Hydrolytic stability of Polyurethane/Polyhydroxyurethane hybrid adhesives

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Abstract

Polyurethane/polyhydroxyurethane (PU/PHU) hybrid materials are potential alternatives to PU materials in adhesive use, when the user needs to be protected from free di-isocyanates. PU/PHU materials have promising mechanical and adhesive properties, but they are susceptible to a higher water uptake than corresponding PU materials. In adhesive use, water and temperature are typically responsible for environmental ageing, which can cause unexpected bond failure. Therefore, the effect of water uptake on mechanical and adhesive strength is crucial. In this study, the water uptake of PU/PHU at various temperatures was studied and the contribution of absorbed water to material properties was investigated. The highly crosslinked amorphous PU/PHU was synthesized from a multifunctional polyethyleneimine (PEI) and a cyclic carbonate terminated prepolymer made from a hexamethylene di-isocyanate (HDI) based isocyanate prepolymer. High water uptake of PU/PHU originated from the hydrophilic amine used as well as the pendant hydroxyl groups in the hydroxy urethane. After the high initial water absorption, a quasi-equilibrium was reached at room temperature. Water immersion at elevated temperature introduced a second water absorption step which eventually caused PU/PHU to become a water-soluble gel. Considering the potential applications of PU/PHU, the cohesive strength had increased after water

immersion cycles, but the adhesive strength was irreversibly reduced resulting in total bond failure after five water immersion cycles. In contrast, longer storage at dry elevated temperature improved the cohesive and adhesive strength. Thus, a careful design of the application is required for PU/PHU adhesives to fully utilize the advantage of the high lap shear strength in dry condition.

Keywords: A. novel adhesives, D. aging, D. mechanical properties of adhesives, water immersion, hybrid polyurethane/polyhydroxyurethane, non-isocyanate polyurethanes

1. Introduction

Polyurethanes (PU) form one fifth of the resin markets for coatings, adhesives and sealants [1]. However, in PU synthesis monomeric di-isocyanates are used, which causes potential health hazards for the user. This has increased the interest to find alternatives for PU where di-isocyanates are not used. These polymers are often referred as non-isocyanate polyurethanes (NIPUs) [2]. One class of NIPU polymers is polyhydroxyurethanes (PHUs), where the synthesis is conducted between poly- or difunctional cyclic carbonates and poly- or diamines instead of polyols and di-isocyanates [2]. In addition to less harmful starting materials, PHU differs from PU by the pendant primary or secondary hydroxyl groups located in the β- carbon of the polymer chain. The hydroxyl groups are considered to increase the adhesion, thermal stability, and chemical resistance of the material, but also increase the water uptake [2–5]. Despite the suitability of PHU to replace PU, the synthesis of PHU is not completely straightforward. The reactivity of cyclic carbonates with amines is low, which leads to low molecular weight polymers unless a higher curing temperature is used [6]. To overcome these drawbacks, it is possible to produce crosslinked structures with multifunctional starting materials [7] or to use novel hybrid materials where different reactive chemistries (e.g. epoxy, PU, acrylics) are combined with PHU [2,8]. One such approach is to use PU/PHU hybrid materials, which avoid sensitizing the user to di-isocyanates in the final stage of the polymerisation but still benefit from the good properties of PU. Such an approach has been applied by Leitsch et al.[8] and Kotanen et al. [9] for use in adhesives.

Although good adhesion is naturally the main materials property in adhesive use, long-term durability and the ageing behaviour of adhesive bond is equally crucial for demanding bonding applications. Ageing causes permanent physical or chemical changes to the polymer, lowering its strength properties and can lead to bond failure. Environmental ageing is greatly influenced by the moisture and temperature resistance of the polymer [10–12]. Water can impact the polymer itself, or may penetrate into the interface, causing adhesion failure [13,14]. Diffusion of water in the polymer is influenced by several factors, including the chemical structure [14], crosslinking density [13], the polarity and surface topography of the polymer [10] as well as the exposure temperature, time and humidity [12]. Absorbed water can cause swelling of the polymer, act as a plasticiser, or cause irreversible hydrolysis or cracking. All these phenomena lower the strength of the polymer and decrease its glass transition temperature (T_g) [11,12,15], which pose a risk for the long term durability and can cause premature failure of the adhesive bond [11]. The combined effect of water and temperature can lead to more severe ageing than either on their own. In addition to the effects of diffused water mentioned above, elevated temperatures can thermally expand the polymer network as well as accelerate chemical reactions such as hydrolysis or unwanted side reactions [12].

The research on PHUs in adhesive use has mainly focused on the mechanical and adhesive properties as well as the thermal stability [4,5,8,16–18]. Some research is available on the water uptake of PHU material itself, which all conclude that the increased water uptake compared to PU is mainly due to the pendant hydroxyl groups in PHU [3,4,16–25]. In addition, in a hydrogel application Gennen et al. [24] found that the crosslinking density, as well as hydrophilicity of the amine applied in the PHU synthesis, contributed to the water uptake of PHU. The high water uptake behaviour of PHU can potentially decrease the mechanical properties of the polymer posing a significant risk for PHU in adhesive applications. However, there is little or no research on the influence of water uptake of PHU on the mechanical and adhesive properties.

In this study the water uptake of crosslinked PU/PHU materials was examined in various conditions. In addition, the influence of absorbed water and temperature on the mechanical and

adhesive properties of PU/PHU was investigated by differential scanning calorimetry (DSC), dynamical mechanic analysis (DMA), and tensile and lap shear testing. In addition to the mechanical properties, structural analysis before and after water exposure was conducted with Fourier transform infrared spectroscopy (FTIR) and gel content measurements. By understanding the hydrolytic stability of PU/PHU material, industrial use can be correctly designed to prevent unexpected or premature failure of the bond. The starting materials for PU/PHU were selected based on previous research on the reactivity of polyamines and cyclic carbonate ended prepolymers [9]. Cyclic carbonate ended prepolymer based on hexamethylene di-isocyanate (HDI) and polyethyleneimine (PEI) were utilized as they were reactive already at room temperature.

2. Materials and Methods

2.1 Materials

Commercially available raw materials were used as received: hexamethylene di-isocyanate (HDI) based isocyanate prepolymer with a pendant hydrocarbon chain (Tolonate XFLO 100, Vencorez, Mw 682 g/mol, isocyanate functionality 2.0), glycerol carbonate (Jeffsol GC, Huntsman, Mw 118 g/mol, hydroxyl functionality 1.0), a bismuth based catalyst and polyethyleneimine (PEI, Lupasol PR 8515, BASF, Mw 2000 g/mol, primary amine functionality 16.8).

