters of the indole diol. Initially, we attempted to propoxylate the obtained indole diol **6.1** or bis-TAD-coupled tetraol derivative **9.1**. This proved to be a non-viable strategy, as we could not avoid propoxylation initiation from the acidic indole or urazole N-H under all conditions.

After this initial set of experiments, the TAD-indole tetraol **9.1** was redesigned by preparing the longer chain amine polyols **2**, **3** and **4** by propoxylation of benzyl amine (Figure **2** and **3**). Hydrogenation of the propoxylated benzyl amine gave ready access to chain elongated versions of amine diol **1**, which were expected to give more soluble TAD-indole adducts. These propoxylation could be carried out in a medium scale reactor, yielding 1-6 kg of product. Also, debenzylation could be carried out at almost kilogram scale (~800 g) in a borosilicate glass reactor. The hydrogenation of these polyols did not require a solvent, as they were low viscosity liquids.

The coupling of the amine polyols (**2-4**) proved to be more challenging. A longer polypropylene glycol chain is strongly preferred in terms of ultimate physicochemical properties of the derived TAD-indole polyols, as this will give higher miscibility and solubility in solvent-free PU foam formulations. However, we found that the efficiency of the indole coupling step strongly depends on the degree of polymerization of the amine precursors (Figures **2** and **4**). The reaction becomes sluggish for **3** (with chain lengths of 5-6 propylene glycol units) and failed to deliver the desired amide coupling product for longer chain length. We surmised that the NH functionality loses its reactivity because of the steric crowding by the large propylene glycol chains. A final solution was found to this problem by first initiating the propoxylation of benzyl amine with a small amount of ethylene oxide, before continuing to grow the chain in the reactor with propylene oxide. As such, **4** was achieved, with diminished steric crowding of its central secondary amine functionality, and a degree of polymerization (and expected physicochemical properties) that is more in line with those of standard flexible PU foam polyols. This amine polyol **4** was indeed successfully coupled to result in the high molecular weight amide **6.4** (Figure **4**).

When the longer chain indole polyols **6.2**, **6.3** and **6.4** were coupled with the bis-TAD cross-linker **8**, the resultant dynamic polyols **9.2**, **9.3** and **9.4** were obtained. The shorter chain polyol **9.2** was obtained as a solid product. In contrast to its non-propoxylated counterpart **9.1**, it did show some improved solubility in PU polyol ingredients. Thus, the solubility was checked in several commercial polypropylene glycols: PPG400, PPG725, PPG1000, and standard flexible PU foam polyol (a trifunctional PPG-based polyol with ~3500 g/mol). Although **9.2** showed some solubility in all of these polyols, full solubility of **9.2** as a 1:1 mixture was only achieved in PPG725, after mixing and heating to 60-70 °C. This solution of **9.2** in PPG725 could be used to make the first solvent-free formulations of dynamic covalent PU elastomers (Figure S-19 and S-20). Likewise, after considerable optimization of the conditions, PU foam formulations could also be achieved, but the resultant PU foams showed properties that are very far from standard material properties for flexible foams (Table S-5 and Figure S-21). The TAD-indole polyol **9.2** is indeed expected to give a quite rigid molecular architecture.

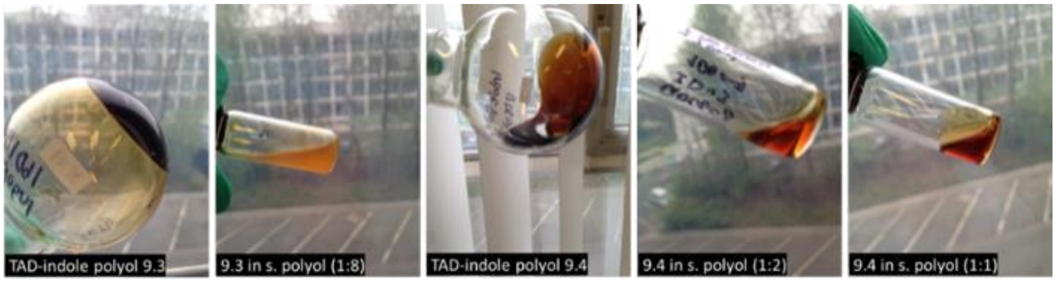


Figure 8. Illustration of comparative viscosity and miscibility (in standard polyol = s. polyol) features of TAD-indole polyol 9.3 and 9.4.

The second generation of propoxylated TAD-indole polyols, **9.3**, was found to be a highly viscous waxy product. Compared to **9.2**, it showed increased solubility in PPG1000 as ~1:5 mixture, but the solubility was still low in the standard polyol. The use of **9.3** in PU formulations was therefore not further investigated in favor of **9.4** (Figure **8**).

