FULL PAPER

Using NMR to Study the Process of Rigid Polyurethane Depolymerization

Juliana Proliciano Maioli, João Vitor Oliveira Soares, Fabricio Uliana, Thays Cardoso Valim, Carla Santana Francisco, Eloi Alves da Silva Filho, Valdemar Lacerda Junior, and Alvaro Cunha Neto*

LabPetro – Research and Methodology Development Laboratory for Crude Oil Analysis, Chemistry Department, Federal University of Espírito Santo, Av. Fernando Ferrari, 514, Goiabeiras, Vitória, ES, CEP: 29075-910, Brazil.

Abstract:

Polyurethanes (PUs) have been widely used in several trade sections. Thereby, large amounts of waste are produced and need to be correctly disposed of. Research on this theme has been helping industries to apply recycling processes that are cheap and efficient. In this work, the glycolysis of a rigid PU was performed using different catalysts. ^{1}H NMR analysis was used to obtain the rate of PU depolymerization. Glycerol (GCL) and diethylene glycol (DEG) were tested as glycolysis agents. The PU was synthesized to be free of additives in the depolymerization process, and its characterization was performed using FTIR and ^{1}H NMR analyses. The use of NaOH as a catalyst showed a better conversion rate, as is already known in the literature. Ionic liquids (LIs) also presented good results, which can be improved by modifying the reaction conditions. To determine the composition of the mixture of products in the depolymerization reaction, diffusion ordered spectroscopy ^{1}H NMR (DOSY-NMR) was used. DOSY-NMR indicated a complex mixture of reaction by-products, differently from the ^{1}H NMR data, which indicated the formation of a simple diamine-terminated by-product.

Keywords: catalysts; chemical recycling; glycerol; NMR; polyurethane

1. Introduction

Polyurethanes (PUs) are a class of polymers that possess various useful properties, such as chemical resistance to corrosion, abrasion, and compression, as well as hardness, thermal conductivity, and a long lifetime of many products. Because of the mentioned properties, it has become a polymer with wide application and market demand. [1–4]

This polymer class is mainly applied in foams for mattresses and automotive upholstery, thermal insulation in refrigerators, and the furniture and footwear industries, among others [5–7]. Large-scale production of these materials generates large amounts of waste. Chemical recycling, a depolymerization process, has been used as a solution to this problem of waste discard. This technique allows the recovery of at least one monomer, which can be purified by traditional methods and reused in the synthesis of new polymers. However, it is required that recycling be carried out in a safe, efficient, and environmentally friendly manner [3, 4, 8–13]. Recycling is only commercially viable depending on its cost/benefit and performance, therefore, it has aroused the interest of researchers in studies that enable its use [9, 14].

Among the chemical recycling processes, glycolysis is the one that stands out in the literature and is carried out by successive reactions of transesterification of the urethane bond. In the glycolysis process, a glycol solvent is used, for example, diethylene glycol, dipropylene glycol, ethylene glycol, polyethylene glycol, propylene glycol, or diethanolamine, and a catalyst, which may be a base, a Lewis acid, an organometallic, or an acetate, at a temperature between 170 and 220 °C [5, 8, 11, 12, 14–20]. The

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*Corresponding author. E-mail: ✉ alvarocunhaneto@gmail.com

reaction time, solvent, and catalyst have an influence on the degree of conversion from polymer to product.