2.2 Synthesis procedures
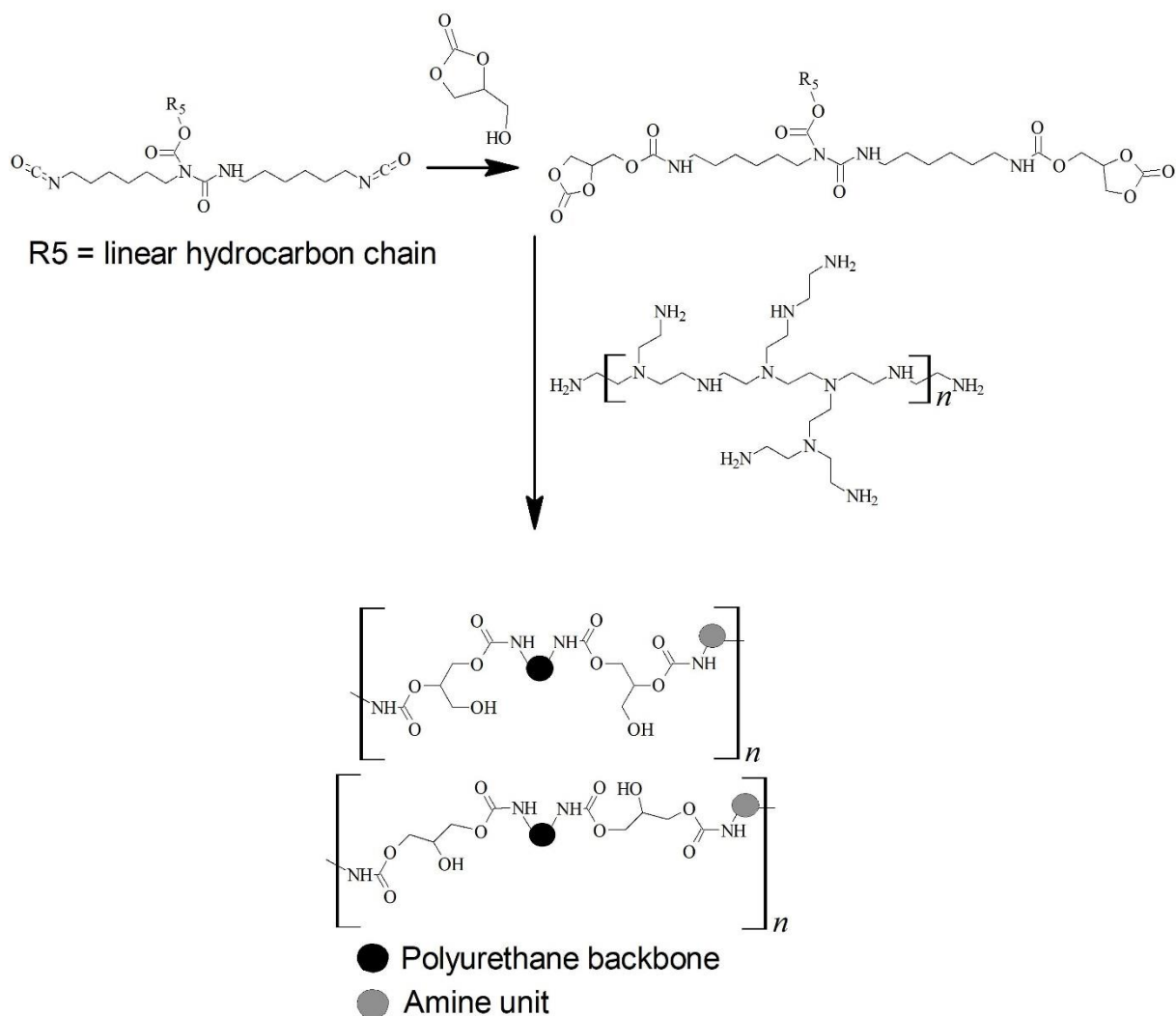
2.2.1 Prepolymer synthesis

The cyclic carbonate terminated prepolymer was synthesized from the corresponding isocyanate terminated prepolymer. First, the isocyanate terminated prepolymer was weighed in a glass reactor followed by the glycerol carbonate in a slight molar excess to ensure that all the isocyanate (NCO) groups will react. The amounts used in the synthesis are listed in Table ESI 1. The NCO/OH ratio was set to 0.93, according to a patent filed in this field [26]. The reaction mass was mixed at 200 rpm and kept at a constant temperature (80 °C). The bismuth catalyst (0.3 wt. %) was added stepwise until the reaction was complete. The advancement of the reaction was followed with FTIR until no NCO absorption bands at 2270 cm^{-1} were detected and the absorption band typical for

cyclic carbonate carbonyl group at 1800 cm^{-1} had appeared. Additionally, nuclear magnetic resonance (NMR) spectroscopy was used for the analysis of the synthetized prepolymer.

2.2.2   PU/PHU synthesis

The synthesis of PU/PHU was performed by mixing the cyclic carbonate terminated prepolymer and polyethyleneimine (PEI) in an equimolar amount, similarly to previous studies [3,4,7,9]. In the equimolar calculations, only the primary amines were considered, as secondary amines are not reactive below 90 °C [27]. Furthermore, in preliminary investigations the equimolar ratio showed the smallest water uptake. First, the prepolymer was heated to 50 °C to lower the viscosity and ease the mixing of the components. The required amount of prepolymer was weighed into a plastic cup followed by PEI in equimolar amount. The mixture was stirred for a minimum of 2 minutes with a glass rod, followed by additional mixing and degassing with the speed mixer (DAC 400 FVZ) for 20 seconds. The amounts used in the reaction are listed in Table ESI 1. Finally, the reaction mixture was cured at room temperature either as a film or as lap shear specimen (see Section 2.3.7). Furthermore, the curing of PU/PHU was monitored with FTIR and testing of PU/PHU was performed after the cyclic carbonate absorption band had disappeared.

A simplified reaction scheme from the isocyanate terminated polyurethane prepolymer to the cyclic carbonate terminated prepolymer and its reaction with PEI is shown in Scheme 1. Two possible structures formed from the synthesis of PU/PHU are shown, where the hydroxyl group is either in the primary or secondary position depending on the ring opening mechanism [2].

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Scheme 1. Synthesis of isocyanate terminated prepolymer to cyclic carbonate ended prepolymer and its reaction with amine to form PU/PHU.

2.3 Characterization of materials

2.3.1   FTIR

FTIR measurements were performed with a Perkin Elmer Frontier FT-IR spectrometer equipped with a Specac attenuated total reflectance (ATR) diamond module. Spectra were collected over a range of 4000 - 550 cm⁻¹ with a resolution of 0.4 cm⁻¹ and with 8 scans per run. The spectra were analysed with the PerkinElmer Spectrum (version 10.4.2.279). A press was used to ensure a close contact with the ATR diamond.

2.3.2 Thermal analysis

Thermogravimetric analysis (TGA) was carried out with the Netzsch TG209 Tarsus Equipment using a heating rate of 20.0 K min^{-1} over a temperature range of 30 - 600°C under nitrogen atmosphere. Netzsch DSC 214 Polyma was used for the differential scanning calorimetry measurement (DSC). The samples were exposed to two heating ramps from -50 °C to 130 °C with heating rate of 10 K min^{-1} in nitrogen atmosphere. Samples were pre dried at 50 °C for 24 hours.

2.3.3 DMA

Dynamic mechanical analysis was conducted with the Mettler Toledo DMA/SDTA861 equipment using shear mode with 1 Hz frequency and heating from -50 to 75 °C with the rate of 3 K min^{-1}. Star SW 15.00 software was used for analysis. Samples were pre dried at 50 °C for 24 hours.

2.3.4 NMR

Nuclear magnetic resonance (NMR) was carried out to analyse the prepolymer structure by proton 1H NMR (500 MHz) and carbon 13C (125 MHz) NMR in CDCl$_3$ solvent using tetramethyl silane as a standard. The NMR spectra were measured on 500 MHz JEOL LNM-ECZ500R spectrometer at room temperature with a broadband inverse Royal HFX probe.

2.3.5 Gel content

The gel contents of PU/PHU were measured similarly to Panchireddy et al.[16] in order to evaluate the crosslinking density of the formed polymer. The materials were weighed after drying at 50 °C for 24 hours and immersed in tetrahydrofuran (THF) for 96 h at room temperature. After the immersion the samples were dried at 50 °C for 24 hours and re-weighed. Three parallel samples were measured. The gel content was calculated using the formula below.

Gel content (%) = w(f)/w(i) x 100%,

where w(f) is the weight of the dried sample after immersion and w(i) is the initial weight of the sample.

2.3.6 Water uptake measurements

Water uptake was measured following the ISO 69 standard. The samples were pre-dried at 50 °C for 24 hours, cooled down in a desiccator and weighed for dry weight. The samples were submerged into distilled water at 23 °C, at 50 °C or at 70 °C and the weight of the samples was recorded at certain time intervals until 28 days (672 hours). The sample size was approximately 600 mm^2 with a thickness of 1 mm. Three parallel samples were measured. The water uptake of PHU was measured using the formula below.