The final generation of TAD-indole polyols, **9.4** was produced in relatively larger scale (0.5 and 1.5 kg, respectively indicated as polyols **9.4-1** and **9.4-2**, see Tables S-2 and S-3). Both polyols were free flowing homogenous liquids. As such, they were directly usable in PU foam and elastomer formulations and were also fully miscible in any ratio with standard flexible PU foam polyol, to which it has a comparable molecular weight. With this achievement, the performance of the TAD-indole dynamic covalent chemistry could be assessed in flexible PU foam products for the first time.

Preparation, optimization and properties of dynamic covalent PU foams

Several polyurethane foams could be prepared from **9.2** and **9.4**. For **9.2**, drastic changes were required in the formulation to be able to achieve an acceptable foaming process (Table S-5 and Figure S-21). These foams lacked good mechanical properties and were more in line with those of rigid (insulation) PU foam, which fell outside of the scope of the research project, thus the optimization (and foam scale up required for this) was not pursued. Instead, our efforts focused on the last generation TAD-indole polyol **9.4**, for which more or less standard industry formulations for PU flexible foams could be applied, with a few changes in catalyst mixtures. The dynamic polyol **9.4** was therefore scaled up to kilogram level to allow extensive foaming trials. It could be added in various ratios to standard PU foam formulations, by replacing an increasing part of the standard non-dynamic polyol (from 0% in the reference foam up to 100% in the completely dynamic foam). However, by replacing 100% of the standard polyol (a trifunctional polyol) with the dynamic covalent polyol **9.4** (a tetra functional polyol), it was observed to be a challenging task to achieve a good foaming process (Figure S-28, right), as the foam shrinkage occurred after an initial rise. This can be rationalized by the higher functionality and degree of cross-linking that results from the use of **9.4** as the sole polyol ingredient, leading to an uncontrollable gelation process. In a subsequent step, normal foaming rise profiles (Figure S-28, left) could ~~only~~ be achieved at a replacement level of 40% (w/w) of the standard polyol by the dynamic polyol **9.4-1**

~~(Table S-6 and Figure 9)~~. The doping level (20-30-40%) also affected the foam properties (Table S-7). For flexible PU foams, specific mechanical properties are desired. Regarding the density of the foam, the target is between 30 and 40 kg/m3. The hardness is expected to be lower than 10 kPa and, preferably, even lower than 4 kPa. The air resistance, related to the cell structure (open vs. closed), is also an important property with a target value below 50 cm H_2O for main comfort applications.

As a blank specimen for initial foam properties and further reprocessing behavior, a standard PU foam was simultaneously prepared as “Reference (REF)” from industrially standard (non-dynamic) polyol. The corresponding ratios; 20/80, 40/60 etc. (Table S-7) for dynamic covalent PU foams are representation of the exchanged volume of standard polyol with dynamic covalent TAD-indole polyol.

As can be seen from Table **S-7**, and as can be expected by the higher functionality of **9.4-1**, the foams are going further away from the specified target values for properties with increasing doping level of the TAD-indole polyol **9.4-1**. Especially, the needed amount of each catalyst got higher in correlation to the amount of dynamic polyol content. The same trend was also observed with **9.4-2**. For foams with a high ratio of **9.4-2** (Table S-9, S-10 and S-11), significant settling and high air resistance were observed, indicative of a lack of balance between blowing and gelation. Higher content (100%) of dynamic polyol **9.4-2** resulted in collapsed foams (Figure S-30), indicating that gelation was not taking place in a proper way, which can indeed be explained by the higher amount of catalyst and a non-optimized foam formulation.

As can be seen from SEM-analysis (Figure S-29), the three covalent dynamic PU foams based on **9.4-1** (20/80, 30/70 and 40/60) display a cellular structure (500 µm-1mm) that is still close to that of the reference foam (with cell sizes around 500-600 µm). The density and hardness of all the foam samples are quite similar as well with a tendency to rise with increasing TAD-indole polyol **9.4-1** contents due to higher cross-linking degree. However, the air resistance values show significant differences (Table S-7 and S-8). This could be attributed to the relative lack of uniformity in cell structure compared to the reference, which can introduce smaller and more closed cells in the structure as well as the higher degree of cross-linking, which favors the gelling reaction over the blowing and thus gives more closed cells.

