

Recycling Polyurethanes through Transcarbamylation

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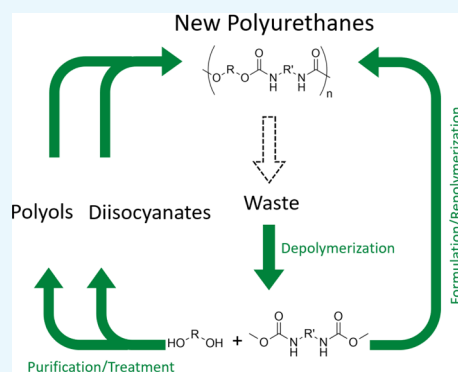


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ABSTRACT: In this paper, we describe a new strategy to recycle polyurethanes (PUs) using base-catalyzed transcarbamylation. PUs were depolymerized qualitatively in the presence of MeOH (methanol)/tetrahydrofuran as a solvent and *tert*-butoxide as a base catalyst. The resulting depolymerized mixture constituted by *O*-dimethylcarbamates and polyols can either be used as the starting material to synthesize new PUs with the transcarbamylation approach or be purified to recover polyols and diisocyanates. The versatility and easy scaling-up of the experimental procedures and high depolymerization outcomes of the presented method make this strategy very attractive for PU recycling.



INTRODUCTION

Polyurethane (PU) is one of the most used polymers all over the world. The global production of PU was 22.9 million tons in 2017 and is increasing by 4.5% per year.^{1,2} As a result of the increasing quantity of PU demand, a large amount of PU waste, particularly foams, was disposed of by landfilling in the last decades. Postconsumer products as well as scraps from postproduction products reach almost 10% of the total production.³ However, increasing landfill costs, decreasing landfill space, environmental issues, and strengthening of public policies and regulations are forcing consideration of alternative options for the disposal of PU materials. PU recycling has experienced growing attention from the research and industrial world;⁴ recycling of any kind of plastic to convert it into valuable products is one of the main challenges of today's society.

PU recycling is an alternative approach to landfilling. There are three kinds of strategies: (i) physical recycling (corresponding to the mechanical transformation of PU foams into flakes, granules, or powder to be used in new materials production); (ii) energy recovery (conversion of PU waste materials into useable heat, electricity, or fuel), and (iii) chemical recycling (consisting of the transformation of polymer chains into valuable chemicals).³ Several processes have been developed to chemically recycle PU foams, such as hydrolysis^{3,5–7} (the first process developed to recycle PU waste in a chemical way, in particular for flexible PU foams), aminolysis^{8–10} (the polymer chain is degraded with low molecular-weight amines), phosphorolysis^{11–19} (a reaction analogous to hydrolysis in which esters of phosphonic or phosphoric acids perform in a similar way to that of water with the formation of a phosphate), and glycolysis^{20–29} (the PU chain is fragmented by glycols producing polyols). Meth-

analysis of PU foams was also investigated by several groups,^{30,31} starting from commercially available PU foams and thermoplastic PU (TPU) elastomer. However, the depolymerization of PU operated at high temperatures (above 200 °C) with supercritical methanol limits its development.

The development of sustainable alternative and environmentally friendly routes to recyclable materials is of great interest, especially when recycling processes are able to obtain the basic valuable chemicals or building blocks which can be reused in the synthesis of chemical material or in the petrochemical industry. In this context, the transcarbamylation reaction is an interesting reaction, allowing the conversion of a carbamate to another carbamate (Figure 1). Several metal catalysts are known to be able to activate the carbonyl group and catalyze transcarbamylation,^{32,33} such as titanium(IV) isopropoxide,³⁴ lanthanum(III) salts,^{35,36} dihalodistannoxanes,³⁵ zinc acetate³⁶ or bismuth triflate,³⁷ inorganic or organic

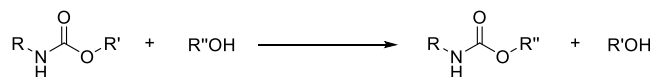


Figure 1. Transcarbamylation reaction of a carbamate (R, R' = aliphatic or aromatic group and R'' = aliphatic group).

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bases such as 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD),³⁸ and even without any catalyst with sulfonyl carbamates.³⁹

Transcarbamoylation can be used as well to synthesize PUs to avoid the use of toxic isocyanates.^{40–43} Recent works have shown that transcarbamoylation is an efficient reaction and can be operated in mild conditions with a soft base at low temperatures (<70 °C) offering promising perspectives in the field of PU recycling.³⁸ Here, we investigate a recycling procedure involving the depolymerization of PU wastes producing dicarbamates and polyols coupled to the repolymerization of these intermediates to regenerate new PUs both using transcarbamoylation reaction in mild conditions (Figure 2).³⁸ The key intermediate in this strategy is the O-

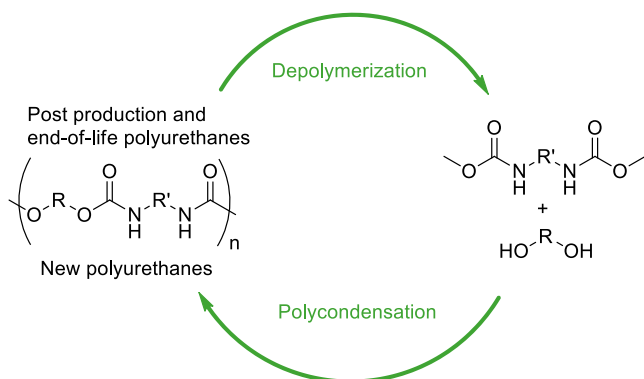


Figure 2. Recycling of PUs through transcarbamoylation.

dimethylcarbamate obtained from the complete depolymerization of PU through transcarbamoylation in the presence of methanol (namely methanolysis). This *O*-dimethylcarbamate is stable to be reformulated or isolated and reactive enough to form a new urethane bond with the elimination of MeOH allowing the regeneration of PU.