Water uptake (%) = (w(w)- w (i)) /w(w) x 100%,

where w(w) is the weight of the wet sample during a selected time interval in immersion and w(i) is initial weight of the dried sample.

After the water uptake test, weight loss of the polymer was calculated similarly to the gel content from a dried sample.

2.3.7 Lap shear strength on stainless steel

Lap shear strength tests were performed for produced PU/PHU material after various environmental treatments of the specimen in order to understand the mechanical performance in wide range of conditions. The treatments used are named and explained in Table 1. Between the test cycles samples were dried at 50 °C for 24 hours.

Table 1. Used environmental treatments in mechanical testing. The material to be tested was the same PU/PHU from cyclic carbonate ended prepolymer and PEI in all treatments.

Treatment name	Temperature	Used cycle	Amount of cycles	Post treatment prior mechanical testing
Pristine	-	-	-	Stabilized at 23 °C 50% RH for 24 hours
W1W	23°C	96 hours in water	1	Measured as wet
W1D	23°C	96 hours in water	1	Drying 50 °C for 24 hours, stabilized at 23 °C 50% RH for 24 hours
W2D	23°C	96 hours in water	2	Drying 50 °C for 24 hours, stabilized at 23 °C 50% RH for 24 hours
W5D	23°C	96 hours in water	5	Drying 50 °C for 24 hours, stabilized at 23 °C 50% RH for 24 hours
W1D,50°C	50°C	96 hours in water	1	Drying 50 °C for 24 hours, stabilized at 23 °C 50% RH for 24 hours
D1, 50°C	50°C	Dry	1	Stabilized at 23 °C 50% RH for 24 hours
D1, 70°C	70°C	Dry	1	Stabilized at 23 °C 50% RH for 24 hours
D5, 50°C	50°C	Dry	5	Stabilized at 23 °C 50% RH for 24 hours
D5, 70°C	70°C	Dry	5	Stabilized at 23 °C 50% RH for 24 hours

Lap shear strength testing was done according to the EN 1465 standard using the Instron 3366 machine with a load cell of 10 kN. The analysis was performed with Bluehill software. Minimum of three parallel tests specimens were tested with a speed of 50 mm/min. Testing was carried out at 23 °C 50% RH. Stainless steel (SS) plates were used. Cleaning with isopropanol was used as a pre-treatment. The length of the specimen overlap was 12.5 ± 0.25 mm and the exact surface area was measured prior the test. Small amount of adhesive was spread between the steel plates and pressed for 24 hours with zero gap. Curing of the adhesive was performed at room temperature until the absorption band for cyclic carbonate at 1800 cm^{-1} disappeared.

2.3.8 Tensile strength and elongation

Tensile strength measurements were performed after the same environmental treatments as in 2.3.7 (Table 1). Tensile strength and elongation at break were measured according to the EN 527-1 standard using the Instron 3345 machine with a load cell of 1 kN and Instron extensometer. The

analysis was performed with Bluehill software. The reaction mixtures were cast into a 1 mm thick films immediately after mixing the components and left curing at room temperature until the absorption band for cyclic carbonate at 1800 cm^{-1} had disappeared. Cured film was cut into a dumbbell shaped specimen. Minimum of three parallel dumbbell specimens were tested at a test speed of 50 mm/min. Testing was performed at 23 °C 50% RH. For all reported values, the samples broke within the narrow area (6 mm) of the dumbbell sample as required by the standard.

3. Results and discussion

3.1 Synthesis of prepolymer

Synthesis of the cyclic carbonate terminated prepolymer was performed from the isocyanate terminated prepolymer and glycerol carbonate using a bismuth catalyst. It was necessary to add the catalyst stepwise during the synthesis, otherwise the reaction did not advance to completion. The reaction of glycerol carbonate with isocyanate terminated prepolymer was monitored with IR spectroscopy. The disappearance of the characteristic absorption band of NCO at 2270 cm^{-1} was detected after 4 hours at 80 °C. The complete conversion of the free carbonate and the structure of the cyclic carbonate prepolymer was additionally confirmed by the NMR spectra. First unsubstituted glycerol carbonate was analysed showing peaks at 4.8 and 4.5 ppm corresponding to the cyclic carbonate, a group of peaks of methylene bridge at 3.95 - 3.65 ppm and the signal of hydroxy proton at 3.1 ppm (Fig. ESI 2 a and b). The assignment was also confirmed with HSQC spectrum (Fig. ESI 3), which shows the lack of correlation to a carbon for the signal at 3.1 ppm. When analysing the cyclic carbonate terminated prepolymer, the proton spectrum shows no hydroxy signal at 3.1 ppm. Indeed, it gives a peak at 3.2 ppm along with other signals at 5 ppm, 4.6 - 4.3 and between 3.8 and 3.1 ppm (see Fig. ESI 4 a and b). According to HSQC spectra all these peaks correspond to the methylene groups of the cyclic carbonate prepolymer, naturally except for the signal at 4.8 which originates from the CH group of the carbonate ring (see Fig. ESI 5). In addition, the ^{13}C spectrum of the cyclic carbonate terminated prepolymer shows no signal isocyanate groups at 120 ppm, which proves that all these groups have been consumed during the

reaction (Fig. ESI 6 and 7). The cyclic carbonate prepolymer was a clear viscous liquid and was used without further purification.

3.2 Structure of PU/PHU materials

PU/PHU material was polymerized using an equimolar ratio of PEI and the cyclic carbonate terminated prepolymer. The reaction mass hardened in 5 minutes after mixing and the material became a transparent solid. This was in line with previous research performed with same starting materials [9]. When compared to a typical PU material reactivity, the reaction was relatively fast, especially as no catalyst was used. The reaction was followed with FTIR until no absorption band from the cyclic carbonate groups were visible in the FTIR spectra (Fig. 1). PU/PHU was further analyzed by measuring the gel content and studying the polymer with TGA, DSC and DMA.
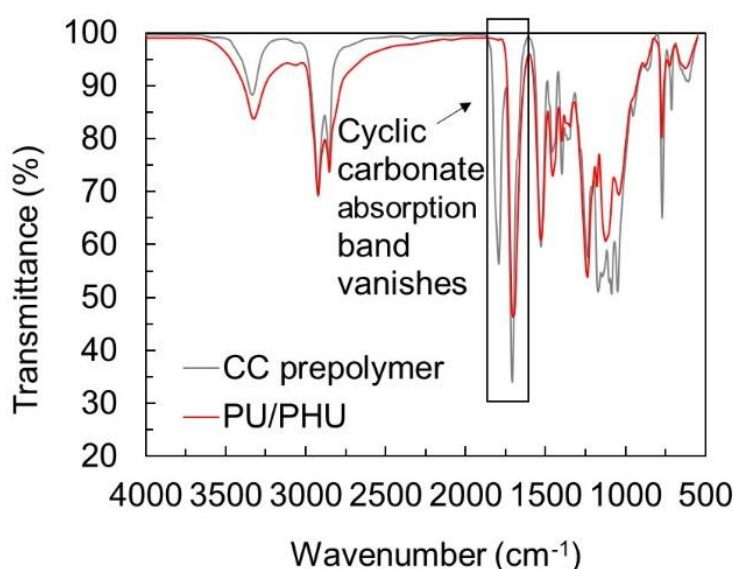
Fig. 1. FTIR spectra of PU/PHU polymer compared to CC prepolymer