Aiming to reduce glycolysis process costs, Nikje and Nikrah [21] tested flexible cold cure PU glycolysis using glycerol (GCL) as solvent and sodium hydroxide (NaOH) as catalyst. GCL is a low-cost by-product of biodiesel synthesis. Reaction time effect studies on the glycolysate product were performed at a temperature of 170–190 °C and it was observed that the product of 1 hour of reaction was the same as the product with 3 hours of reaction. Simón *et al*. [22] compared the use of crude GCL and 99% GCL as the glycolysis agent, using stannous octoate as the catalyst. The results were also compared with using diethylene glycol (DEG) in the same conditions, which is cited as the best glycolysis agent. The authors concluded that there is no difference in the products and yields when using the crude GCL or the 99% GCL and that the polyol obtained in the glycolysis using GCL is purer than when using DEG. Simón *et al*. [23], using another flexible PU type, compared the glycolysis process and observed that using crude GCL solvent produced better yields than 99% GCL and mainly when using DEG. Kopczynska and Datta [7] studied flexible PU glycolysis testing various catalysts (triethylamine, potassium acetate, 1,4-diazabicyclo[2.2.2]octane, sodium hydroxide, dibutyltin dilaurate, and stannous octoate) in the presence of crude GCL as solvent. There were reactions that formed products with two phases while others were single phase. The chemical characteristics of the product did not change when the catalyst was changed. Datta *et al*. [24] verified the influence of different proportions between elastomer PU/GCL on the product reaction. The authors recognized that it is possible to depolymerize the PU waste in proportions up to 10:1 by mass, obtaining the same depolymerization products as in smaller proportions. However, if there is interest in the separation of polyol there is a greater difficulty. Jutrzenka Trzebiatowska *et al*. [25] tested GCL at various purity levels and observed that when the purity level is between 40 and 62% the product obtained is of lower value added because secondary reactions occur in the medium due to the impurities in the GCL. Part of the recovered polyol was used to synthesize new cast PU, which was obtained with good mechanical characteristics.

In this present work, different catalysts were tested in the glycolysis not yet reported in the literature, such as hexadecyltrimethylammonium bromide (CTAB), niobium pentoxide (Nb_2O_5), hydrated niobium oxide (Nb_2O_5H), niobium pentachloride ($NbCl_5$), and niobium ammoniacal oxalate, as well as the ionic liquids (LIs) 1-butyl-3-methylimidazole trichloromanganate (LIMn) and 1-butyl-3-methylimidazole trichlorozincate (LIZn), and GCL and DEG were used as the solvents. The number of repeating units or degree of polymerization was obtained from the ^{1}H NMR spectra. The conversion rate was also calculated using ^{1}H NMR spectra for each depolymerization reaction and applied to the diffusion ordered spectroscopy ^{1}H NMR (DOSY-NMR) technique to determine the composition of the products.

2. Results and Discussion

2.1 Characterization of the synthesized PU

The PU infrared spectrum (Figure 1) presents bands at 3310 cm^{-1}, corresponding to the N–H bond stretching; 1697 cm^{-1}, corresponding to the C=O bond stretching; 1522 cm^{-1}, attributed to the C–N bond stretchingand N–H bond angular deformation, and 1223 cm^{-1} attributed to C–O bond stretching, which are characteristic of the polymer structure according to Motokucho *et al*. [13].
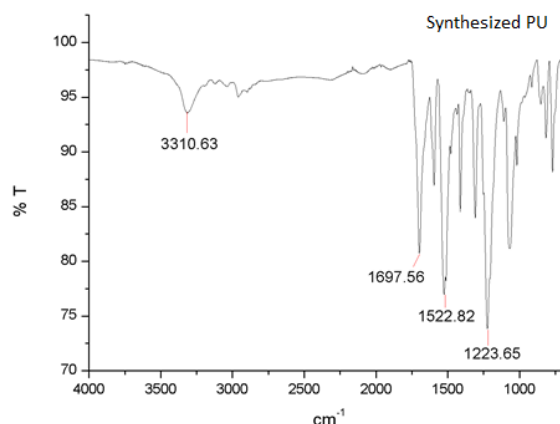

Figure 1. Infrared spectrum of synthesized PU.

The ^{1}H NMR spectrum (Figure 2) also shows signals from PU. Signals designated as *a* and *i*, are assigned to the CH_2 in the β position to the urethane group (-NH-CO-OCH$_2$**CH$_2$**-) and the

