

Chemical Recycling of Flexible Polyurethane Foams to Recover High Quality Polyols

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Abstract

Polyurethane foams are widely used commodity materials, but most of them end up in landfills at the end of their life, which is not in line with the circular economy approach. Here we introduce microwave-assisted aminolysis as an efficient chemical recycling process for polyurethane foams. Amino reagents containing primary and tertiary amino groups in the structure, which act both as a reagent and a catalyst, are shown to be particularly effective in degrading urethane groups in the foam structure. The recycled polyols have structural and molar mass characteristics that basically make them perfect analogues of the corresponding virgin polyether polyols. Therefore, the production of high-quality polyurethane foams exclusively from the recycled polyols is possible without having to adapt the synthesis process. The flexible foams synthesised from recycled polyols have comparable mechanical properties to those produced from virgin polyols, which has not been achieved with any recycled polyol so far.

Introduction

Plastic materials are key components of almost every technology today. The production of plastics consumes substantial feedstock resources and after their service life they represent a waste that has become a growing environmental problem in terms of pollution and related climate change due to inadequate circular economy¹. Chemical recycling of polymers is an alternative to traditional methods of treating plastic waste (landfill, incineration, mechanical recycling) by converting them into feedstock suitable for re-polymerization into the same materials or into new materials of higher value (up-cycling)²⁻⁴. Chemical recycling is particularly suitable for polymers with chemically labile groups in the backbone such as polyesters, polyamides, polyurethanes (PUs), and polycarbonates⁵⁻⁷. Depolymerisation of these polymer types is usually carried out by solvolysis using nucleophilic solvents in the presence of a catalyst.

PUs are the sixth most produced polymer, with PU foams (PUFs) accounting for about 67% of global PU consumption^{8,9}. The global PUF market is forecast to increase from 15 million tons in 2020 to 20 million tons in 2025 as mattress, furniture, electronics, automotive, and construction industries grow¹⁰. Consequently, both the consumption of fossil resources (polyols, diisocyanates) and the amount of PUF waste are expected to increase. Therefore, there is a clear need for alternative solutions to sustain growth projections for PUF production and prevent waste accumulation. Since mechanical recycling is not the most suitable for the cross-linked PUF structure, chemical recycling has recently become a very interesting research topic^{8,11-13}. Chemical recycling of PUFs made from polyether polyols is based on the cleavage of the urethane bonds, leaving the ether groups in the polyether polyol intact. Depending on the mechanism of urethane bond degradation, recycling technologies are mainly classified into hydrolysis^{14,15}, (hydro)glycolysis¹⁶⁻²⁴ and, more recently, acidolysis^{7,11,25-28}. To achieve efficient degradation of urethane groups, the process of PUF recycling must be carried out at high temperatures (200°C and above) by heating the reaction mixtures by conventional heating or, less commonly, by microwaves (MW)^{7,17,29,30}, which allows an equally effective degradation process in a much shorter time. The high reaction temperatures required for efficient process highlight the importance of thermal degradation of urethane groups in PUF recycling^{7,23}. The general consensus is that the urethane groups start to thermally dissociate into the isocyanate and hydroxyl precursors above 150°C and in particular above 200°C^{31,32}. However, under certain reaction conditions, urethane groups can also irreversibly degrade by decarboxylation, which is undesirable as the resulting allyl-functionalized polyol cannot undergo further polymerization with diisocyanates. Due to the high reactivity of thermally formed isocyanate groups, they further react with the nucleophiles present in the reaction system. Therefore, the choice of the degradation reagent in PUF recycling is extremely important. The order of reactivity of isocyanate group in the uncatalysed reaction typically decreases in the following order: primary aliphatic amines > secondary aliphatic amines > aromatic amines > primary alcohols > water > secondary alcohols > carboxylic acids > ureas > urethanes^{33,34}.

Currently, split-phase glycolysis is considered to be the most efficient PUF recycling method^{23,35}. Since both glycolysis and thermal degradation of urethane groups are reversible reactions, a large excess of glycol reagent per urethane group is required to shift the equilibrium toward the desired product formation. Despite the purification of recycled polyols (RPs) obtained in this way, high-performance flexible PUFs cannot be synthesized exclusively from the glycolysis-derived RPs^{7,23}. Moreover, a major drawback of glycolysis carried out under conditions that allow a high degree of degradation of the urethane groups (DD_{urethane}) is the use of a large amount of glycol reagent, which after the reaction contains a lot of aromatic diamines along with other side products originating from glycolysis and/or thermal degradation of PUF hard segments. Therefore, the residual glycol medium must be recovered by cost-intensive thermal methods, otherwise it is a waste product^{23,35}. In contrast, chemical recycling of PUFs by acidolysis with carboxylic acids can be performed with much smaller amounts of the degradation reagent, since the reaction of carboxyl group with the urethane and isocyanate group is irreversible and leads to the formation of a more thermally stable amide bond after decarboxylation of carbamic acid. Nevertheless, acidolysis can in no way produce RPs that would be close equivalent to the virgin polyols (VPs) in terms of functionality⁷. The reason is that the degradation of the urethane bonds does not occur quantitatively at low amounts of the acidic reagent used, which results in the aromatic amine-functionalized polyols. At higher amounts of the acid used, the DD_{urethane} increases, however esterification as a side reaction inevitably takes place, resulting in polyol chains terminated with carboxyl groups. Importantly, the degree of functionalization of the RP by the amino and, in particular, the carboxyl end groups significantly affects the quality and performance of the flexible PUFs synthesized from the acidolysis-derived RPs⁷. An even less studied PUF degradation process is aminolysis, which can be carried out in the presence^{30,36-38} or absence of a catalyst^{11,38-41}. In aminolysis, the polyol in the urethane group is exchanged with the amine, which can be aliphatic diamines or polyamines with primary and in some cases also secondary amino groups in the structure^{30,38,41,42}. The degradation of PUFs with alkanolamines has also been reported, but the reaction is slower than with primary/secondary amines due to the lower basicity of nitrogen in alkanolamines^{36,38,39,41}. Therefore, the reaction requires harsher reaction conditions. In the case of alkanolamines, both alcoholysis and aminolysis have been proposed as possible mechanisms of PUF degradation³⁹. Depending on the reaction conditions, the result of PUF aminolysis is either a liquefied PUF in the case of a single-phase process or a polyether polyol liquid phase containing aromatic diamine and other aminolysis side

products in the case of a split-phase process³⁶. The exact functionality and molar mass characteristics of the recovered polyols and detailed characterization of obtained aminolysis products are not reported^{36,41}. Aminolysis products as whole reaction mixtures were mainly used for various less demanding applications, e.g., as curing agents for epoxy resins⁴¹, for synthesis of polyurethane urea-based coatings³⁰, etc., while aminolysis-derived RPs were used only for the synthesis of rigid PUFs¹¹ since their poor quality prevents the production of flexible PUFs.

Existing methods of chemical recycling of PUF waste suffer from incomplete degradation of urethane groups and lack of selectivity for degradation of urethane bonds alone, as urea bonds in PUF hard segments also degrade, resulting in differently functionalized polyols containing various side products²³. For this reason, RPs are used only as partial replacements of VPs in formulations for the production of new flexible PUFs^{23,35}. The aim of our work was to develop a cost- and energy-efficient recycling process for flexible PUFs distinguished by a high DD_{urethane} in order to produce RPs that are close equivalent to VPs in terms of functionality, molar mass, and purity since only in this way RPs are suitable for re-polymerization into flexible PUFs of the same quality and performance as those produced from VPs. In addition, the process must ensure the production of high quality RPs, even if the PUFs are subjected to multiple recycling cycles in order to avoid down-cycling.