In order to address the foaming challenges, a limited amount of additional foaming trials was conducted, using slight changes such as addition of surfactants and tweaking the relative amount of the catalyst mixture (Table S6-S9 and Figure S28-S29). Although in this case a higher degree of replacement (up to 60%) of the standard polyol with TAD-indole polyol **9.4-2** could be achieved without collapse of the foam, the air resistance values remained high, related to settling and non-uniformity in the cell structure. Additionally, mechanical properties were not good for these high doping level foams. It is expected that the foam properties could be improved by lowering the functionality of the non-dynamic polyol, targeting an average functionality of about 3.0, but this was not done for these initial trials. Before attempting such further optimization, we were interested in the recycling properties of these first dynamic covalent PU foams (Figure **9**), and thus in whether the dynamic covalent cross-linking concept is applicable in PU foams.

Thermal reprocessing of dynamic covalent PU foams

The main objective of our research was to assess the utility of the TAD-indole dynamic covalent chemistry platform in helping the sustainable development of innovative PU foam products. The main idea is that the foamed network polymer can be recycled into a PU elastomer, much like current thermoplastics are recycled by pelleting and remolding. In a further horizon, if the dynamic network bonds retain their reactive character, it could be possible to 'refoam' these PU elastomers by a physical blowing process, as is currently used for thermoplastic PU (TPU)[61,62] and this foaming strategy was not limited to PU elastomers, it has also been successfully applied to thermoset PU foams[34] and thermoset NIPUs[63]. In line with our earlier work with PU elastomers[17,19,25,54] thermal compression molding was used because of their low density. As the PU foam fragments are hard to fit into a classical mold, a qualitative reprocessing was done between two flat plates in a press, heated to 130 °C, and pushed together at 100 bar pressure for 10 min. This technique was chosen since it allows for simple assessment of the dynamic nature of network bonds in the polymer network.

The results for the qualitative PU foam recycling experiments are shown in Figure **9**. The first surprising observation was that the reference foam showed a good first reprocessing into a transparent elastomer.

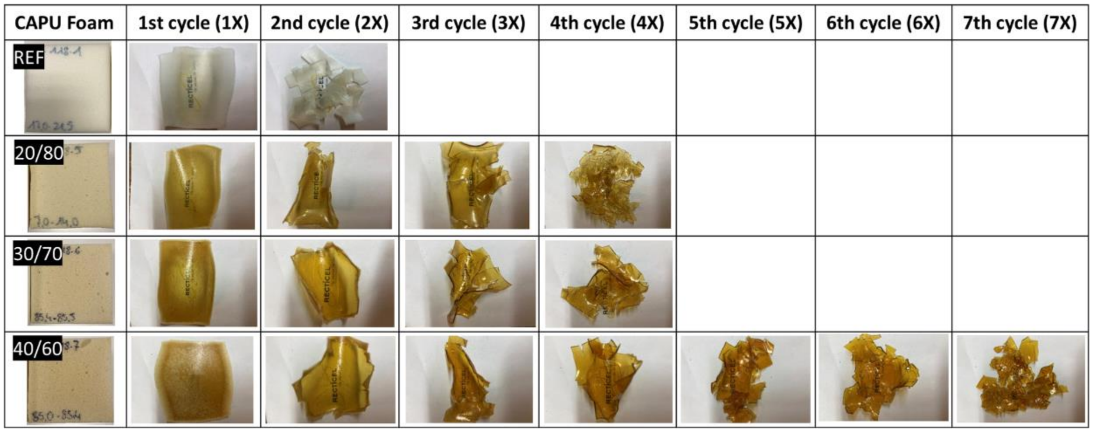


Figure 9. A combined image of PU foams (first column) prepared with the standard polyol (REF) and varying ratio of the polyol 9.4-1 (20/80, 30/70 and 40/60) and elastomer-to-elastomer recycling performances of covalent adaptable PU elastomers (up to 7 cycles)

Indeed, urethane functionalities are known to show a degree of dynamic covalent behavior, as is known in so-called ‘blocked isocyanate’ applications, and as has also been investigated within the framework of dynamic covalent PU networks.[20,23,40,42,44–46,64] However, after one thermal compression of the reference PU foam, breaking up the reference elastomer into pieces, and stacking them again for a second treatment in the thermal press, healing or recycling was not observed anymore. This observation is quite general in such thermal reprocessing of PU networks.[17,25,54] A urethane bond may dissociate into hydroxyl and isocyanate moieties, but the reactive isocyanates are expected to give a complex 'rebonding' profile, as these can react with a wide range of alternative nucleophiles and can oligomerize. Furthermore, the catalysts that are inducing the reactive behavior may have limited thermal and hydrolytic stability.