MATERIALS AND METHODS

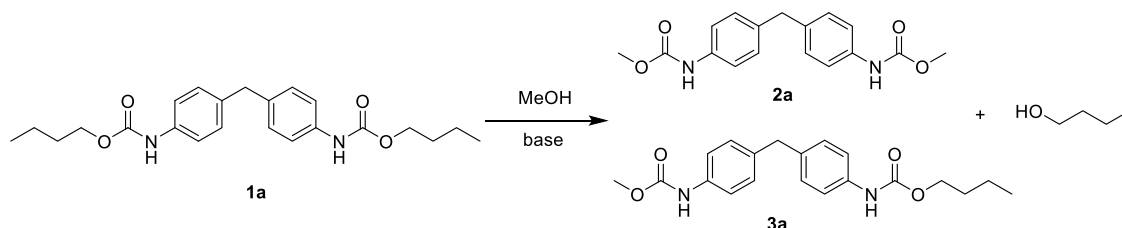
All solvents used were dry solvents purchased from Sigma-Aldrich. All reagents were purchased from Sigma-Aldrich and used without further purification. ¹H NMR spectra were recorded with a Bruker Avance III (400 MHz). DMSO-*d*₆ or CDCl₃ was used as the solvent and tetramethylsilane as the internal standard. Chemical shifts (δ) and coupling constants (*J*) are given in parts per million and in hertz, respectively. High-performance liquid chromatography (HPLC) was monitored using an HP Agilent 1050 series HPLC with a diode array detector. HPLC analysis was performed on a Vydac 218TP column (C18, 5 μ m, 4.6 mm i.d. \times 250 mm) by using a linear gradient of A [0.1% trifluoroacetic acid (TFA) in H₂O] and B (MeCN containing 0.1% TFA) at a flow rate of 1.0 mL/min with UV detection at 254 nm. All solvents were HPLC grade. The volume of the sample injected was set at 5 μ L. The molecular weights (*M_w*) and molecular weight distributions of polymers (polydispersity index) were evaluated by size exclusion chromatography (SEC) using an Agilent 1260 Infinity Series GPC (ResiPore 3 μ m, 300 \times 7.5 mm), 1.0 mL/min, UV (250 nm), and refractive index (PLGPC 220) detector. All measurements were performed with tetrahydrofuran (THF) as the eluent at a flow rate of 1.0 mL/min at 35 °C. Monodisperse poly(styrene) polymers were used as calibration standards. Attenuated total reflection-IR was used to characterize the infrared absorption spectra of PU

samples. The infrared spectra were recorded on a Nicolet Magna 550 spectrometer equipped with a diamond probe.

Synthesis of Model *O*-Dibutylcarbamates 1a and 1b. Diisocyanate [methylene diphenyl 4,4'-diisocyanate (MDI) or 1,6-diisocyanatohexane (HMDI)] (16 mmol) was added to 40 mL of dry 1-butanol at ambient temperature slowly. Dibutyltin dilaurate (10 μ L, 0.016 mmol) was added, and the reaction mixture was stirred at 50 °C for 3 h. The 1-butanol was evaporated under reduced pressure to give a white solid. The residue was purified by silica column chromatography eluting with hexane/ethyl acetate EtOAc (75/25). The fractions were concentrated under reduced pressure to give the product **1** (Figure S1). *O*-Dibutylcarbamate **1a**: white solid (5.8 g, 91% yield). ¹H NMR (400 MHz, chloroform-*d*): δ 7.31–7.26 (m, 4H), 7.12–7.07 (m, 4H), 6.59–6.51 (m, 2H), 4.15 (t, *J* = 6.7 Hz, 4H), 3.88 (s, 2H), 1.69–1.62 (m, 4H), 1.46–1.35 (m, 4H), and 0.95 (t, *J* = 7.4 Hz, 6H). *O*-Dibutylcarbamate **1b**: white solid (6.2 g, 95% yield). ¹H NMR (400 MHz, DMSO-*d*₆): δ 6.98–6.86 (m, 2H), 3.97–3.83 (m, 4H), 3.50–3.41 (m, 2H), 1.69 (dd, *J* = 39.9, 12.7 Hz, 4H), 1.56–1.19 (m, 20H), 1.19–1.03 (m, 4H), and 0.89–0.84 (m, 6H).