Results

Aminolysis was chosen as a method of PUF recycling because amines are highly reactive toward the isocyanate group^{33,34} formed during thermal degradation of PUF-constituent groups (urethane, urea, biuret, allophanate). Since thermal degradation of PUFs is a reversible process, the type and amount of amine reagent used is important in driving the reaction to the desired product formation. In this respect, we rely on the fact that the reaction of thermally released isocyanate with the amino group of the reagent to form the urea group is much faster than the recoupling of the isocyanate with the hydroxyl group of the polyol back to the urethane group, and that the urea is more thermally stable than the urethane group. To improve the selectivity of the reaction of the isocyanate group with the amino group, we have used reagents that contain in their structure, in addition to the primary amino groups, a tertiary amino group that is known to activate the isocyanate group and greatly increase the rate of nucleophilic addition of compounds with active hydrogen to the C = N bond³³, e.g., tris(2-aminoethyl)amine (TREN) and hyperbranched polyethylenimine (PEI) (Fig. 1). Such reagents have not been previously reported for PUF recycling. The degradation experiments were first performed on a model flexible PUF synthesized from a polyether polyol composed of propylene oxide (PO) repeating units attached to a glycerol core to obtain information on the type of the end groups of the recovered polyols by MALDI-TOF mass spectrometry. All chemical degradation reactions of PUFs were performed by MW-heating of the reaction mixtures. A certain amount of polyether polyol (virgin or recycled) was used as a medium because of its ability to absorb MWs and convert them into heat. Its presence also ensures efficient and uniform stirring of the reaction mixtures to prevent foam caking. The experiments were carried out in an inert nitrogen atmosphere to avoid darkening of the reaction mixtures due to oxidation processes^{7,23,43}.

Aminolysis as a function of temperature and time

In aminolysis experiments with TREN, which contains three primary amino groups and one tertiary amino group in the structure, and poly(propylene oxide) (PPO)-based PUF, a slight excess of amino per urethane group was used (1.25 equivalents (Eqs)). The weight ratio of PUF/medium/reagent was 6 g/3 g/0.24 g.

With increasing temperature and time, the content of remaining urethane groups in the RPs decreases down to 8 mol% with a simultaneous increase in the content of toluenediamine (TDA) up to 5.4 wt%, as determined by ¹H NMR according to equations (1) and (2), respectively. However, none of the reaction conditions leads to complete degradation of the urethane groups (Table S1). After 40 min at 210°C, and after 30 min at 220°C and 230°C, the molar mass characteristics of RPs are comparable to that of VP of the same type (Table S1). Nevertheless, with increasing reaction temperature or time, a continuous decrease in the ratio of UV to RI signals of the RPs is observed in the SEC/UV-MALS-RI chromatograms (Fig. S1), which is a consequence of the decreasing fraction of polyol species containing UV-active aromatic amine chain ends (TDA moiety attached to the polyol via the urethane group), resulting from incomplete urethane group degradation. The typical MALDI-TOF mass spectrum of RP shows four peak populations; the main peak series corresponds to the desired hydroxyl-functionalized polyol, while the three smaller peak populations show the polyol chains terminated at one or two chain ends by the aromatic amine group due to incomplete urethane group degradation, and by an allyl group due to the thermal degradation according to the undesired pathway (Fig. 2a). Typical ¹H NMR signals of differently functionalized polyol chains are found at 4.40 ppm for the hydroxyl group, 5.08 and 5.22 ppm for the allyl group, and at 1.87, 1.96 and 2.00 ppm for the methyl groups of three isomeric aromatic amino end groups attached to the polyol via the urethane bond (Fig. 2b, Table S2). The formation of allyl-functionalized RP is a consequence of the established equilibrium between the urethane group and its isocyanate and hydroxyl precursors, which favours the slower irreversible pathway of thermal degradation of urethane group to primary amine, olefin, and carbon dioxide due to insufficient amount of added amine reagent³¹.

Aminolysis as a function of the type and amount of amine reagent

To improve DD_{urethane} and shift the thermal equilibrium toward the desired formation of aliphatic urea, aminolysis of PPO-based PUF was performed with larger amounts of TREN (i.e., amino per urethane group from 1.50 to 4.00 Eqs, corresponding to TREN per PUF from 4.8 to 13.2 wt%). It was determined that increasing the temperature above 220°C or extending the reaction time beyond 30 min did not significantly improve the DD_{urethane} (Table S1), so further reactions were performed at 220°C for 30 min. The allyl-functionalized polyol was not detected by ¹H NMR or by MALDI-TOF MS at amino to urethane group ratios of 2.25 and above. With increasing amount of TREN from 1.50 to 4.00 Eqs of amino per urethane group, the content of remaining urethane groups in the RP decreases from 9.7 to 1 mol%, but with a concomitant increase in released TDA from 3.9 to 10.2 wt% (Table 1; entries 1–4;

Figs. 3 & S2), corresponding to a conversion of toluene diisocyanate (TDI) used in the PUF formulation to TDA from 10.5 to 29.0 mol%. Moreover, the isolation of RP is facilitated with increasing amounts of TREN, because the final reaction mixtures are dispersions at low amounts of TREN used, whereas at amino to urethane group ratios of 2.25 (7.3 wt%) and more, a two-phase system is obtained consisting of a liquid polyol phase and the residual solid hard segments that settle after centrifugation, allowing easy decantation of the crude RP from the reaction mixture (Fig. S3). In this way, ~85 wt% of the crude RP can be isolated.

To identify the importance of the presence of both primary and tertiary amino functional groups in the structure of the same reagent molecule, the degradation of PPO-based PUF with hexamethylenediamine (HMDA), containing only primary amino groups in the structure, was studied in the presence and absence of a tertiary amine catalyst, i.e., triethylenediamine (DABCO), commonly used in PUF synthesis (Table 1; entries 5 & 6, Fig S4). The degradation of PUF with HMDA at 4.00 Eqs of amino per urethane group (15.3 wt% HMDA per PUF) results in 7.3 mol% remaining urethane groups in RP, while the value for TREN at the same ratio of primary amino per urethane group is 1 mol%. Compared to aminolysis of PUF with HMDA only, the additional use of DABCO catalyst improves the DD_{urethane} but RP still contains more residual urethane groups than RP recovered from PUF with TREN (3.7 vs. 1.0 mol%), at the same ratios of primary and tertiary amino per urethane group (4.00 and 1.36 Eqs, respectively). This shows the importance of the presence of primary and tertiary amino groups in the structure of the degradation agent, which acts as both a reagent and a catalyst.