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terminal hydroxyl (-CH2**CH2**CH2-OH), respectively. The signal referred to as *b* indicates the methylene group between the aromatic rings (-Ph-C**H2**-Ph-). Signal *c* is assigned to the α-position CH2 of the urethane group (-NH-CO-OC**H2**-). Signal *d* is assigned to the terminal hydroxyl (-O**H**), and the signals designated *e* and *f* are assigned to the aromatic ring hydrogens. Finally, the signal *g* is assigned to the -N**H**-. Thus, the PU synthesized formation could be verified. Other signals at 8.0 and 2.75 ppm were attributed to the DMF, which was not completely removed in the methanol wash process.
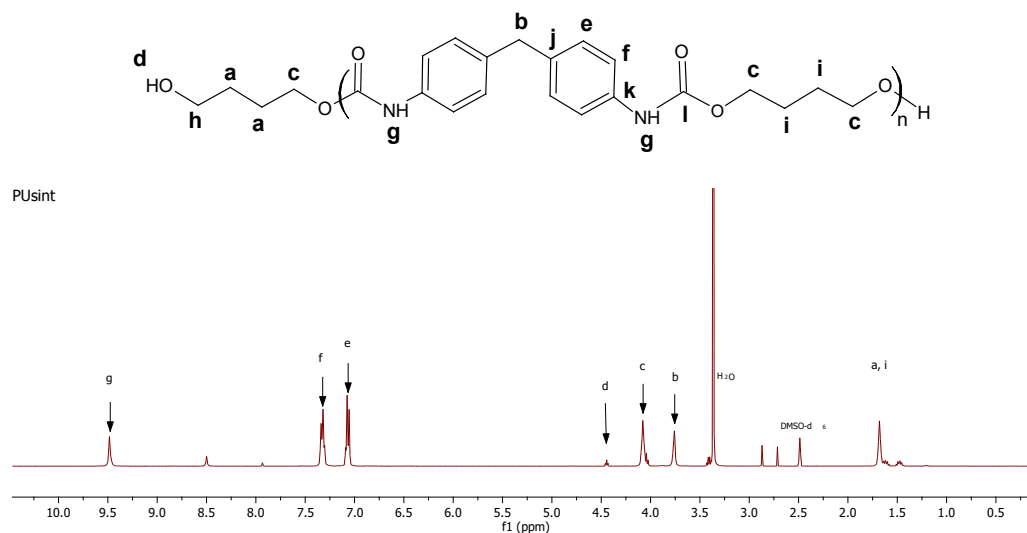

Figure 2. ^{1}H NMR spectrum of the synthesized PU, in DMSO-d$_6$.

The comparison of the integrations in Figure 2 indicate the degree of polymerization of the polymer. For the synthesized PU, the values of degree of polymerization show an average of five units of the monomers for each polymer molecule. The homogeneity of monomers distribution in the polymer formation is observed in Figure 3. In the ^{1}H NMR-DOSY spectrum of the polymer in DMSO-d$_6$, a small set os molecules appear with a diffusion coefficient between 0.6 and 1.4 x10^{-10} m^2 s^{-1}.
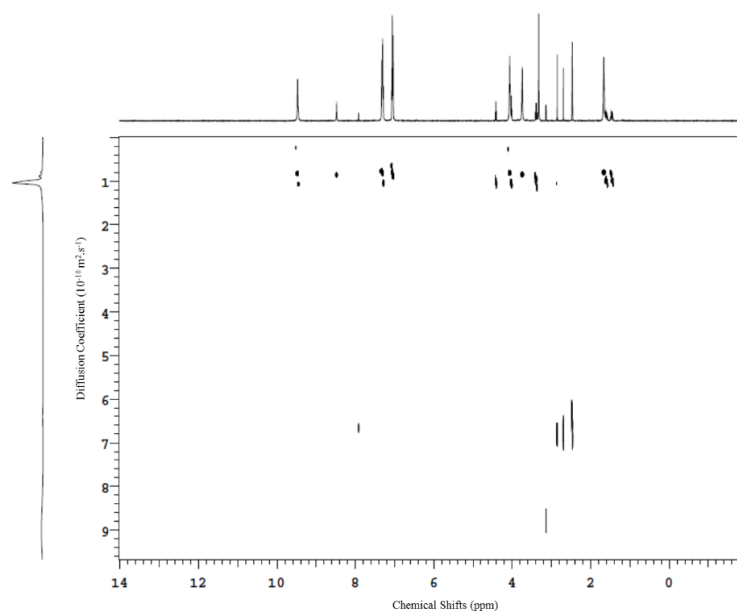

Figure 3. ^{1}H NMR-DOSY spectrum of the synthetized polymer in DMSO-d$_6$.