The possible repeating unit of PU/PHU is presented in Fig. 2 and shows a highly crosslinked polymeric structure. The high crosslinking density was proven by the high gel content in THF, 99.1%. In addition, no further crosslinking was seen in the DSC spectra at elevated temperatures (Fig. ESI 8). As evident from Fig.2, PU/PHU has multiple hydrogen bonding sites originating from the urethane, hydroxy urethane, and secondary amine groups. When analyzing the polymer with DSC (Fig. ESI 8), only one glass transition temperature (Tg) at 18.7 °C was detected. Other

transitions such as melting or crystallization were not visible, indicating that the structure was amorphous. This finding was supported by DMA analysis (Fig. ESI 9), where only one Tg at 25.6 °C was observed from the Tan delta curve. The reason for the amorphous behaviour could be the crosslinked and branched PU/PHU structure making it difficult to form ordered crystalline segments. This mainly originates from the highly functionality PEI, although the pendant hydrocarbon chain in cyclic carbonate prepolymer and the pendant OH group from the hydroxy urethane group further prevent the crystalline segments from becoming more ordered. Evidently, the synthesized PU/PHU does not contain the typical morphology of PU, where the polymer is segmented with highly oriented crystalline parts held together by hydrogen bonding in a matrix of soft amorphous segments [28].
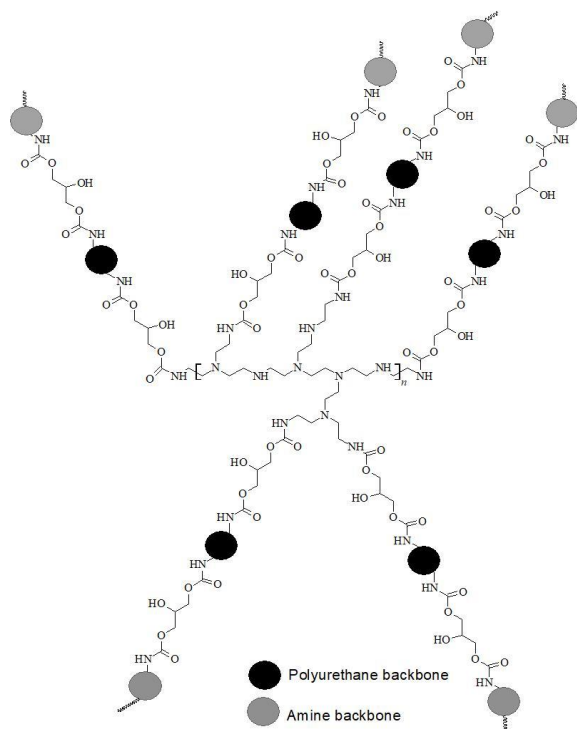
Fig. 2. Schematic presentation of the possible repeating unit of PU/PHU network of with functionality 16.8 (PEI) and 2 (prepolymer).

The thermal stability of PU/PHU was examined with TGA (Fig. 3). In the spectra, three evident decomposition phases were visible, similar to the literature on hybrid PHUs [29]. The first decomposition at 200 - 330 °C was caused by the hydroxy urethane and urethane linkage

dissociation and the second and third between 330 °C and 520 °C were due to the breakage of hydrocarbon chains [29,30]. In addition, in the first decomposing step, some part of the degradation originated from the PEI used in PU/PHU [31]. As in other research related to PHU polymers, 5% or 10% of degradation has been used as a measure for thermal stability [5,30,32–34]. The results observed (5% and 10% degradation of PU/PHU prior to 230 °C and 250 °C respectively) were found to be similar to previous research.
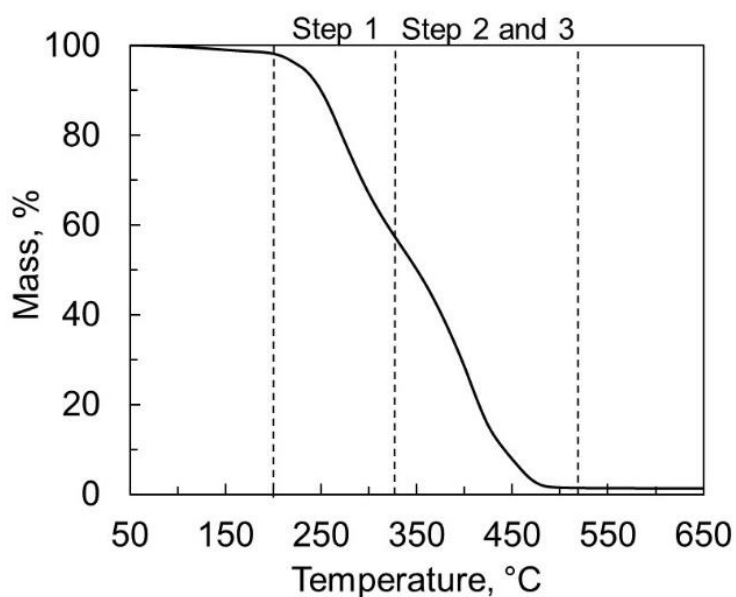
Fig. 3. Thermogravimetric analysis of PU/PHU where three decomposition steps were detected

3.3 Water uptake of PU/PHU over time

The water uptake of PU/PHU was measured at different temperatures (23 °C, 50 °C and 70 °C) for 28 days (672 hours) or until the sample was too degraded to be measured. Direct water immersion was considered as the most severe case of moisture stress. The results are presented in Fig. 4 (data available in Table ESI 2). Initially the rate of water uptake of PU/PHU was high. After 48 hours, the water uptake of PU/PHU reached a quasi-equilibrium and after that the water uptake of PU/PHU did not significantly increase. At room temperature the water uptake of PU/PHU reached 29% after 672 hours. The high initial absorption of water could be explained by the hydrophilic amine groups in the water soluble PEI used for the PU/PHU reaction. In addition, the vast amount of hydrogen bonding sites in the PU/PHU structure can interact with polar water molecules and

introduce water into the structure. The glass transition temperature of PU/PHU (18.7 °C / 25.6 °C from DSC/DMA) was observed close to the test temperature (23 °C), which can generate unexpected behaviour as well as lead to increased water absorption due to increased mobility between polymer chains. After 672 hours of immersion in water, the total mass change was found negligible, only less than 1%. This is in accordance with the high gel content (98.9%) measured after the water immersion indicating that significant chemical changes did not occur. Furthermore, when the sample was analyzed with FTIR after one month of immersion, absorption bands closely matched the original spectra and no difference in the absorption bands were detected (Fig. 5 a).
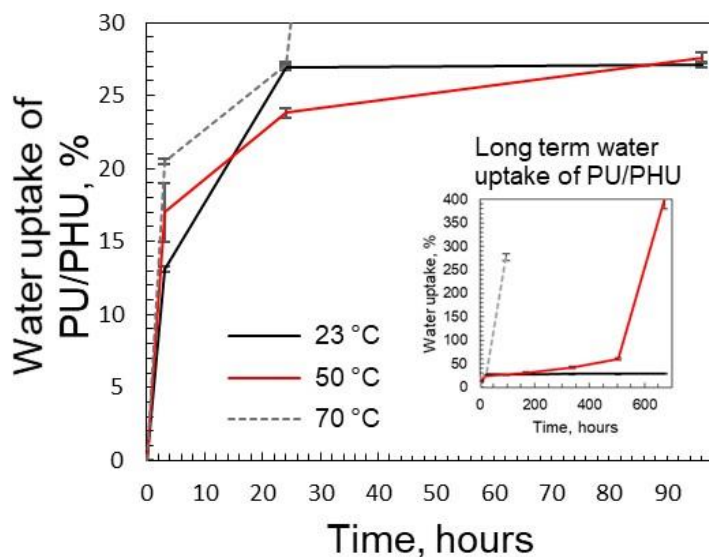
Fig. 4. Water uptake of PU/PHU material at different temperatures as a function of time

When measured at 50 °C or 70 °C, the water uptake of PU/PHU initially followed same water uptake as at room temperature (Fig 4.). However, at 50 °C, the observed equilibrium was shorter, and a secondary water uptake process was detected. Therefore, at 672 hours of immersion, the material was clearly swollen and tacky and the measured water uptake was around 400%. It seemed that the absorbed water alongside with the elevated temperature led to an additional but delayed water uptake mechanism. The rapid rate of water uptake in the secondary uptake step could originate from the degradation of PU/PHU via chain scission due to extensive physical swelling or via hydrolysis of the carbamate bond, resulting in increased free volume between the polymer chains. After the water uptake test, PU/PHU was analyzed with FTIR (Fig. 5 b) and a few

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changes in the absorption bands of carbonyl, amine and C-O stretching were detected, indicating that there were changes in the molecular structure of PU/PHU compared to the pristine material.