Synthesis of Model *O*-Dimethylcarbamates 2a–e. Diisocyanate [MDI, hexamethylene diisocyanate (HDI), HMDI, 2,6-tolylene diisocyanate (2,6-TDI), or 2,4-tolylene diisocyanate (2,4-TDI)] (5 mmol) was added to 10 mL of dry methanol at ambient temperature slowly. Dibutyltin dilaurate (5 μ L, 0.008 mmol) was added, and the reaction mixture was stirred at 50 °C for 3 h. Methanol was evaporated under reduced pressure to give a white solid. The residue was purified by silica column chromatography eluting with hexane/EtOAc (75/25). The fractions were concentrated under reduced pressure to give the corresponding desired product **2a–e** (Figure S2). *O*-Dimethylcarbamate **2a**: white solid (1.52 g, 97% yield). ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.52 (s, 2H), 7.33 (d, *J* = 8.2 Hz, 4H), 7.12–7.04 (m, 4H), 3.77 (s, 2H), and 3.62 (s, 6H). *O*-Dimethylcarbamate **2b**: white solid (1.45 g, 89% yield). ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.05–6.96 (m, 2H), 3.05–3.45 (m, 8H), 1.71 (dd, *J* = 40.5, 12.8 Hz, 4H), 1.54–1.38 (m, 8H), and 1.30–1.05 (m, 8H). *O*-Dimethylcarbamate **2c**: white solid (1.04 g, 90% yield). ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.09–7.01 (m, 2H), 3.49 (s, 6H), 2.95–2.90 (m, 4H), 1.38–1.31 (m, 4H), and 1.23–1.19 (m, 4H). *O*-Dimethylcarbamate **2d**: white solid (1.14 g, 96% yield). ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.91 (s, 2H), 7.13 (d, *J* = 1.6 Hz, 3H), 3.64 (s, 6H), and 2.04 (s, 3H). *O*-Dimethylcarbamate **2e**: white solid (1.15 g, 97% yield). ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.53 (s, 1H), 8.79 (s, 1H), 7.48 (d, *J* = 2.2 Hz, 1H), 7.18–7.13 (m, 1H), 7.07–7.03 (m, 1H), 3.63 (d, *J* = 1.8 Hz, 6H), and 2.10 (s, 3H).

Methanolysis of *O*-Dibutylcarbamate 1. The urethane **1** (0.224 mmol) was dissolved in methanol (2 mL). A base [NaOH, KOH, LiOH, NaH, 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU), TBD, *tert*-butoxide (*t*-BuOK), 1.0–2.0 equiv per urethane group] was added, and the reaction mixture was heated at 55 or 65 °C with continuous agitation for 20 h. The solvent was evaporated, and water (15 mL) was added and extracted with EtOAc (3 \times). The combined organic layers were washed with brine, dried on magnesium sulfate, and the solvent was evaporated. The residue was purified by silica column chromatography eluting with hexane/EtOAc (75/25). The fractions were concentrated under reduced pressure to give the product **2**.

Table 1. Optimization of the Transcarbamoylation Reaction Conditions^a

entry	base	equiv ^b	temp. (°C)	conversion ^c	2a/3a ^c	isolated yield ^d (%)
1	KOH	2.0	65	66% (20 h)	76/24	45
2	NaOH	2.0	65	78% (20 h)	90/10	73
3	LiOH	2.0	65	68% (20 h)	80/20	57
4	NaH	2.0	65	79% (20 h)	90/10	70
5	<i>t</i> -BuOK	2.0	65	85% (20 h)	97/3	80
6	TBD	2.0	65	86% (20 h)	97/3	79
7	Et ₃ N	2.0	65	1% (20 h)	ND	trace
8	DBU	2.0	65	65% (20 h)	85/15	60
9	<i>t</i> -BuOK	2.0	65	79% (14 h)	88/12	75
10	<i>t</i> -BuOK	2.0	65	61% (8 h)	71/29	ND
11	<i>t</i> -BuOK	1.5	65	76% (20 h)	86/24	75
12	<i>t</i> -BuOK	1.0	65	48% (20 h)	60/40	ND
13	<i>t</i> -BuOK	2.0	55	38% (20 h)	50/50	ND

^aReactions were run with 0.224 mmol of **1** in 2 mL of MeOH with 0.448, 0.672, or 0.896 mmol of base for 8–20 h at 55 or 65 °C. ^bEquivalent per urethane group. ^cConversion of compound **2a** group determined by LC/MS analysis of the crude products. ^dIsolated yield (by column chromatography) of compound **2a**. ND: not determined.

General Procedure for the Depolymerization of PU 4a–e. PU **4a–e** (300 mg) was suspended in THF (2 mL) and methanol (2 mL), 2.0–2.7 equiv per carbamate group of *t*-BuOK was added to the solution, and the solution was kept at continuous agitation under 65 °C for 20 h. The solvent was then evaporated, and water (20 mL) was added to the reaction mixture and extracted with EtOAc (3×). The combined organic layers were washed with brine, dried on magnesium sulfate, and the solvent was evaporated. The residue was purified by silica column chromatography with hexane/EtOAc (75/25). The fractions were concentrated under reduced pressure to give the product **2a–e**.

Optimization of Transcarbamoylation-Based Polycondensation 2a–e with PTMO. *O*-Dimethylcarbamate **2** (0.235 mmol), PTMO 2000 (450 mg, 0.224 mmol), and TBD (10 mg, 0.07 mmol) were added to 10 mL of dry toluene. The temperature was progressively increased to 130 °C under nitrogen flow (to remove MeOH) and stirring. Then, the polymerization reaction was conducted over 16 h. Finally, after it was cooled to room temperature, the obtained PU **4a–e** was solubilized in THF and precipitated in cooled methanol.