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2.2 PU depolymerization reaction

The PU conversion rate to the product was calculated using the signals referring to the aromatic ring hydrogens, which appear near 7.0 ppm, between 6.30 and 7.50 ppm. These signals were chosen because they do not overlap with any other. The products' spectra presented signals between 6.98–7.10 and 7.22–7.37 ppm, referring to hydrogens *e* and *f* of the starting material. They also presented signals between 6.35–6.51 and 6.73–6.90 ppm, referring to the aromatic ring hydrogens' signals of the depolymerized product, specifically to MDI, according to Motokucho *et al.* [13]. The reaction product signals that appear below 7.0 ppm undergo this shift due to the ligands' changes occurring near to the aromatic ring. This change can be explained by the transesterification reactions of PU.

In Appendix A (in Supporting Information), the spectra of the reaction products using GCL as a solvent are arranged, and a region enlargement of the aromatic ring signals. Notably, all products presented similar behavior where conversion was not complete, except for the products where NaOH was used as a catalyst, in which the signals *e* and *f* from the starting material did not appear.

Appendix B (in Supporting Information) presents the reaction products' spectra that have used DEG as a solvent. Spectra also presented signals from the starting material, as well as the products using GCL as a glycolizing agent.

Based on the spectra, the signal regions at 6.35–6.51 and 6.98–7.10 ppm were chosen for their respective integrations and calculation of the depolymerization reaction conversion rate. Integrating the signal below 7.0 ppm converted to a percentage using Equation 1, shows graphically the conversion rate regarding the reaction time for each catalyst used, in GCL and DEG. Table 1 presents the integration data for the samples using GCL, while Table 2 presents the integration data for the samples using DEG.

Figure 4 presents the graphs of the conversion rate as a function of the reaction time. Thereby, it has been found that when GCL is used as a solvent, the extent of PU conversion into product reaches 100% using NaOH as the catalyst before 30 min of reaction, as already suggested by Nikje and Nikrah [21]. When other catalysts are used,

the LIMn provides the highest conversion, approximately 80% in up to 1 h of reaction, the LIZn reaches its best conversion in 1.5 h, whereas the CTAB increases its catalytic activity throughout the reaction. The reaction without catalyst (Scat) also obtained good degradation, considering the high GCL reactivity because it has three hydroxyls in its structure. With the higher potential conversion presented for the uncatalyzed reaction, the niobium salts were not used as a catalyst for this glycolysis process. Despite niobium salts acting as Lewis acids with good catalytic activities in many organic reactions, their behavior in glycolysis reactions was not known in this work [26].

When DEG was used as a solvent for the depolymerization reaction, the conversion rate considerably decreased, even when using LIMn and CTAB as catalysts, which presented good catalytic activity. The test with the three catalysts obtained conversion rates close to each other, which is shown in Figure 4 (b).

Because the catalysts mentioned above had not yet been studied in the glycolysis reactions of PUs, except for NaOH, and that the solvent choice was important in the depolymerization reaction yield, there is an interest in studying better reaction conditions to achieve even higher conversion rates.
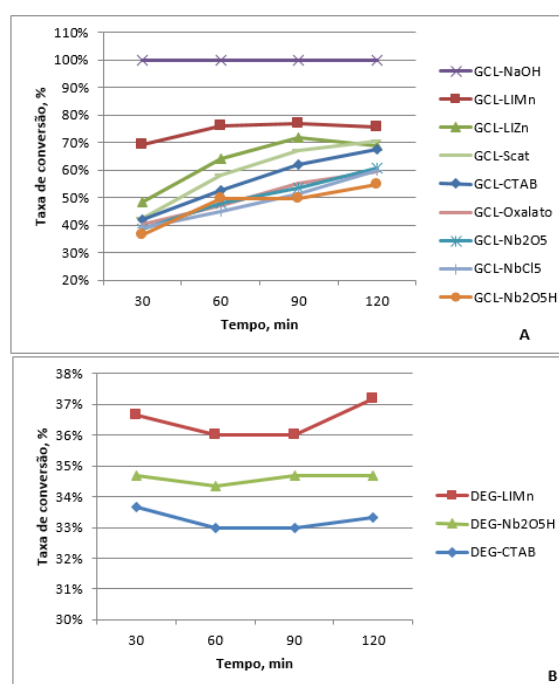

Figure 4. Graphs of PU conversion rates in product for each catalyst in (a) GCL and (b) DEG.

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Table 1. Integration of the aromatic ring hydrogen signals and the PU conversion rate into the product for each sample in GCL.