Interestingly, and as expected, the PU elastomers obtained after the first thermal compression of the TAD-indole doped foams showed an improved qualitative recycling profile (Figure **9**). The PU foams wherein 40% (w/w) of the standard 'non-dynamic' polyol was replaced by dynamic covalent polyol **9.4-1** could be recycled up to seven times before healing started to be visibly hampered. Clearly, the dynamic nature of the TAD-indole bonds is retained.

There is a significant difference between the outcome of these PU foam recycling experiments, and those previously obtained from the corresponding PU elastomer recycling trials (Figure S-16-S-20). First, the reference elastomers do not show any thermal healing behavior at 130 °C, while the reference PU foams do show this. Both the network architecture, molecular constitution and catalyst mixture are different, so any of these factors could have improved the 'intrinsic reprocessability' of the foams. Secondly, the reprocessed TAD-indole based elastomers show similar properties to those of the original PU sample after thermal remolding up to 3 times, while the foam derived reprocessed samples show a gradual decrease in material properties. Any chemical degradation process linked to the limited recyclability of our PU foams is thus not related to the TAD-indole linkage as such, but to its combination with the catalyst package and macromolecular architecture of the PU foam.

It is assumed that the catalyst mixture, which needed to be increased in order to achieve good foaming for the TAD-indole-doped foams, can cause a significant dynamic behavior of the urethane bonds. The investigation of the thermal and mechanical properties of the PU foams and the recycled PU elastomers, described in the next section, confirmed this observation.

Thermo-mechanical and rheological properties of foam-to-elastomer reprocessed dynamic covalent PU elastomers

The foam-to-elastomer reprocessed PU samples, as well as the next generation samples of elastomer-to-elastomer recycling, were characterized to evaluate the efficiency of the reprocessing. The combination of tensile strength, FTIR, DSC and TGA analysis allowed to conclude on the potential degradation or side reactions happening in the polymer during reprocessing.

The results of thermal characterization from DSC and TGA analysis of selected samples from the reprocessed dynamic covalent PU elastomers demonstrate that significant changes are absent. TGA analysis showed a degradation temperature at 5% mass loss (T_{deg},5%) around 286°C and a sharp degradation profile was reached around 320°C for all samples. Individual TGA graphs and summary of the thermal characterization are shown in the supporting information (Figure S-34-S-37 and Table S-13).

The mechanical properties of the recycled PU elastomer samples are a better measure for the extent and efficiency of the dynamic reprocessing of the network structure. We conducted tensile strength tests with selected samples and determined soluble fractions and swelling degrees to assess the network integrity in the different samples.

Tensile measurements (Figure S-38-S-40) revealed that the mechanical properties of dynamic covalent PU elastomers (after the first reprocessing cycle) were all comparable to those of the reference elastomer. As the bulk of the network (60-80%) is indeed the same, this is expected. However, all reprocessed elastomers demonstrated a large deviation from the initial (1X) reprocessed sample after consecutive reprocessing cycles (much larger force at break, and a shorter elongation at break). This is a pattern that is typically associated with a rise in cross-linking density, which could be explained through side reactions of released isocyanate groups at elevated temperature. The build-up of permanent cross-links could thus be related to the competitive 'dynamic urethane' reactivity that is seen in the reference material. Moreover, there was a large spread of properties over different samples taken from the same 2X reprocessing batches. As the amount and nature of the side reactions can be quite different in PU-based systems, it is not possible to interpret these results in more detail.

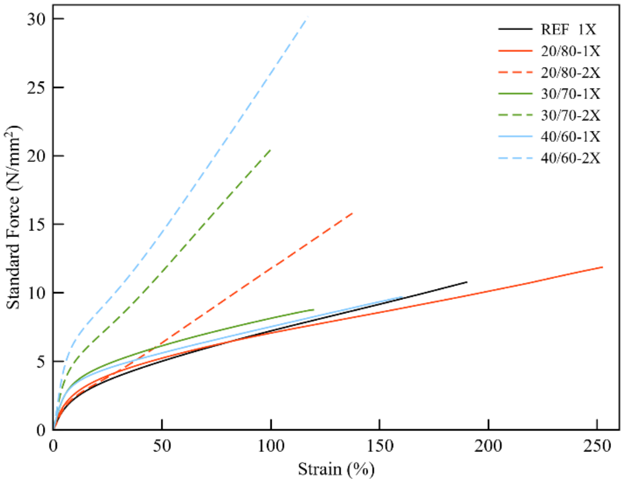


Figure 10. Combined representative tensile strength measurement, 1X and 2X of PU elastomers with varying ratio of the TAD-indole polyol 9.4-1 (20/80-40/60).