Increasing the water uptake temperature to 70 °C shortened the equilibrium further and already after 96 hours of water immersion the material had become gel-like, and exact weight measurements could not be performed further. After 672 hours of water immersion at 70 °C the sample had completely dissolved or dispersed into water. The residual material was collected after evaporating the water and analyzed with FTIR. The spectra of the residual material in Fig. 5 c was quite distinct from the original one. Biggest changes were observed in the carbonyl absorption band of the PU/PHU, indicating severe hydrolysis of the PU or PHU carbamate bond. In addition, the amine related bands and the C-O band had changed. All these indicate dramatic irreversible changes in the PU/PHU network. In addition, the solvated material stayed as a soft gel after the water was evaporated, indicating that the material was not only swollen and solvated due to high water uptake, but the polymer chains had also broken into smaller fragments and the original integrity of the material could not restored. Based on the findings, increasing the temperature together with the water immersion had a detrimental effect on the polymer network and caused irreversible damage. At elevated temperature the solvency power of water is additionally increased, which can further improve the solubility of the fragments.
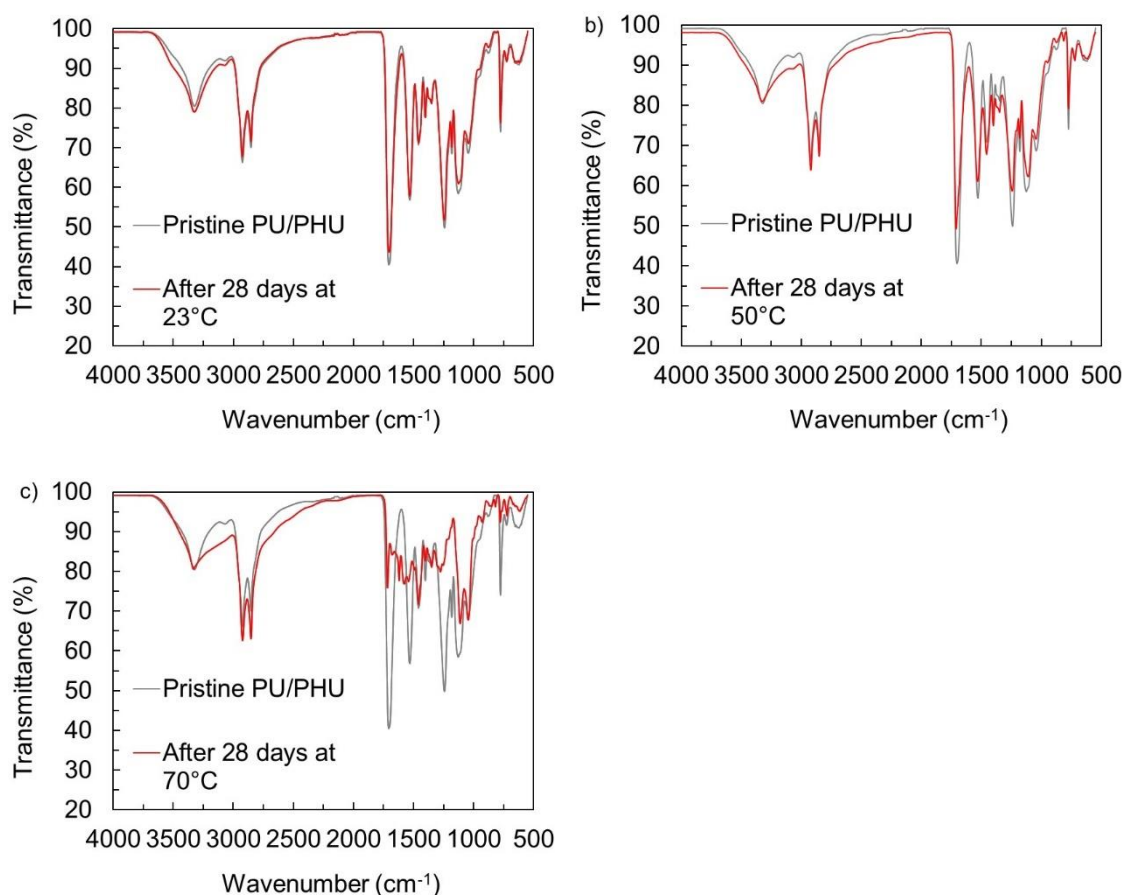
Fig. 5 FTIR spectra after 28 days (672 hours) of immersion in water a) at 23 °C, b) at 50 °C, c) at 70 °C compared to pristine PU/PHU material

Based on the findings, the synthetized PU/PHU was hydrophilic with high water uptake, as expected. The hydrophilicity of the amine particularly impacts the water uptake [24], as the amine was water soluble. Even though the used isocyanate terminated polyurethane prepolymer was relatively hydrophobic, the pendant OH groups from hydroxy urethane increased the water uptake of PU/PHU [2]. The water uptake of PU/PHU had high initial rate, followed by almost an equilibrium with slow water uptake at room temperature. The absorbed amount of water (29%) at room temperature was high compared to pure PU material, which typically has water uptake around 2-5% [35,36]. This is due to the difference in the starting materials of PU and PHU as an amine is needed for the cyclic carbonate to react into polyhydroxyurethane without the use of di-isocyanates. However, the result was in accordance with other research conducted on PHU in the adhesives use, where the results were varying from 5% [25] to 57% [4] after 96 hours of water

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immersion at room temperature depending on the starting materials. Considering the industrial use, the high amount of water absorbed poses a significant risk for the material behaviour and based on the fast rate of water uptake, the effects of the absorbed water would be seen relatively quickly. Furthermore, increasing the temperature resulted in second water uptake step after a short equilibrium state, leading the material to eventually become a soluble gel. Therefore, elevated temperatures pose even greater risk for the material. Thus, the application of PU/PHU needs to be well designed to avoid continuous water immersion particularly at high temperatures.