Samples	Signal integration above 7.0 ppm	Signal integration below 7.0 ppm	Integration total	Conversion rate
GCL-CTAB 1	1.37	1.00	2.37	42.19%
GCL-CTAB 2	0.95	1.05	2.00	52.50%
GCL-CTAB 3	1.00	1.63	2.63	61.98%
GCL-CTAB 4	0.97	2.03	3.00	67.67%
GCL-LIMn 1	0.92	2.08	3.00	69.33%
GCL-LIMn 2	0.95	3.05	4.00	76.25%
GCL-LIMn 3	0.93	3.07	4.00	76.75%
GCL-LIMn 4	0.97	3.03	4.00	75.75%
GCL-LIZn 1	1.03	0.97	2.00	48.50%
GCL-LIZn 2	1.08	1.92	3.00	64.00%
GCL-LIZn 3	1.00	2.55	3.55	71.83%
GCL-LIZn 4	0.93	2.07	3.00	69.00%
GCL-NaOH 1	*	1.00	1.00	100.00%
GCL-NaOH 2	*	1.00	1.00	100.00%
GCL-NaOH 3	*	1.00	1.00	100.00%
GCL-NaOH 4	*	1.00	1.00	100.00%
GCL-Nb_2O_5 1	1.58	1.00	2.58	38.76%
GCL-Nb_2O_5 2	1.04	0.96	2.00	48.00%
GCL-Nb_2O_5 3	0.93	1.07	2.00	53.50%
GCL-Nb_2O_5 4	1.00	1.56	2.56	60.94%
GCL-Nb_2O_5H 1	1.91	1.09	3.00	36.33%
GCL-Nb_2O_5H 2	1.01	0.99	2.00	49.50%
GCL-Nb_2O_5H 3	1.01	0.99	2.00	49.50%
GCL-Nb_2O_5H 4	0.90	1.10	2.00	55.00%
GCL-$NbCl_5$ 1	1.57	1.00	2.57	38.91%
GCL-$NbCl_5$ 2	1.23	1.00	2.23	44.84%
GCL-$NbCl_5$ 3	0.97	1.03	2.00	51.50%
GCL-$NbCl_5$ 4	1.00	1.49	2.49	59.84%
GCL-Oxalate 1	1.47	1.00	2.47	40.49%
GCL-Oxalate 2	1.06	0.94	2.00	47.00%
GCL-Oxalate 3	1.00	1.24	2.24	55.36%
GCL-Oxalate 4	1.00	1.46	2.46	59.35%
GCL-Scat 1	1.36	1.00	2.36	42.37%
GCL-Scat 2	1.00	1.39	2.39	58.16%
GCL-Scat 3	0.98	2.02	3.00	67.33%
GCL-Scat 4	1.00	2.42	3.42	70.76%

* signs not observed.

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**Table 2.** Integration of the aromatic ring hydrogen signals and the PU conversion rate into product for each sample in DEG.

Samples	Signal integration above 7.0 ppm	Signal integration below 7.0 ppm	Integration total	Conversion rate
DEG-CTAB 1	1.99	1.01	3.00	33.67%
DEG-CTAB 2	2.01	0.99	3.00	33.00%
DEG-CTAB 3	2.01	0.99	3.00	33.00%
DEG-CTAB 4	2.00	1.00	3.00	33.33%
DEG-LIMn 1	1.90	1.10	3.00	36.67%
DEG-LIMn 2	1.92	1.08	3.00	36.00%
DEG-LIMn 3	1.92	1.08	3.00	36.00%
DEG-LIMn 4	1.69	1.00	2.69	37.17%
DEG-Nb$_2$O$_5$H 1	1.96	1.04	3.00	34.67%
DEG-Nb$_2$O$_5$H 2	1.97	1.03	3.00	34.33%
DEG-Nb$_2$O$_5$H 3	1.96	1.04	3.00	34.67%
DEG-Nb$_2$O$_5$H 4	1.96	1.04	3.00	34.67%