General Procedure to Recycle TPU (Pellethane 2363-80AE). Pellethane 2363-80AE (300 mg) was suspended in THF (3 mL) and methanol (3 mL), *t*-BuOK (60 mg, 0.54 mmol) was added to the solution, with continuous agitation under 65 °C for 20 h; the solvent was evaporated, and water (20 mL) was added to the reaction mixture and extracted with EtOAc (3×). The combined organic layers were washed with brine and dried on magnesium sulfate, and the solvent was evaporated. The residue was dissolved in dry toluene (20 mL), with a nitrogen inlet, monomer **2** (9 mg, 0.03 mmol), and TBD (10 mg, 0.07 mmol) added to the solution; the temperature was progressively increased to 130 °C under nitrogen flow (to remove MeOH) and stirring. Then, the polymerization reaction was conducted over 16 h. Finally, after

it was cooled to room temperature, the obtained PU was solubilized in THF and precipitated in methanol to get regenerated PU (220 mg, yield: 74%).

RESULT AND DISCUSSION

We first investigated the reactivity of transcarbamoylation. Dibutyl(methylenebis(4,1-phenylene))dicarbamate **1a** was chosen as the model substrate for aromatic carbamates to optimize reaction conditions including bases, temperatures, and reaction times. The results are summarized in Table 1. According to the previous work carried out by our group,³⁸ we first used 2 equiv per urethane group of potassium hydroxide (KOH) as the base at 65 °C in the presence of methanol (Table 1, entry 1). The reaction afforded a mixture of compounds **1a**, **2a**, and **3a** (detected by HPLC) conducting a yield of 45% in disubstituted dicarbamate **2a**. In order to increase the yield of the compound **2a**, other inorganic bases such as sodium hydroxide (NaOH), lithium hydroxide (LiOH), and sodium hydride (NaH) as well as organic bases such as potassium *t*-BuOK; TBD, triethylamine (Et₃N), and DBU (Table 1, entries 2–8) were screened. Most of the bases evaluated (NaOH, KOH, LiOH, NaH, DBU, TBD, and *t*-BuOK) afforded dimethylcarbamates with good conversions. It was shown that the reaction is base-dependent, *t*-BuOK and TBD providing the highest yield (80 and 79% respectively). The impact of the reaction time (Table 1, entries 5, 9, and 10), equivalent of base (Table 1, entry 5, and entries 11–12), and reaction temperature (Table 1, entry 5, and entry 13) was studied. The yield of **2a** decreased with the reduction of reaction time or the amount of base. The best condition is 2 equiv of potassium *t*-BuOK as the base at 65 °C reacted for 20 h (Table 1, entry 5) and was kept for the rest of the study. Furthermore, the reactivity of aliphatic diurethane with the use of the dicarbamate **1b** as model substrate of aliphatic PU was also investigated resulting in the same observations (see the

Table 2. Depolymerization of PUs^a

entry	4	n	m	M _w	t-BuOK (equiv) ^b	conversion ^c (%)	isolated yield ^d (%)
1	4a	5	14	6500	2.0	79	75
2	4b	5	14	5250	2.0	65	53
3	4c	6	14	8200	2.0	71	63
4	4d	3	14	4700	2.0	78	74
5	4e	4	14	5900	2.0	78	65
6	4a	8	27	20,000	2.0	77	73
7	4a	11	27	28,000	2.0	81	78
8	4a	10	40	33,600	2.0	78	70
9	4a	11	27	28,000	2.3	90	85
10	4a	11	27	28,000	2.5	83	83
11	4a	11	27	28,000	2.7	85	81

^a300 mg of PU was suspended in 4 mL of solvent (MeOH/THF, 1/1), stirred at 65 °C, and *t*-BuOK was added then reacted for 20 h. ^bEquivalent per urethane group. ^cDetermined by ¹H NMR analysis of the crude products. ^dIsolated yield (by column chromatography) of dicarbamate 2.