Aminolysis of PUF was also performed using hyperbranched PEIs with number-average molar masses of 600 and 1800 g mol⁻¹ (Table 1; entries 7–9, Fig S5). Hyperbranched PEIs contain primary and tertiary amino groups as well as secondary amino groups in the structure. After aminolysis of PUF at 220°C for 30 min with 11.0 wt% PEI-600 per PUF, corresponding to 1.70 Eqs of primary amino and 1.30 Eqs of secondary amino groups per urethane group, the degradation of urethane groups was almost complete, as only 1.1 mol% urethane groups were detected by ¹H NMR in the RP. However, the formation of allyl-functionalized polyol was completely prevented only when 14.2 wt% reagent per PUF was used (2.10 Eqs –NH₂ and 1.70 Eqs –NH– per –NHCOO– group). The more pronounced formation of allyl-functionalized polyol during aminolysis with PEI was attributed to its higher molar mass compared to TREN and consequently to its lower mobility. This explanation was confirmed by higher molar mass PEI-1800, which did not completely prevent the formation of allyl-functionalized polyol even when 14.8 wt% PEI-1800 per PUF was used, corresponding to 1.90 and 1.80 Eqs of primary and secondary amino groups per urethane group, respectively.

The optimal aminolysis procedure using TREN or PEI-600 was also applied to the recycling of post-industrial and post-consumer PUF wastes containing unknown additives. These PUFs were prepared from a commonly used copolyether three-arm-star polyol with ethylene oxide (EO) and PO repeating units attached to a glycerol core. The results related to the contents of residual urethane group and TDA in the RPs are very similar to the values obtained for the PPO-based PUFs (Table 1; entries 10–13). Moreover, the molar mass characteristics of the RPs are comparable to those of the corresponding VP, indicating successful recycling of the PUFs prepared from (co)polyether polyols (Fig. S6). Finally, the PUFs synthesized from 100% RPs were again subjected to aminolysis with TREN and PEI-600 under optimal experimental conditions (Table 1; entries 14 & 15, Fig. S7). The structural properties and molar mass characteristics of the twice-recycled polyols are comparable to those of the corresponding VP, indicating that down-cycling is not an issue of the disclosed aminolysis process.

The typical yield of RP from PUF aminolysis at high DD_{urethane} is ~95%, which represents the decanted polyol (85%) and RP isolated from the remaining PUF hard segments by dissolution in ethyl acetate (10%), taking into account that PUF5611 and PUF4811 consist of 66.1% and 65.9 wt% polyol, respectively. The crude PPO- and copolyether polyol-based RPs were purified by extraction with acidic water followed by water to remove amino-functionalized low molar mass impurities (mainly TDA) derived from the degradation of the PUF hard segments. The yield of RP after purification is ~85%.

Two-step aminolysis

Previous results indicate that a 4-fold excess of amino per urethane group is required to achieve almost complete degradation of urethane groups in the structure of PUFs. To reduce the amount of reagent, aminolysis with TREN was performed in two steps. In the first step, only 7.3 wt% of TREN per PUF was used (amino per urethane group of 2.25), an amount that prevented the formation of allyl-functionalized polyol and resulted in 5.8 of remaining urethane groups after 30 min at 220°C (Table 1; entry 2). Subsequently, 6 g of thus obtained crude RP was subjected to the second aminolysis cycle, in which TREN was added in a 4-fold excess of TREN amino per polyol remaining urethane groups (1.2 wt%; Table 1; entry 16). In this way, complete degradation of urethane groups without formation of allyl-functionalized polyol chains was achieved with 34 wt% less TREN reagent compared to the one-step aminolysis procedure, only the degradation time is prolonged by 20 min. In addition, two-step aminolysis results in RPs containing 2.5 wt% less TDA than the RPs obtained by one-step aminolysis. Similar results were obtained for two-step aminolysis of copolyether polyol-based PUF4811 (Table 1; entries 17 & 18). Complete degradation of urethane groups in the structure of PUF5611 was also achieved by two-step aminolysis using HMDA in an amount of 15.3 wt% (amino per urethane group ratio of 4.00; Table 1; entry 5) in the first step and TREN in an amount of 1.8 wt% (amino per urethane group ratio of 6.00; Table 1; entry 19) in the second step. Purified PPO- and copolyether-based RPs obtained by the two-step aminolysis procedure are perfect equivalents of the corresponding VPs in terms of structural and molar mass characteristics as well as purity, as shown by the results of ¹H NMR, SEC/UV-MALS-RI, HPLC, MALDI-TOF MS and other characterization techniques (Figs. 4, S8, S9, S10 & S13, Tables S3 & S7).

Synthesis of flexible PUFs from RPs

At high DD_{urethane} the content of residual urethane groups in RPs is comparable to the content of aromatic amino functional groups, because oligomers are not present in RPs. Purified PPO-based RPs containing 6.9 and 0 mol% residual urethane groups (Figs. 4, S8 & S9, Table S3) were used to synthesize new flexible PUFs without adjusting the PUF formulation or synthesis conditions compared to PUF prepared from 100% VP (Table S4). The PUF prepared

from fully hydroxyl-functionalized RP exhibit an open-cell morphology, just like the PUF prepared from VP (Fig. S11). In contrast, PUF prepared from partially aromatic amino-functionalized polyol shows a more closed-cell morphology and a slightly smaller average pore size.

Compression tests show comparable mechanical properties (compressive moduli and stress at 40% compression) of PUFs made from VP and fully hydroxyl-functionalized RP, while PUF made from partially aromatic amino-functionalized RP shows higher compressive modulus and stress at 40% compression, which can be attributed to a more closed-cell morphology (Table S6, Figs. S11 & S12). Flexible PUFs are widely used cushioning materials, so good recovery after prolonged compression is desirable. Compression set property as a potential predictor of height and load bearing loss reflecting changes in the PUF network was measured at 50% strain at 70°C for 22 h and determined according to equation (S1). PUFs synthesized from VP and fully hydroxyl-functionalized RP have comparable compression set values, while PUF prepared from partially amino-functionalized RP has a higher value (Table S6), indicating slightly lower durability of this particular PUF, but still within specifications for standard flexible foams⁴⁴. These results indicate that aromatic amino end groups of RP, similar to carboxylic end groups of RP derived from acidolysis⁷, affect the polymerization process, albeit to a lesser extent, as indicated by the shorter gelation time during PUF synthesis from RP compared to PUF from the corresponding VP (Table S5). As a result, the morphological and mechanical properties of flexible PUFs from RP with a low content of only 6.9 mol% amino end groups deteriorate.

PUFs were also synthesized from fully hydroxyl-functionalized copolyether polyol-based RP by replacing 0, 20, 50, and 100 wt% of VP in the PUF formulation with RP obtained by a two-step aminolysis procedure (Figs. 5, S14, Table S7). The characteristic times during the synthesis of copolyether polyol-based PUFs were only slightly affected by the RP content in the PUF formulation (Table S8), while the mechanical properties of all synthesized PUFs were highly comparable, even when the PUF was synthesized exclusively from RP (Table S9).

Discussion

Structurally perfect equivalents of VPs, enabling the synthesis of high-quality flexible PUFs exclusively from RPs, were obtained by aminolysis of flexible PUFs with amine reagents containing both primary and tertiary amino groups in the structure and acting as both reagent and catalyst. The unique structure of such reagents prevents the recombination of isocyanate and hydroxyl groups formed during thermal degradation of PUFs back into the urethane bond by forming a urea group between the reagent and the isocyanate group; this degradation mechanism appears to be more likely than direct aminolysis of the urethane groups, as indicated by the fact that high degrees of degradation of the urethane groups can only be achieved at reaction temperatures that allow extensive thermal degradation of the urethane groups (above 210°C). The amount of reagent that allows complete degradation of urethane groups is much lower than that normally required for typical solvolysis, especially when aminolysis is carried out in a two-step process (8.7 wt% TREN per PUF). Aminolysis produces a small amount of aromatic amine side products, but their formation is inevitable in any PUF recycling process. While in glycolysis most of the aromatic amines formed are dissolved in the glycol phase, in aminolysis, where no extra medium is used, they are dissolved mainly in the polyol phase. Amine impurities that affect the polymerization process and PUF quality can be easily removed from RPs by extraction with acidic water without using inorganic salts. The yield of RPs from the PUF aminolysis recycling process is high (>95%), even after purification of the RPs (85%). In addition, the high-quality of the RPs is not affected by subjecting the PUFs to multiple recycling cycles, indicating that down-cycling is not an issue of the described aminolysis process. For this reason, and due to the fact that aminolysis-derived RPs are structurally equivalent to VPs, RPs can be used in the aminolysis process as a medium instead of VPs, making the proposed aminolysis process a sustainable solution for PUF recycling.