Differently from the unidimensional ^{1}H NMR, the DOSY-NMR experiments show a complex by-products' mixture. In Figure 2, the signals that refer to hydrogens in the amino groups in the 4,4′-methylenedianiline (MDA) indicate a complete depolymerization reaction. However, the ^{1}H NMR-DOSY spectra in Figure 5, showed a complex mixture of by-products. Along the vertical axis, signals with diffusion coefficient between 1.6 and 3.0×10^{-10} m^2.s^{-1} can be observed, indicating that the depolymerization reaction was not completed.
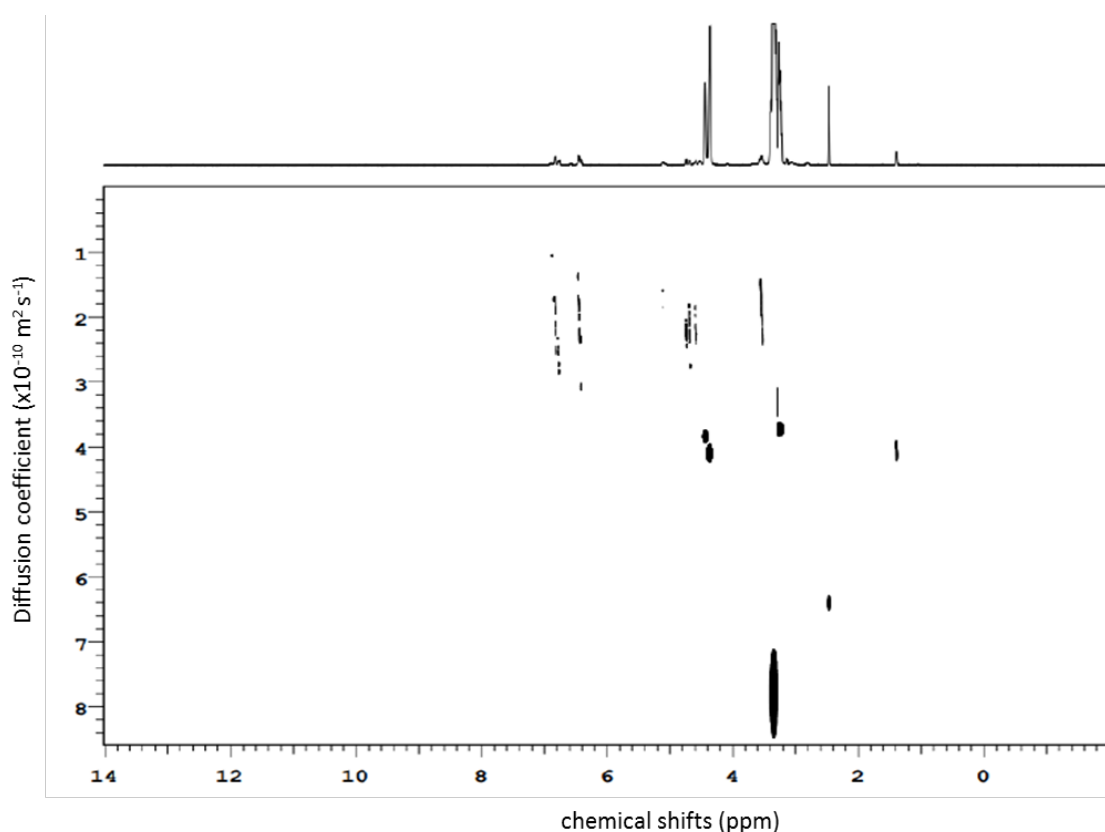
Figure 5. ^{1}H NMR-DOSY spectrum of the depolymerized polymer in GCL-NaOH, in DMSO-d$_6$.

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Although the signals of the depolymerization product MDA appears on the spectrum, can be observed that there are several structures not yet completely depolymerized, contrary to observed in the unidimentional spectrum.

3. Material and Methods

3.1 Materials

For the synthesis of rigid polyurethane, 1,4-butanediol (BD) (Sigma-Aldrich, 99%) and 4,4′-methylene diphenyl diisocyanate (MDI) (Aldrich, 98%) were used as raw materials. *N,N*-Dimethylformamide (DMF) (Synth, PA) was used as the solvent for the reaction, and methanol (Vetec, PA) as the precipitating agent and in the washing of the polymer.

In the depolymerization process, the synthesized PU was used in its pulverized form. GCL (Alphatec) and DEG (Neon) were used as glycolysis agents. CTAB, LIMn, LIZn, NaOH, Nb_2O_5, Nb_2O_5H, $NbCl_5$, and niobium ammoniacal oxalate, were tested as catalysts.