Table 3. Optimization of Transcarbamoylation-Based Polycondensation^a

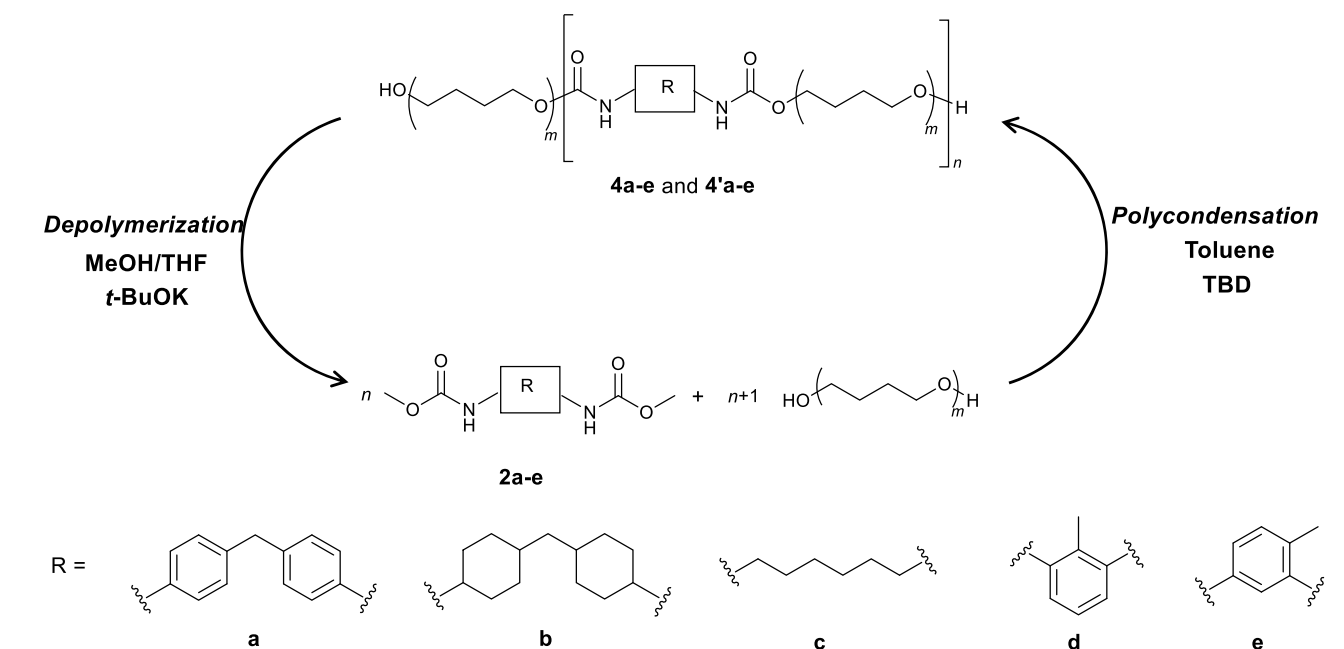
entry	2a (equiv)	base (equiv)	temp. (°C)	reaction times (h)	solvent	M _w (g/mol) ^b	M _w /M _n ^b	yield (%)
1	1.0	TBD (0.05)	130	8		6600	1.11	trace
2	1.0	TBD (0.05)	130	8	toluene	8900	1.21	35
3	1.0	TBD (0.15)	130	8	toluene	11,200	1.31	33
4	1.0	TBD (0.25)	130	8	toluene	11,200	1.51	34
5	1.0	TBD (0.15)	130	16	toluene	11,200	1.38	54
6	1.0	TBD (0.15)	150	16	toluene	11,200	1.55	56
7	1.1	TBD (0.15)	130	16	toluene	15,800	1.35	55
8	1.2	TBD (0.15)	130	16	toluene	15,800	1.41	51
9	1.1	TBD (0.15)	130	20	toluene	13,500	1.53	57
10	1.1	<i>t</i> -BuOK (0.15)	130	16	toluene	8900	1.45	52
11	1.1	TBD (0.05)	reflux	16	THF	4300	1.08	trace

^aReactions were performed under nitrogen flow with 0.224, 0.235, or 0.269 mmol diurethane 2a, 0.05–0.25 equiv per urethane group of TBD, and 0.224 mmol PTMO in 10 mL of anhydrous toluene or THF with corresponding base at appropriate reaction time and temperature. ^bDetermined by SEC.

Supporting Information, Table S1 for details). It is noteworthy that in our trials no byproducts such as aromatic amines were detected by liquid chromatography/mass spectrometry (LC/MS) due to the mild reaction conditions used. The excellent reactivity of aromatic and aliphatic dicarbamates subjected to transcarbamoylation reaction with methanol is consequently particularly interesting to develop depolymerization strategies of PU in mild conditions.

After the optimization of the transcarbamoylation reaction with the model dicarbamates, several PUs were synthesized to perform transcarbamoylation-based depolymerizations. PUs obtained from different diisocyanates (see the Supporting

Information) were reacted with *t*-BuOK using methanol (MeOH) and THF as solvents at 65 °C to produce the corresponding *O*-dimethylcarbamate and polytetrahydrofuran (PTMO). The results are shown in Table 2. Two equivalents of a base were used as the standard, and 5 different PUs (4a–4e) which are widely used in PU industry were chosen (Table 2, entries 1–5) to investigate the depolymerization by the described process. For all those PUs, depolymerization was observed affording the corresponding *O*-dimethylcarbamates (2a–2e) regardless of the chemical structure of the PUs (Table 2, entry 1–5) and their molecular weights (conversion ranging from 77–81%; Table 2, entries 1 and 6–8). It is worth

Table 4. Recycling PUs through Depolymerization and Polycondensation^a

entry	depolymerization of PU into monomers					repolymerized PU			
	4	R	$M_w/M_n^{b,f}$	M_w^b	yield (%) ^c	4'	$M_w^{d,f}$	$M_w/M_n^{d,f}$	yield (%) ^e
1	4a	2a	1.21	28,000	85	4'a	18,100	1.34	51
2	4b	2b	1.24	28,000	73	4'b	10,800	1.30	31
3	4c	2c	1.24	22,000	89	4'c	13,000	1.35	65
4	4d	2d	1.38	14,000	91	4'd	8900	1.42	56
5	4e	2e	1.33	20,000	81	4'e	10,000	1.33	41