Table 1

Molar mass characteristics (weight-average molar mass, M_w , and dispersity, $\mathcal{D} = M_w/M_n$), urethane group content, aromatic amino end-group content, and TDA content in RPs recovered from PUFs by aminolysis using different amine reagents in different amounts. All experiments were performed at a PUF/VP weight ratio of 6/3 at 220°C for 30 min, except in the case of two-step aminolysis, where the RPs were treated with TREN in the second aminolysis step at 220°C for 20 min.

Entry	PUF Type	Amino/Urethane Group Ratio				PUF/VP/ Reagent (g/g/g)	Reagent /PUF (wt%)	Urethane Group Content (mol%)	Amine End-group Content (mol%)	TDA Content (wt%)	Double Bonds	M_w (kg mol ⁻¹)	\mathcal{D}
		TREN	HMDA	PEI-600	PEI-1800								
1	PUF5611	1.50	/	/	/	6/3/0.29	4.8	9.7	8.4	3.9	Yes	3.2	1.03
2	PUF5611	2.25	/	/	/	6/3/0.44	7.3	5.8	5.8	6.0	No	3.1	1.02
3	PUF5611	3.00	/	/	/	6/3/0.58	9.7	3.7	3.6	7.7	No	3.1	1.02
4	PUF5611	4.00	/	/	/	6/3/0.79	13.2	1.0	0.9	10.2	No	3.0	1.02
5	PUF5611	/	4.00	/	/	6/3/0.92	15.3	7.3	6.9	7.1	No	3.1	1.02
6	PUF5611	/	4.00	/	/	6/3/0.92 + 0.30 DABCO	15.3	3.7	3.5	7.1	No	3.0	1.02
7	PUF5611	/	/	3.00	/	6/3/0.66	11.0	1.1	1.1	8.7	Yes	3.0	1.03
8	PUF5611	/	/	3.80	/	6/3/0.85	14.2	1.0	0.9	8.8	No	3.0	1.02
9	PUF5611	/	/	/	3.70	6/3/0.89	14.8	2.7	1.9	7.5	Yes	3.0	1.02
10 ^a	PUF4811	4.00	/	/	/	6/3/0.68	11.3	*	0.6	9.3	No	3.5	1.02
11 ^a	PUF4811	/	/	3.80	/	6/3/0.74	12.3	1.3	1.3	10.3	No	3.5	1.02
12 ^a	Post-consumer PUF	4.00	/	/	/	6/3/0.68	11.3	*	0.2	10.1	No	3.5	1.02
13 ^a	Post-consumer PUF	/	/	3.80	/	6/3/0.74	12.3	*	0.7	8.7	No	3.5	1.02
14	PUF5611 from RP	4.00	/	/	/	6/3/0.79	13.2	*	0.7	9.5	No	3.0	1.02
15	PUF5611 from RP	/	/	3.60	/	6/3/0.79	13.2	*	1.0	8.4	No	3.0	1.02
16	RP5611 II-step	4.00	/	/	/	6 RP/0.07 TREN	1.2	0	0	7.7	No	3.0	1.02
17 ^a	PUF4811 I-step	2.25	/	/	/	6/3/0.38	6.3	6.4	6.2	6.4	No	3.5	1.02
18 ^a	RP4811 II-step	4.00	/	/	/	6 RP/0.07 TREN	1.1	0	0	8.5	No	3.5	1.02
19 ^b	RP5611 II-step	6.00	/	/	/	6 RP/0.105 TREN	1.8	0	0	9.6	No	3.0	1.02
The content of urethane groups, TDA, and amino end-groups in RP was calculated according to equations (1), (2), and (3), respectively.													
* The intensity of the ¹ H NMR signal of the polyol methyne group adjacent to the urethane group at 4.88 ppm is too low for accurate quantification.													
^a The molar mass of 3.5 kg mol ⁻¹ and the chemical composition of the copolymer polyol VP4811 were considered in the calculations of the urethane and amino group contents and the TDA content.													
^b First-step of aminolysis carried out as in entry 5.													

Methods

Chemical reagents. The virgin polyether polyols (VPs) ALCUPOL® F-5611 (VP5611), ALCUPOL® F-4811 (VP4811) as well as PUFs prepared from them were supplied by Repsol S.A. VP5611 is a trifunctional PO based homopolyether polyol with a hydroxyl number of 56 mg KOH g⁻¹ and a molar mass of 3.0

kg mol⁻¹, containing mixture of isomers (C7-9-alkyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate; CAS 125643-61-0) as a phenolic antioxidant and benzenamine, *N*-phenyl-, reaction products with 2,4,4-trimethylpentene; CAS 68411-46-1) as an amine antioxidant. VP4811 is a trifunctional copolyether polyol consisting of PO and EO repeating units, with an EO content of 12 mol%. It has a hydroxyl number of 48 mg KOH g⁻¹, a molar mass of 3.5 kg mol⁻¹ and it contains the same phenolic and amine antioxidants as VP5611. PUF5611 and PUF4811 were synthesized from the corresponding ALCUPOL® polyol (F5611 and F-4811, respectively (66.1 and 65.9 wt% polyol per PUF5611 and PUF4811, respectively), an isomers mixture of 2,4- and 2,6-toluene diisocyanate (TDI) with isomer ratio of 80/20 (TDI index of 107), and water as a foaming agent to chemically produce CO₂. Kosmos® 29 (tin(II) octoate), TEGOAMIN® 33 and TEGOAMIN® BDE were used as gelling and foaming catalysts, while silicone TEGOSTAB® BF 2370 was used as a surfactant to control cell size and opening.