3.4 Changes in the mechanical properties after hydrolytic stress

Since PU/PHU was susceptible to water uptake, it is of great importance to understand how the absorbed water will affect the mechanical performance such as the cohesive strength and the adhesive strength of PU/PHU. Thus DMA, FTIR and gel content analysis as well as tensile strength, elongation at break, and lap shear tests on stainless steel were performed before and after different environmental treatments (treatments are listed in Table 1, results in Fig. 6 a-c). Numerical values for test results can be found in Table ESI 3.
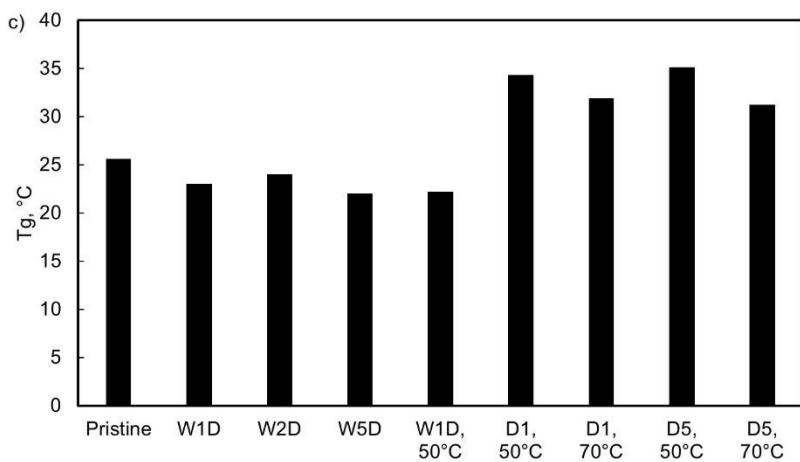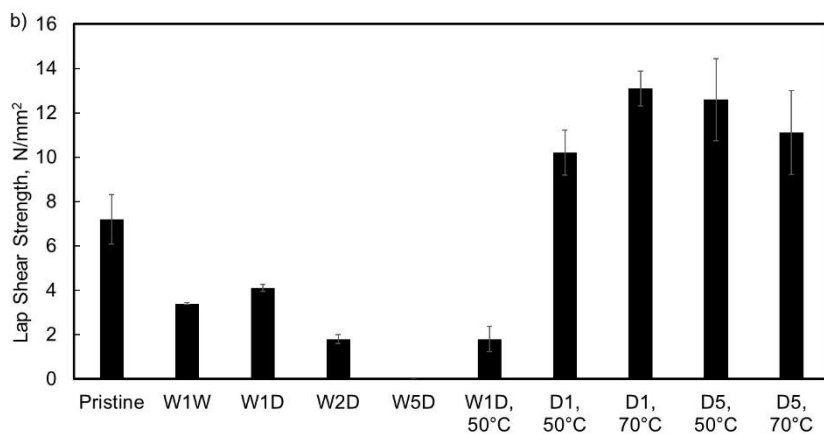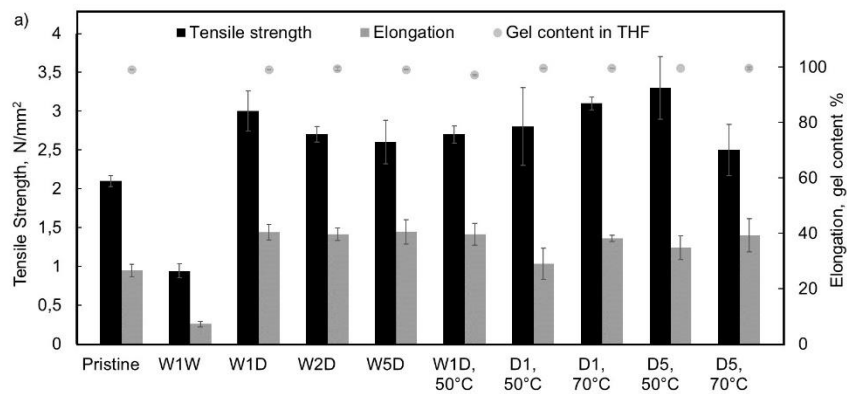
Fig. 6. a) Tensile strength, elongation and gel content, b) lap shear strength on stainless steel, c)

Tg of PU/PHU measured from DMA tan delta after different environmental treatments

When evaluating the tensile strength and elongation (Fig. 6 a), the weakest strength and the lowest

elongation was measured from the wet sample (W1W) as expected due to the plasticizing effect of

water. The strength was reduced 45% from the reference sample, which is not surprising considering the high amount of absorbed water (27 %). However, in addition to a lower tensile strength, also the elongation was decreased. Interestingly, when the sample was dried after the water immersion (W1D), the tensile strength and elongation were improved compared to the pristine material. This could be due to the re-organization of the polymer network after the water was removed. Water can act as plasticizer or solvent, but it will also interact with the hydrogen bonding sites. In PU/PHU, due to the fast crosslinking reaction, internal stresses are possible and reorganizing the hydrogen bonds leads to a better organized network and relaxation of the material. Furthermore, as all reagents were used without purification, water could remove some impurities from the network. This was not detected in the gel content measurements, however.

Repeating the water exposure (W2D, W5D) caused slight reduction of the tensile strength and elongation, yet all the water immersed samples were better than the pristine material up to 5 cycles. Comparing these results to Tg measured from tan delta peak in DMA measurements (Fig. 6 c), the plasticizing effect of water is seen as a lower Tg value after immersion tests. However, when analyzing the FTIR spectra after treatments (Fig. ESI 10), no changes in the absorption band locations or intensities were found after these short immersions in water and the gel contents stayed on the same level (Fig. 6 a). After one water immersion cycle at elevated temperature (W1D, 50 °C), the strength was at the same level as after two cycles at room temperature i.e. the strength improved compared to pristine PU/PHU and the observed Tg was on same level as after five test cycles at room temperature. In addition, no hydrolysis was detected based on FTIR absorption bands and all the absorption bands were similar as in the reference (Fig. ESI 10). This is in accordance with the findings in the water absorption tests, since at 50 °C the second water uptake step had not yet started after 96 hours. Based on the findings, short term immersion in water at elevated temperature did not have a severe ageing effect on the polymer properties.

The effect of dry elevated temperature at 50 °C or 70 °C after different test cycles (D1, 50°C, D1, 70°C, D5, 50°C and D1, 70°C) was examined. The strength and elongation results were improved compared to the pristine material after all cycles at elevated temperatures, and all the samples

after these treatments had similar strength values within the standard deviation. As the cyclic carbonate absorption band had disappeared during the synthesis phase (Fig. 1), it was considered that the better results were due to relaxation and improved orientation of the network. The relaxation of PU/PHU is supported by the fact that the height of the Tan delta peak was increased when heat treatment was repeated five times, indicating better energy dissipation (Fig. ESI 11) and gel contents were over 99 % (Fig. 6 a). Furthermore, there was an increase in the Tg values, which occurred already after one treatment cycle. As with other FTIR measurements, no change in the FTIR spectra before and after the heat treatments were detected (Fig. ESI 12).

To study the application specific behaviour of PU/PHU, lap shear strength on stainless steel was tested (Fig. 6 b). Initial results were on a high level, but after the water immersion treatments, the lap shear strength was clearly decreased compared to the pristine material regardless of whether the samples were wet (W1W) or dried after immersion in water (W1D, W2D). All samples had adhesive failure type, which is typical when stainless steel is used without grit blasting. During the fifth cycle in water immersion (W5D), the adhesion failed, and zero lap shear strength was reported. As water molecules can easily penetrate into the bond line of the lap shear test specimen [13,14], it can interfere and replace the physical interactions such as hydrogen bonds and Van der Waals forces between the substrate and the adhesive. This is partly irreversible, which was visible from the low tensile strength results after drying the samples. When performing the water immersion at 50 °C (W1D, 50 °C), the result was similar to after two immersions in water at room temperature (W2D), indicating that the elevated temperature accelerated the effect of water. After dry elevated temperature cycles at 50 °C or 70 °C (D1, 50°C, D1, 70°C, D5, 50°C and D1, 70°C), the results were significantly improved compared to the pristine material, which resulted in partly cohesive failure type. This shows that the physical interactions including hydrogen bonding were improved at elevated temperatures. This effect can be seen after relatively short treatment at 70 °C and is not improved when the sample is stored for a longer period, even showing a slight decrease within the standard deviation. At 50 °C the best result was observed after 5 cycles at elevated temperature.

Based on these results, the PU/PHU material itself is not so sensitive to short term water immersion even though the water uptake of PU/PHU is high. On the contrary, the tensile strength and elongation were both increased. However, in application specific testing, the results were more critical. A significant irreversible decrease was observed in the lap shear strength after the water immersion and repeated immersion led to permanent bond failure. When comparing treatments performed only at elevated temperature, both the cohesive and adhesive strength of PU/PHU was improved compared to the pristine material.