^aDepolymerization conditions as described in Table 2. Polymerization: the same process as described in Table 3 (with extra 0.1 equiv of monomer 2). ^bPU synthesized by diisocyanate approach. ^cIsolated yield (monomer 2, by column chromatography) of depolymerization, calculated for the urethane group. ^dPU synthesized by transcarbamoylation. ^eYield of polymerization. ^fDetermined by SEC.

noting that with the increase of the amount of the base, the conversion rate and yield were improved, leading to the obtention of monomer 2a with high yields. We first optimized the base catalysis conditions (Table 2, entries 7 and 9–11). The best amount of *t*-BuOK was found to be 2.3 equiv (Table 2, entry 9). A remarkable fact is that THF can be substituted by MeOH by just increasing reaction times (THF being a good swelling solvent): for example, PU 4a ($M_w = 6500$ g/mol, 300 mg) reacted in 4 mL of MeOH at 65 °C for 20 h leads to 2a with a 73% yield.

One important advantage of methanolysis is the production of *O*-methylcarbamate, a useful reactive intermediate that can be used to regenerate PUs through transcarbamoylation associated to the release of MeOH which can be easily eliminated by evaporation during the reaction.^{40–42} We tried to achieve repolymerization to prepare PU by using the dicarbamate 2a and PTMO (2000); they were subjected to transcarbamoylation, with an organic base TBD to catalyze the reaction.⁴³ The results are shown in Table 3. We first tried a solvent-free condition; however, only a trace amount of PU was observed (Table 3, entry 1) possibly due to its poor solubility in liquid PTMO (2000). A solvent is required to observe the formation of PU, and toluene was therefore chosen as the solvent for the rest of the study (Table 3, entries 2–10). The effect of the quantity of base (TBD) to catalyze the reaction was then studied. When 0.15 and 0.25 equiv per urethane group of base were used (Table 3, entries 3 and 4), the molecular weights and yields increased. As expected, the

increase of the reaction time improved the polymerization yield (from 33 to 54%) (Table 3, entries 3 and 5), while there was no noticeable improvement under a higher reaction temperature (Table 3, entry 6). The use of an excess of dicarbamate improves polycondensation: 1.1 and 1.2 equiv have been tested, leading fortunately to PU with molecular weight of 15,800 g/mol (Table 3, entries 7 and 8). Attempts to use longer reaction time or some other base (*t*-BuOK) or solvent (THF) failed to improve the reactivity of transcarbamoylation (Table 3, entries 9–11).

Based on these optimal reaction conditions, we turned our attention to validate the cycle depolymerization/repolymerization on different PU structures (Table 4, entries 1–5). Five PUs 4a–4e (see the Supporting Information) were synthesized as starting material to screen the applicability of our chemical recycling processes. Depolymerization was performed according to the procedure described in Table 2, and after extraction, the products of depolymerization were used in the repolymerization reaction. Polycondensation was conducted at 130 °C under catalysis of TBD (0.15 equiv per urethane group) in toluene, with 1.1 equiv of monomer 2. Five different structures of PUs (scaffold corresponding to MDI, 2,6-TDI, 2,4-TDI, HMDI, and HDI) have been evaluated. Because of the high reactivity of the structure 2a (Table 4, entry 1), the M_w of the repolymerized PU (4'a) provided the best results in our system ($M_w = 18,100$ g/mol); all structures were able to achieve the original PU structure, although other compounds