Tris(2-aminoethyl)amine (TREN; Sigma-Aldrich, Germany), polyethylenimine with number-average molar mass of 600 and 1800 g mol⁻¹ (PEI-600 and PEI-1800; Sigma-Aldrich, Germany), hexamethylenediamine (HMDA; Sigma-Aldrich, Germany) and triethylenediamine (DABCO; Aldrich, Germany) were used in degradation reactions. Acetonitrile (ACN; ≥99.9%; Riedel de Haën, Germany), methanol (MeOH; ≥99.9%; Merck, Germany), formic acid (FA; ≥98%; Fluka, Germany), ammonium formate (AmFm; ≥97%; Fluka, Germany), MQ-water (MQ) with 18.2 MΩ resistivity and polyethylene glycol (PEG) with weight-average molar mass of 4.0 kg mol⁻¹ were used to perform HPLC and size-exclusion chromatographic (SEC) experiments. Deuterated dimethyl sulfoxide (DMSO-*d*₆; Euriso Top, Germany) and trifluoroacetic acid (TFA; 99%; Aldrich, Germany) were used for ¹H NMR experiments. Hydrochloric acid (HCl; Euriso Top, Germany), ethyl acetate (EtOAc; Honeywell, USA) and MQ-water (MQ) were used for purification of RPs. Imidazole (Sigma-Aldrich, Germany), pyridine (Sigma-Aldrich, Germany), phenolphthalein (Merck, Germany), phthalic anhydride (Merck, Germany), potassium hydrogen phthalate (KHP; Acros Organics, USA), sodium hydroxide (NaOH; Honeywell, USA), and ethyl alcohol (EtOH; Carlo Erba, Italy) were used to determine hydroxyl number and acid value of RPs. Aquastar water standard 0.01% (Supelco, Germany), Aquastar CombiCoulomat reagent (Supelco, Germany) and chloroform (CHCl₃; Honeywell, Fluka) were used to determine water content in RPs. Tetrahydrofuran (THF; p.a.), 2,5-dihydroxybenzoic acid (≥ 99.0%), sodium trifluoroacetate (≥ 98.0%) and poly(methyl methacrylate) standards (PMMA; MALDI validation set, Fluka Analytical) were used to perform MALDI-TOF mass spectrometry experiments. TDI Ongronate (TDI 80/20), Kosmos® 29 (tin(II) octoate catalyst), B11 tertiary amine catalyst and silicone 2370 were used for flexible PUF synthesis and were obtained from Plama-pur, Slovenia. All chemicals were used as received.

PUF degradation. PUF was cryogenically ground into powder using a vibratory ball mill (Tehtnica Millmix 20 Domel, Slovenia). The reaction mixture consisted of ground PUF, amine degradation reagent (TREN, HMDA, PEI-600 or PEI-1800) with or without additional catalyst (DABCO) in case of HMDA, and corresponding VP as a medium (VP5611 or VP4811). The mixture was added to a 30 mL glass reactor vessel with magnetic stirrer and then tightly sealed with PTFE-coated silicone septa. The weight ratio of PUF to medium was kept constant; that is 6 g to 3 g. Prior to degradation, the reaction mixtures were purged with nitrogen to prevent oxidation of the amino groups and darkening of the polyol products. The reaction mixture was initially a thick paste that required a preheating step (heating to 175°C in a period of 3 min) to allow partial PUF liquefaction and efficient stirring. The reaction mixtures were heated with microwaves in a laboratory microwave reactor Monowave 400 (Anton Paar GmbH, Austria). The main heating cycle consisted of heating to a predetermined temperature (210, 220, or 230°C) in a span of 5 min and maintaining this temperature for a defined time (20, 30, or 40 min). After completion of the degradation experiment, the vials were cooled to room temperature by a stream of compressed air. The resulting reaction mixtures were centrifuged at 9000 rpm for 10 minutes to separate the upper polyol phase (crude polyol) from the lower solid phase (residues of the hard segments). For the second cycle of aminolysis, TREN was added to a crude polyol in excess to the remaining urethane groups, the content of which was determined from ¹H NMR spectra of the crude polyol in DMSO-*d*₆ with added TFA. The reaction mixture was subjected to a second heating cycle for 20 min at 220°C.

Purification of RPs. The isolated crude polyol was purified by liquid-liquid extraction, in which the solution of RP in ethyl acetate (EtOAc, c = 1 g mL⁻¹) was washed with 0.1 M HCl followed by water to remove low molar mass side products such as TDA isomers and trace amounts of urea and reagent. EtOAc was removed from the RP by evaporation at 60°C. The purified RPs were analysed by ¹H NMR, FTIR, SEC/UV-MALS-RI and MALDI-TOF MS. The lower solid phase composed mainly of residues of PUF hard segments functionalized with the amino groups of TDA and/or reagent and residual polyol, which was isolated from residues of PUF hard segments by extraction with EtOAc and further purified in a similar manner as described above.

Synthesis of flexible PUFs. Various amounts of VP (0, 20, 50, or 100%) were replaced by RP in the PUF formulation. The flexible PUFs were synthesized according to the standard 'cup' procedure described in our previously published work⁷. The synthesized flexible PUFs were cut into test specimens (2.5 × 2.5 × 1.0 cm³) for analysis of morphology and mechanical properties.

Characterization methods for polyols

Nuclear magnetic resonance (NMR). ¹H NMR spectra were recorded at room temperature in DMSO-*d*₆ with or without the addition of TFA using a Bruker AVANCE NEO 600 MHz instrument (Bruker Corporation, USA). Chemical shifts (δ) are given in ppm relative to a DMSO-*d*₆ residual peak.

Content of residual urethane groups in the RPs was determined from their ¹H NMR spectra recorded in DMSO-*d*₆ with added TFA to shift the signal of the amino groups, which overlaps with the signal of the polyol methyne groups adjacent to the urethane groups, to higher chemical shifts. The content of residual urethane groups in the RPs was determined according to equation (1) from the integral of the signal of the polyol methyne protons (–NHCOO–CH–) adjacent to the residual urethane groups at δ 4.88 ppm (c) and the integral of the polyol methyl signal (–CH₃; a) at δ 1.04 ppm, assuming 50 PO repeat units in the polyol arms and a functionality of the polyol of 3.

$$\text{Urethane group (–NHCOO–) content (mol\%)} = \frac{I(-CH<)_{c} \times 50}{I(-CH_{3})_{PO}} \times 100 \quad (1)$$

The TDA content in crude RPs was determined from the ^1H NMR spectra recorded in $\text{DMSO-}d_6$ according to Eq. (2) from the signal intensities of the methyl groups of the TDA isomers (δ 1.79 for 2,6-TDA and 1.88 ppm for 2,4-TDA; signals **e** and **h**, respectively) and the methyl group (**a**) of the PO repeating unit of the polyol at δ 1.04 ppm.

$$\text{TDA content (wt\%)} = \frac{I(-\text{CH}_3)_{\text{TDA}} \times M(\text{TDA})}{(I(-\text{CH}_3)_{\text{PO}} \times M(\text{PO}) + I(-\text{CH}_3)_{\text{TDA}} \times M(\text{TDA}))} \times 100 \quad (2)$$

The content of amino ($-\text{NH}_2$) end groups in the RPs was determined from ^1H NMR spectra of the purified RPs recorded in $\text{DMSO-}d_6$ according to equation (3) from the intensity of the methyl signals ($-\text{CH}_3$) of the TDA isomer moieties attached to the polyol via the urethane groups (δ 2.00, 1.96 and 1.87 ppm for both isomers; denoted as **d**) and the intensity of the methyl signal (**a**) of the polyol at δ 1.04 ppm, assuming that 50 PO repeat units are present in the polyol with a functionality of 3.

$$-\text{NH}_2 \text{ content (mol\%)} = \frac{I(\text{CH}_3)_d \times 50}{I(-\text{CH}_3)_{\text{PO}} \times 3} \times 100 \quad (3)$$

Matrix-assisted laser desorption / ionization time-of-flight mass spectrometry (MALDI-TOF MS) measurements were performed using a Bruker UltrafleXtreme MALDI-TOF mass spectrometer (Bruker Daltonics, Germany). Polyol samples were dissolved in THF ($c = 10 \text{ mg mL}^{-1}$) and mixed with a solution of the matrix, 2,5-dihydroxybenzoic acid in THF ($C = 30 \text{ mg mL}^{-1}$) and sodium trifluoroacetate in THF ($c = 10 \text{ mg mL}^{-1}$), in a volume ratio of 1/10/3. A 0.4 μL of the prepared solution was spotted onto the target plate (dried-droplet method). The mass spectra of the samples were recorded in reflective positive ion mode. Calibration was performed externally using a mixture of PMMA standards dissolved in THF covering the measured molecular weight range. Sample preparation for the standard mixture was the same as for the samples. The standard mixture was spotted to the nearest neighbour positions.