4. Conclusions

Understanding the water uptake of PU/PHU and its impact on polymer strength and adhesive properties is crucial for adhesive use, as one of the major causes for premature bond failure is the environmental ageing caused by water and temperature. The synthesized highly crosslinked amorphous PU/PHU was prone to high water uptake due to its hydrophilic nature and multiple sites for hydrogen bonding. This was caused by the hydrophilic amine used in the synthesis as well as the pendant OH group from the polyhydroxyurethane group. The water uptake of PU/PHU was rapid followed by a quasi-equilibrium. Therefore, in the application the effect of absorbed water could cause irreversible damage to the adhesion relatively quickly. Increase of the water immersion temperature to 50 or 70 °C resulted in a second water uptake step with an increased rate of water uptake. A longer immersion at elevated temperature had a detrimental effect to PU/PHU and it started to lose its integrity after one month at 50 °C and eventually solvated after one month at 70 °C. This was caused by extensive physical swelling due to absorbed water and polymer hydrolysis, resulting in chain scission and irreversible changes in the polymer network.

The impact of water uptake on strength properties is important for application design in the adhesive use. PU/PHU material itself was not dramatically affected by short immersion period in water even at elevated temperature of 50 °C. The strength and elongation were in fact improved over the pristine material. As the curing reaction of PU/PHU was very fast even without a catalyst, the improvement of tensile strength and elongation were considered to be caused by the relaxation and removal of internal stresses due to better organization of the hydrogen bonding network after

the water was removed. At dry elevated temperatures, PU/PHU showed improved tensile strength and elongation via polymer network relaxation.

In application testing, the lap shear strength of PU/PHU was irreversibly reduced after five cycles of water immersion, resulting in adhesion failure. However, storage in dry conditions at 50 or 70 °C increased the adhesion strength, which is beneficial for some adhesive applications. More research could be conducted to analyze the best surface treatment to protect the bond line from water absorption. The tendency to have high water uptake is typically seen as a drawback in demanding adhesive applications. However, when designed with care, this kind of adhesive could offer unique properties in e.g. structures that require high adhesion in dry conditions but are not susceptible to moisture during their service life and later on could be rather easily de-bonded with the help of heat and moisture.

Appendix A. Supplementary material

Supplementary data is available.

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Supplementary material for Hydrolytic stability of Polyurethane/Polyhydroxyurethane hybrid adhesives