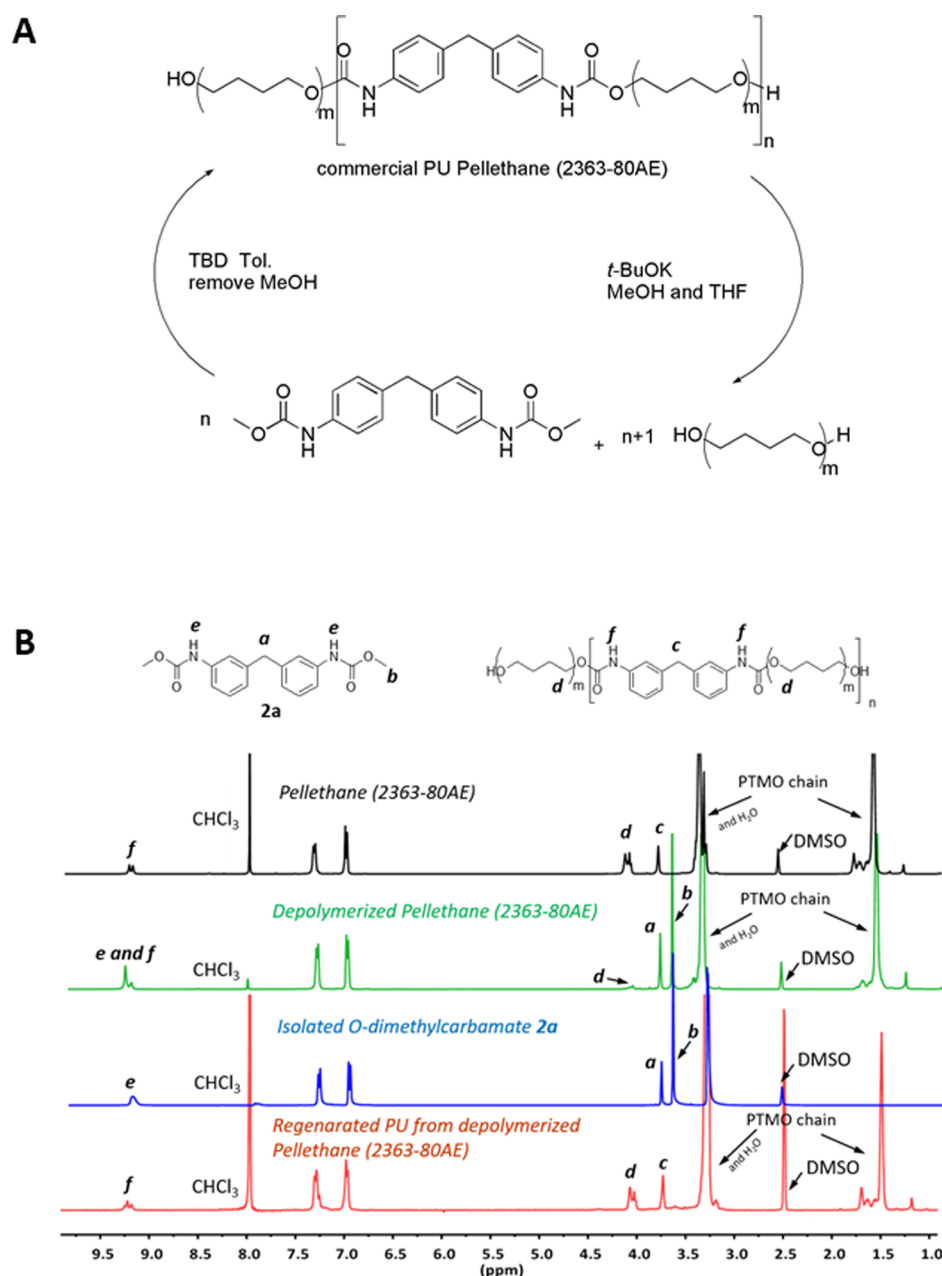


Figure 3. (A) Depolymerization of commercial TPU (Pellethane 2363-80AE) and regeneration of PU. (B) ¹H NMR spectra of raw Pellethane 2363-80AE (black), depolymerized Pellethane (green), the isolated *O*-dimethylcarbamate 2a (blue), and the regenerated PU (red).

4'b–4'e were not as remarkable as 4'a (the M_w are 8900–13,000 g/mol).

Encouraged by these results, we have extended our investigation to recycle commercial TPU (Pellethane 2363-80AE, $M_w = 110,331$ g/mol, $M_w/M_n = 2.10$). Pellethane was first depolymerized to afford the *O*-dimethylcarbamate 2a and PTMO (Figure 3A), which can be identified clearly by NMR in the spectrum of the crude of the depolymerization reaction [Figure 3B, ¹H NMR spectra of raw Pellethane (black trace), depolymerized Pellethane (green trace), *O*-dimethylcarbamate 2a (blue trace)]. This mixture was then incubated with TBD to regenerate PU successfully [Figure 3B, crude of the regenerated PU (red trace)] which was isolated by precipitation ($M_w = 19,500$ g/mol, $M_w/M_n = 1.40$). Alternatively to this route, the *O*-dimethylcarbamate 2a can be isolated due to its stability and possibly converted

subsequently into MDI^{44,45} offering new perspectives to regenerate diisocyanates to feed back into the classical PU industry.

With the aim to recycle PU scraps, we then turned our attention to the PU foams coming from waste electronic and electrical equipment (WEEE; foams from fridge/freezer) as well as construction and demolition waste (foams of insulating panels). Following this strategy, foams were first depolymerized using transcarbamoylation (see the Supporting Information). We can clearly observe in the NMR spectra of the crudes of depolymerization, shown in Figure 4A, the characteristic signals of *O*-methylurethane at 3.62 ppm as well as aromatic signals at 7.1 and 7.3 ppm corresponding to mainly *O*-dimethylcarbamate 2a originating from 4,4'-MDI-based PU (a major constituent of rigid foam) as well as other aromatic signals associated probably to different possible MDI