Size-exclusion chromatography coupled with a multidetection system consisting of a UV-detector, a multi-angle light scattering photometer (MALS), and a refractive index (RI) detector (SEC/UV-MALS-RI). The molar mass characteristics (M_w , M_n , dispersity: $\mathcal{D} = M_w/M_n$) and purity of RPs were determined using SEC connected to a UV detector operating at a wavelength of 280 nm (Agilent Technologies, USA), a DAWN multi-angle light scattering photometer (Wyatt Technology Corp., USA), and an Optilab interferometric refractometer (RI) (Wyatt Technology Corp., USA). Separations were performed at room temperature using a TSKgel Alpha-2500 SEC column (7.8 mm ID \times 30.0 cm L, pore size 7 μm , and exclusion limit 10 kDa) with a precolumn (Tosoh Bioscience GmbH, Germany). Methanol (MeOH) was used as the solvent and mobile phase at a flow rate of 0.7 mL min^{-1} . Toluene was used to calibrate the 90° LS detector, while the other detectors were normalized with the standard polyethylene glycol (PEG) with a weight-average molar mass of 4 kDa and a dispersity of 1.02. The typical RP concentration in MeOH was $1.0 \times 10^{-2} \text{ g mL}^{-1}$, while the injection volume was typically 100 μL . The specific refractive index increment (dn/dc) required to calculate the molar masses of RPs was determined from VP5611 or VP4811, assuming 100% mass recovery of the samples from the column. Astra 8 software was used for data acquisition and analysis (Wyatt Technology Corp., USA).

Declarations

Competing interests

Based on these results a patent application (No.: LU501979) authored by E. Ž., D. P., M. G., and B. Z. has been submitted by National Institute of Chemistry, Slovenia.

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Figures

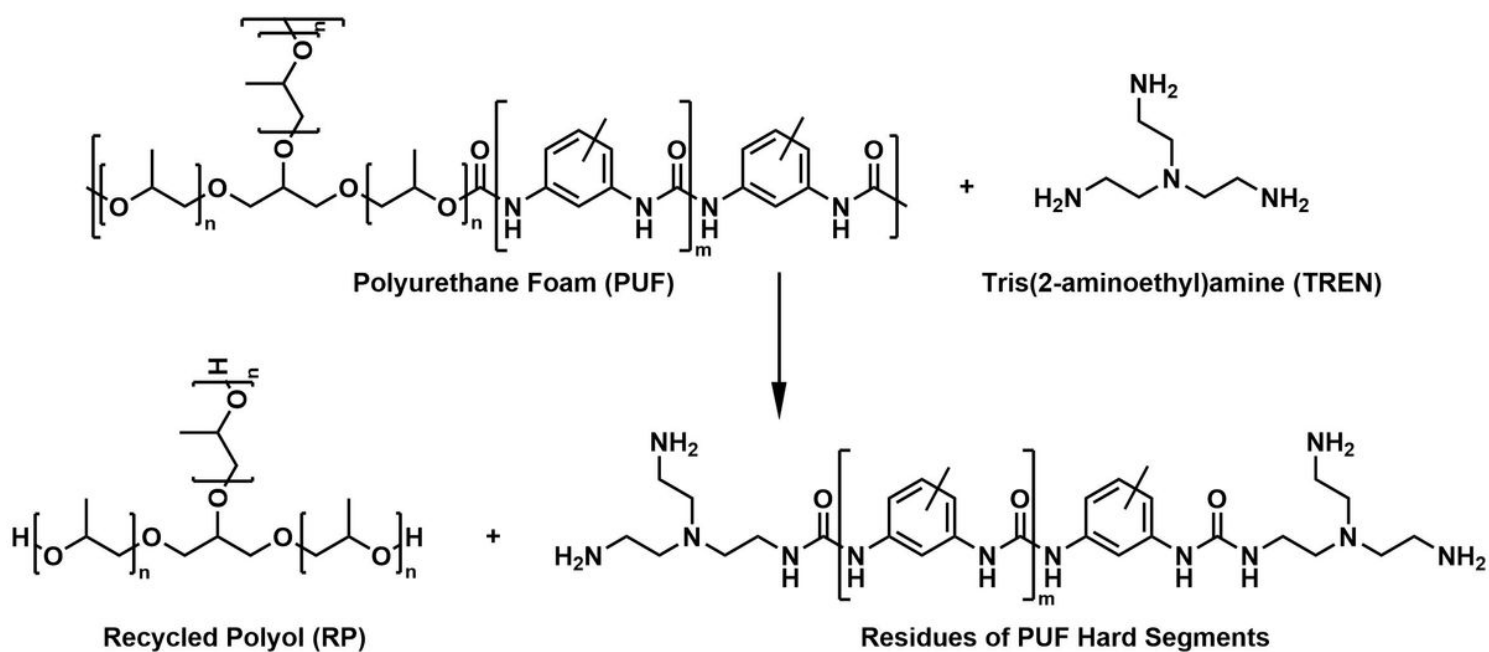


Figure 1

Reaction scheme of aminolysis of PUF with TREN leading to RP and residues of PUF hard segments terminated via urea bond with TREN.