3.2 Synthesis of PU

The rigid PU was synthesized according to Motokucho *et al.* [13]. MDI (8.88 g, 35.50 mmol) in DMF (70.0 mL) was placed in a two-neck round-bottom flask coupled with a reflux condenser, and the reaction was heated at 60 °C. BD (3.26 g, 36.2 mmol) was added and temperature reaction kept at 80 °C for 1.5 h. The reaction mixture was poured into methanol and the precipitated white solid was washed with methanol in a Soxhlet extractor and oven dried.

3.3 Depolymerization reactions

Depolymerization reactions were performed in a two-neck round-bottom flask coupled with a reflux condenser, under stirring at 195–205 °C, for 2 h. The reactions were carried out using PU (3 g), glycolysis agent (15 g), and catalyst (0.03 g). The PU depolymerization rate was analyzed at each 30 min by an aliquot reaction. Nine reactions were used with GCL as solvent, eight of them used catalysts. From the reactions that used DEG as solvent, only the catalysts LIMn, CTAB, and Nb_2O_5H, were used for comparison purposes with the use of GCL (Tables 1 and 2).

3.4 Characterization

3.4.1 Analysis by infrared spectrometer

The PU was characterized by infrared spectroscopy using a spectrometer SPECTRUM 400 FT-IR/FT-NIR, in the region of 650 to 4000 cm^{-1}, in attenuated total reflectance mode, using a ZnSe crystal, with a resolution of 4 cm^{-1}, recording the average of 16 scans.

3.4.2 Analysis by Nuclear Magnetic Resonance (NMR)

3.4.2.1 Unidimensional ^1H NMR

The ^1H NMR experiments were performed on a spectrometer Varian/Agilent model VNMRS 400 MHz, operating at 9.4 T with a 5 mm probe BroadBand$^1H/^{19}F/X$, using deuterated dimethyl sulfoxide (DMSO-d_6) as solvent at 25 °C.

The conversion rate was determined by integration of the signals referred to the aromatic ring hydrogens (region of 7.0 ppm) and converted to a percentage value, according to Equation 1.

$$\% = \frac{signal\ integration\ below\ 7.0\ ppm}{total\ integration} x\ 100$$

Eq.1

Total integration is the sum of the integrations of the signals at 6.35–6.51 and 7.07–7.09 ppm.

The degree of polymerization of the synthesized PU was determined from the ^1H NMR spectra comparing the integration of the hydrogen *j* and the average value of the hydrogens *a–g*.

3.4.2.2 Diffusion ordered spectroscopy (DOSY) by NMR

For the DOSY-NMR experiments, solutions of 20 mg of the bulk depolymerization reaction were prepared in DMSO-d_6 as solvent. The experiments were performed in the same spectrometer, equipped with a 5 mm BroadBand$^1H/^{19}F/X$ probe, generating an 18 G cm^{-1} field strength.

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The *Doneshot* sequence was employed to measure the self-diffusion of the depolymerization by-products, using 25 linear steps from 0 to 18 G cm^{-1}. The gradients were calibrated according to the manufacturer, using the HOD/D$_2$O (99%) standard solution at 25 °C.

4. Conclusions

The proposed study concluded that a better way to do the glycolysis of rigid PU is using GCL as the solvent and NaOH as the catalyst, which has achieved rates of 100% PU conversion in a product. However, the use of LIs (LIMn and LIZn) presented good catalytic activity, which had not been reported in the literature as catalysts for this type of reaction. The use of diethylene glycol and its good performance in glycolysis reactions are well known in the literature [8, 11, 12, 14, 17, 19]. However, for the catalysts tested with the PU used in this work, it did not obtain good results. Thus, it is possible to promote the chemical recycling of rigid PU with low cost and good yields, considering that GCL can be obtained as a by-product of biodiesel synthesis.

Notably, NMR spectroscopy, besides being a great tool in organic compound structural elucidation, also shows itself as a good tool to indicate the amount of product formed in relation to the starting material, in the polymer depolymerization process. The DOSY experiments showed a complex mixture of by-products, which could not be observed in the unidimensional technique.

Supporting Information

[^{1}H NMR Spectra](#)

Acknowledgments

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