In the swelling degree and soluble fraction results (Table S-12), the 20/80-1X and 2X did not show a significant change. On the other hand, the 30/70-1X and 2X showed an increase, which was counterintuitive. Lastly, the 40/60-1X and 2X samples showed the highest decrease of swelling degree (102% to 83%). However, all the soluble fraction values were the same. In other words, these values did not give a clear indication of an increasing or decreasing cross-link density. For most recyclable PU elastomers, no more change in swelling degree was seen in the elastomer-to-elastomer reprocessing after the first cycle. Similarly, infrared analysis did not show significant differences for these samples (Figure S-31-S-33), even though the material properties visibly deteriorate (Figure **10**).

To assess the dynamic nature of the cross-links in the foam-to-elastomer recycled PU materials, frequency sweep experiments were performed between 100 °C and 140 °C using a strain of 10%. The rheology measurement temperature range and strain values were determined based on previous literature.[25] The data from the rheology measurements reveal a complex and difficult to interpret dynamic behavior of the networks, as both the reference sample as well as the dynamic covalent PU samples showed anomalous behavior (Figure S-41-S-44). These data are in stark contrast with previous results obtained for TAD-indole based PU elastomers. One of the explanations here may lie in the fact that the term 'polyurethane' is actually a euphemism to describe the polymer material class known as PU foams. Most flexible PU foams are indeed produced using an excess of isocyanates and water. Part of these isocyanates are hydrolytically cleaved into CO_2 and a terminal amine, which in turn form urea bonds. The excess isocyanates will thus give rise to biurets and allophanates, which are dynamic bonds. The thermal reversibility of any bonded isocyanate is not expected to be a reliable process to develop dynamic polymer networks, as the released isocyanate can recombine in a number of ways, including with network moisture or with itself.

CONCLUSIONS

We demonstrated a kg-scalable synthesis of a dynamic covalent polyol based on thermoreversible TAD-indole chemistry. This polyol can be used in solvent-free PU formulations, and its constituent TAD and indole compounds were shown to be scalable up to industrially relevant levels. This is an important step forward for the industrial applicability of the TAD-indole dynamic covalent chemistry platform. The developed monomers behaved as expected in fully solvent-free PU elastomer formulations, thus clearing an important hurdle in the potential industrial development of this chemistry. However, uptake of the technology in flexible PU foam formulations, which was the main objective of this research program, proved to be more challenging. Foam formulations based on the developed TAD-indole based polyols, which were never achieved before with previous monomers, only showed a limited improvement of intrinsic recycling potential, at the cost of a significant deterioration of the main PU foam properties. Whereas technical difficulties might be resolved by refining the foam formulations, or possibly by rethinking the way foam materials are prepared (i.e., stepping away from reactive isocyanates), it is clear that short term adoption of the TAD-indole technology in the PU foam manufacturing industry will require further refinements. One of the problems in PU foam materials was the fact that even the regular 'non dynamic' PU foams show a high degree of thermal reactivity, which may interfere with the TAD-indole reactivity. This may be related to the prevalence of non-urethane type bonds[65,66] and additional additives and catalyst present in typical foam formulations, compared to more standard 'elastomer' PU formulations that were assayed before and gave much more promising results. Nevertheless, we expect that our results can serve to guide future efforts in the sustainable development of PU foams, and especially can be of use for the development of various dynamic covalent polymers based on the versatile TAD-indole chemistry platform and the scalable building blocks developed herein.

ASSOCIATED CONTENT

Supporting Information. Details about instrumentation, synthetic procedures, properties of obtained materials with images, NMR spectra, IR spectra, DSC, TGA thermograms, tensile strength measurements and stress-relaxation data.

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The draft manuscript was written by KU, and reviewed by all authors. All authors contributed to revising the manuscript. All authors have given approval to the final version of the manuscript. JW, FDP and LI were involved in the design of the overall approach of the research. JW and LI were responsible for the coordination of the research and project tasks.

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Notes

The authors declare no competing financial interest.

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KEYWORDS

polyurethane foams, dynamic materials, foam reprocessing, triazolinediones, indoles, thermosets, dynamic covalent chemistry, polyols

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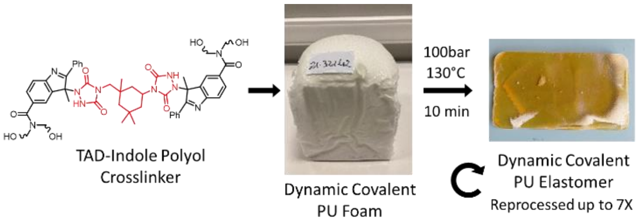

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SYNOPSIS

We developed a scalable macromolecular polyol (5-50 kg) with an embedded dynamic covalent linker that improves the intrinsic recyclability of polyurethane foam materials.