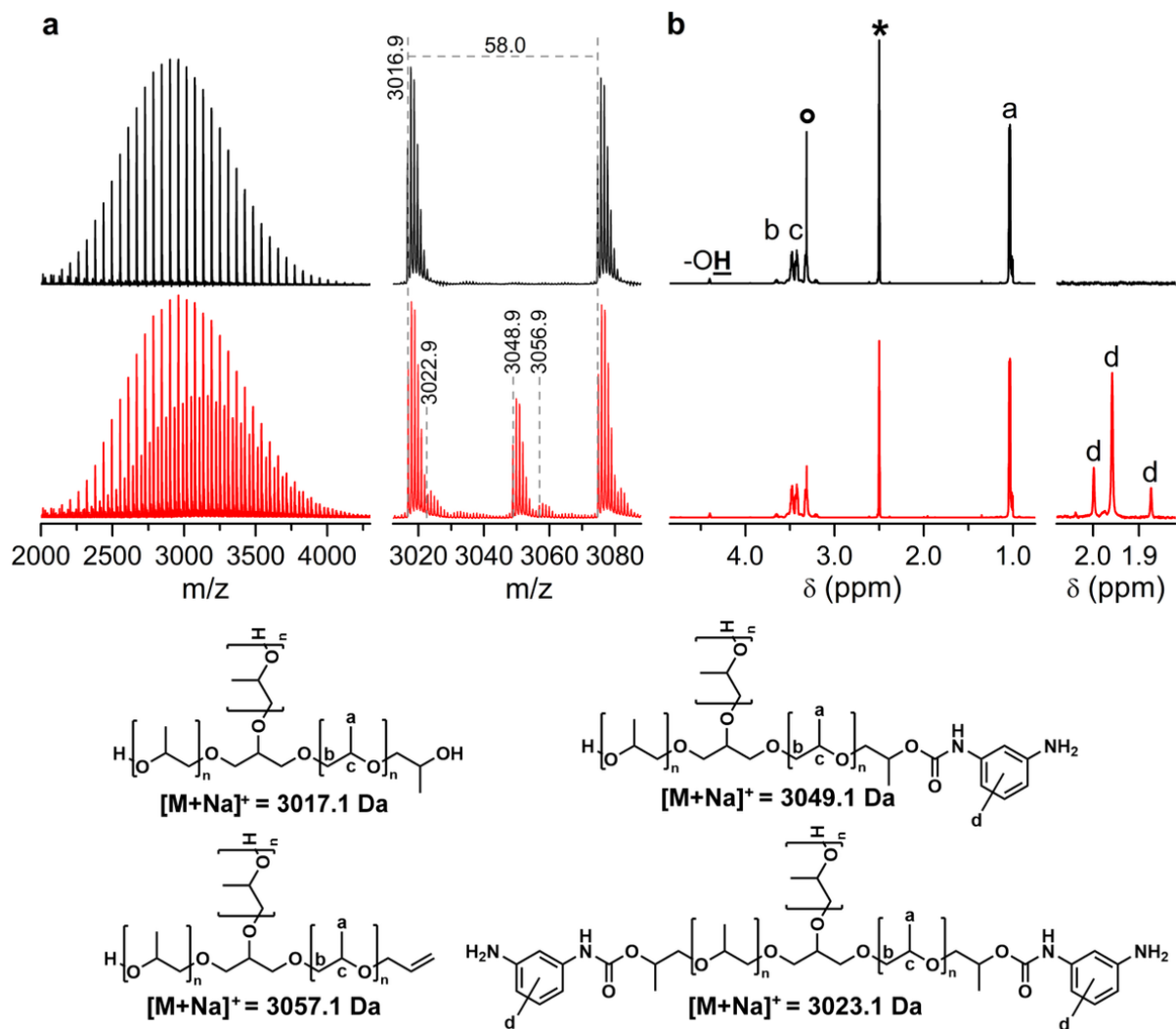


Figure 2

a) MALDI-TOF mass spectra of RP (bottom) after incomplete urethane group degradation and virgin polyol VP5611 of the same type (top). The MALDI-TOF mass spectrum shows four peak populations corresponding to the proposed polyol structures with different end-groups. The measured monoisotopic signals of these populations are shown in the magnified regions of the mass spectra. b) ^1H NMR spectra of the typical RP (bottom) and the corresponding VP5611 (top) with proton assignment. The ^1H NMR spectra were normalized to the methyl group of the PO repeating units. The residual DMSO solvent peak and water in the ^1H NMR spectra are indicated with an asterisk and a circle, respectively. The magnified region shows the signals of the methyl groups of three isomeric aromatic amino end groups of RP (indicated by d).

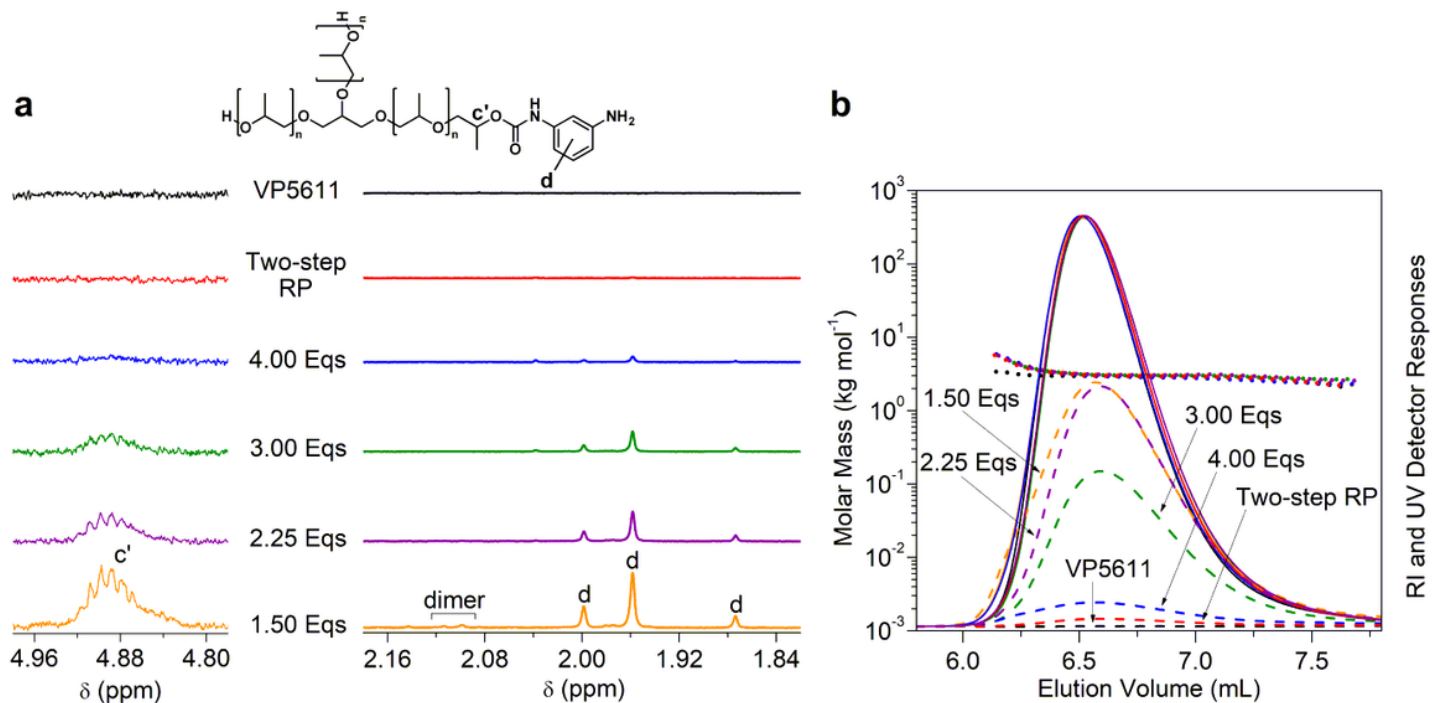


Figure 3

a) Magnified ^1H NMR spectra in the region of the polyol methyne signal adjacent to the urethane group (indicated by c'; spectra recorded in DMSO-d_6 with added TFA to shift the signal of the amino end groups of the polyol overlapping with c' to a lower magnetic field) and the signals of the methyl groups of three isomeric aromatic amino end groups (indicated by d; spectra recorded in DMSO-d_6), and b) SEC/UV-RI chromatograms of RPs recovered from PPO-based PUF by aminolysis with TREN at 1.50, 2.25, 3.00, and 4.00 Eqs amino per urethane group, RP obtained by a two-step aminolysis process, and the corresponding VP5611 virgin polyol (black). The ^1H NMR spectra were normalized to the methyl group of the PO repeating units. The solid and dashed curves in the SEC/UV-RI chromatograms represent the RI and UV detector responses, respectively, while the dotted lines show the molar mass as a function of elution volume.