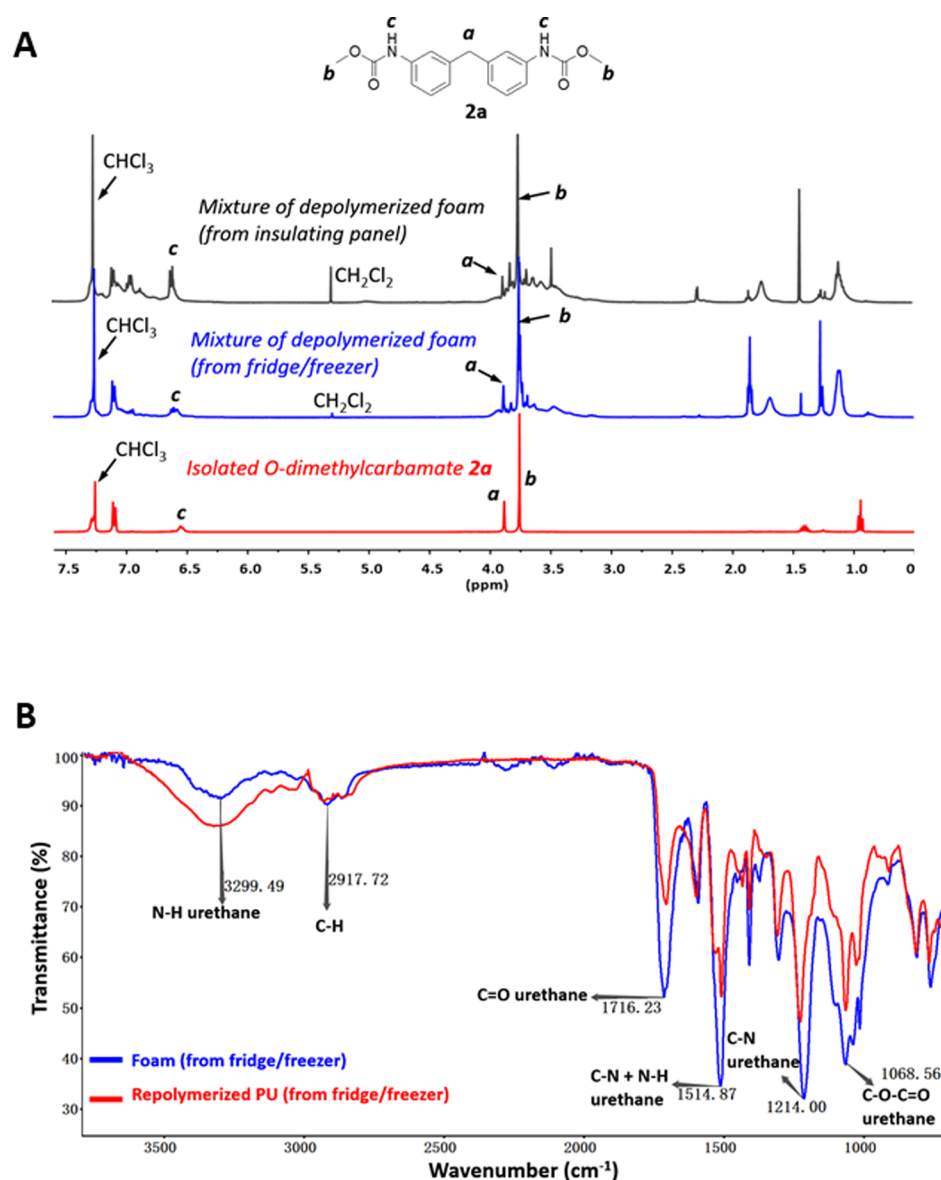


Figure 4. (A) Methanolysis of waste PU. ^1H NMR analysis of depolymerized foam (insulating panel, black; fridge/freezer, blue; monomer **2a**, red); (B) IR of foam from fridge/freezer (blue) and corresponding regenerated PU (red).

derivatives (isomers, polymeric forms) or aromatic polyols in the case of scrap from insulating panels. Unfortunately, because of the complex composition of the waste foams (e.g., mixtures of polyols, undefined additives: brominated flame retardant, etc.), carbamate **2a** is the only constituent identified by ^1H NMR.

The mixture resulting from depolymerization containing carbamates and polyols can then be used to regenerate new PUs. Reconstituted PU was prepared by polycondensation using TBD, starting from depolymerized foams from WEEE and removing unpolymerized materials and unincorporated substances after precipitation, PU was obtained, with characteristic signals in IR spectrum (Figure 4B).

Alternatively in the case of a more complicated mixture of depolymerization (foams of insulating panel), because of too much uncertain compositions in some rigid foams^{46–48} (e.g., polymeric MDI, undefined PUs; mixture of polyols, brominated flame retardant; catalysts; salts...), purification is preferred by the isolation of the carbamate **2a** with a yield of

16% (wt %) that could be further reformulated or further transformed into diisocyanates, associated to the classical recovery of polyols done in glycolysis for example.

CONCLUSIONS

In this report, a new chemical recycling process of PU (TPU and PU foams) is presented based on the transcarbamoylation reaction. PUs are depolymerized under mild and efficient conditions using a base and THF/MeOH as the solvent at 65 °C to provide quantitatively polyols and *O*-dimethylcarbamates making this strategy simple and easy to scale up. It is also noteworthy that THF can be substituted by MeOH offering great prospects. The obtention of *O*-dimethylcarbamates makes this strategy also very attractive since this intermediate is able to react with polyols to regenerate PUs using transcarbamoylation releasing MeOH. The reactivity of this intermediate also offers huge versatility in the outputs of this strategy since the mixture obtained from depolymerization can be used directly to regenerate new PUs through polyconden-

sation or by modifying the formulation (e.g., by adding polyols) to rectify or confer new properties or performances to the regenerated PU.⁴⁹ Alternatively, each constituent resulting from depolymerization can be isolated, particularly the *O*-dimethylcarbamates which due to their stability can be further reacted to synthesize new PUs (nonisocyanate routes)⁴⁹ or converted to diisocyanates to be fed back into the classical PU industry to generate virgin PUs. The last route is of interest in the case of the composition of PUs that is not suitable for the market or does not satisfy new regulations due to the presence of toxic substances (e.g., brominated flame retardant).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.0c04855>.

Experimental procedures and characterization data, ¹H NMR spectra of compounds, and gel permeation chromatography (PDF)

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Notes

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