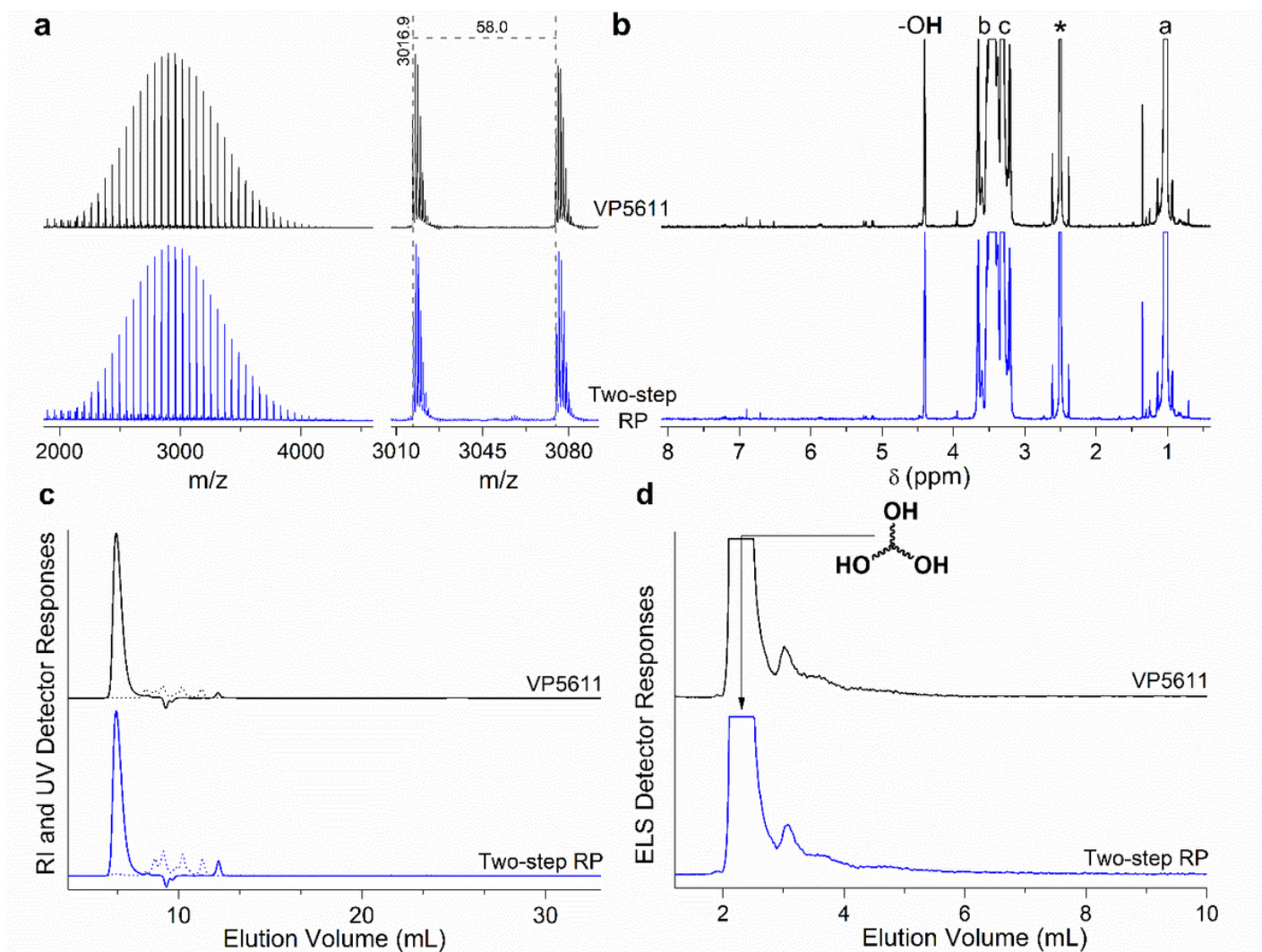


Figure 4

Comparison of a) MALDI-TOF MS, b) ^1H NMR, c) SEC/RI-UV, d) HPLC characterization results for purified RP recovered from PPO-based PUF by a two-step aminolysis procedure with TREN and the corresponding VP5611. The measured monoisotopic signals of the fully hydroxyl-functionalized polyol in MALDI-TOF mass spectra are shown in the magnified regions of a). The ^1H NMR spectra were normalized to the methyl group of the PO repeating units. The peak assignment refers to the structures in Table S2. The residual DMSO solvent peak in the ^1H NMR spectra is indicated with an asterisk. The solid and dashed curves in c) represent the RI and UV detector responses, respectively.

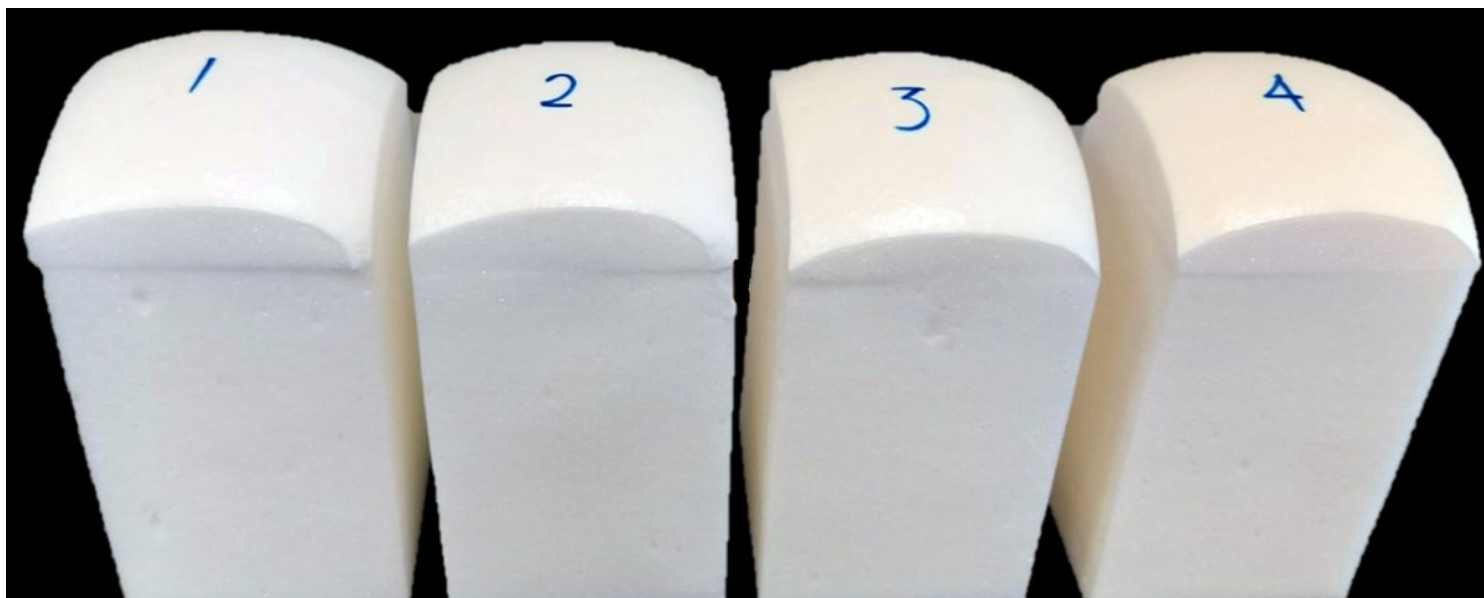


Figure 5

Photos of PUFs where different amounts of VP4811 in the PUF formulation were replaced with fully hydroxyl-functionalized RP4811: 1) 0%, 2) 20%, 3) 50%, and 4) 100%.

Supplementary Files

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