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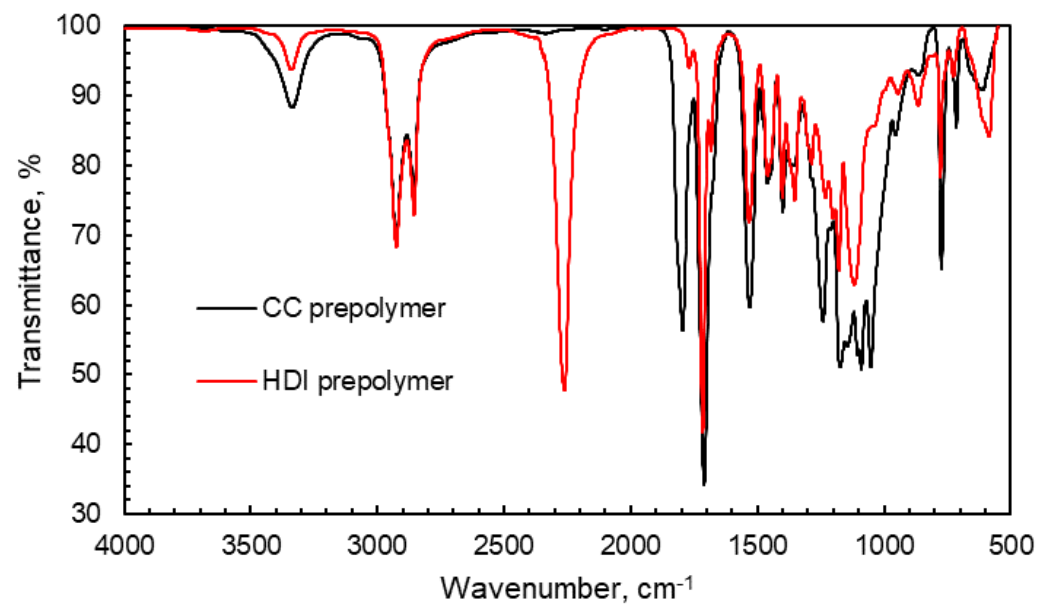
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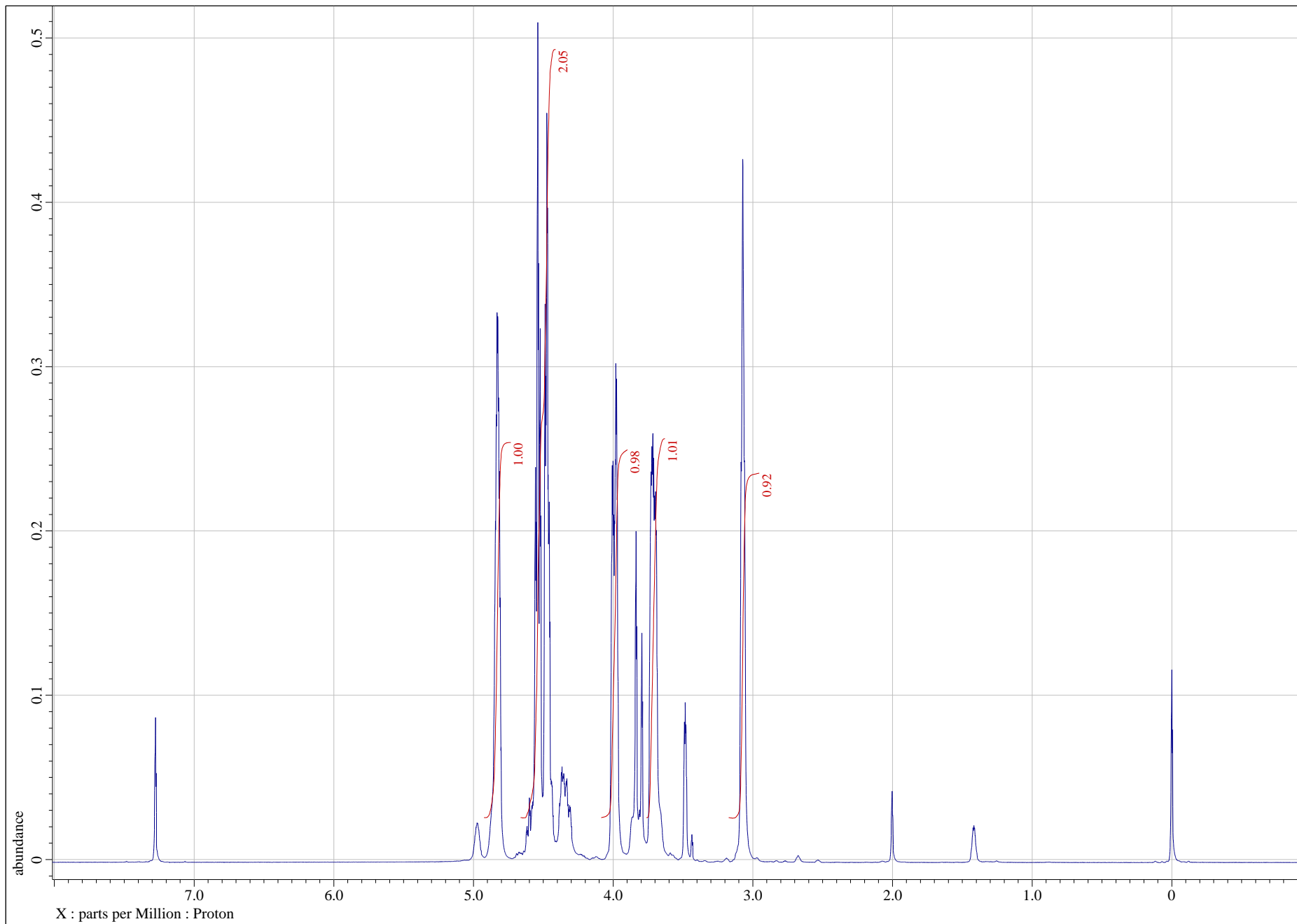
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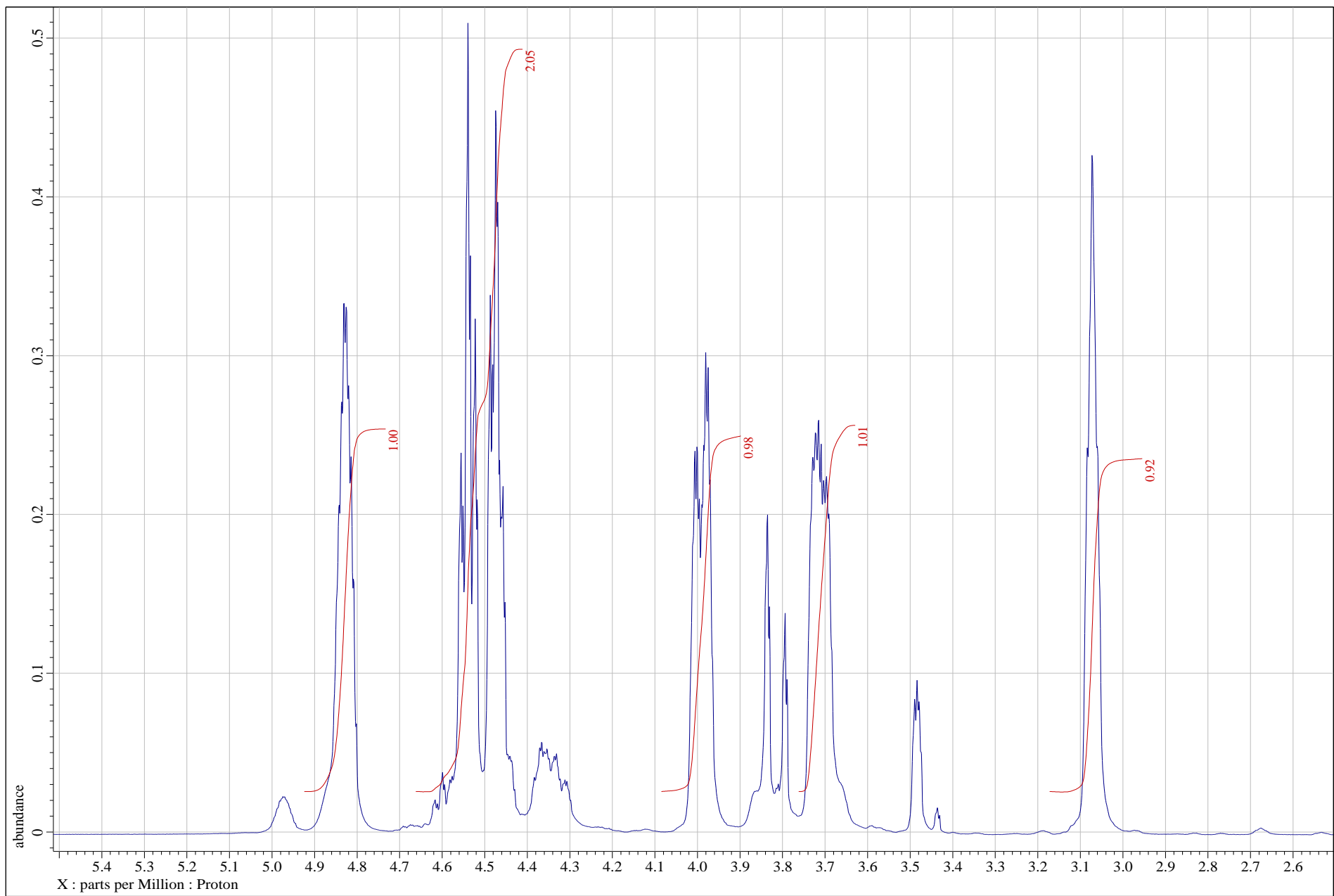
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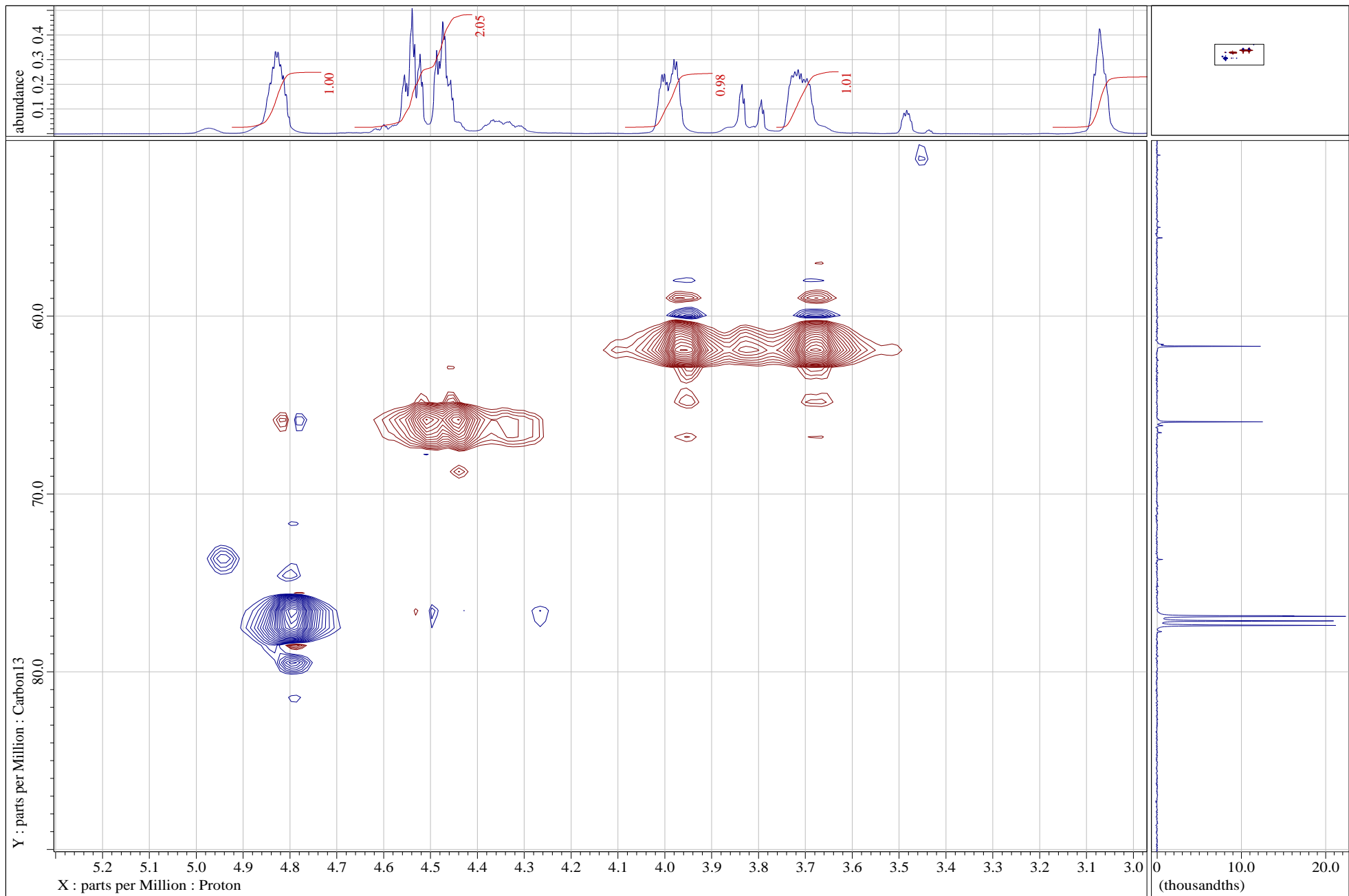
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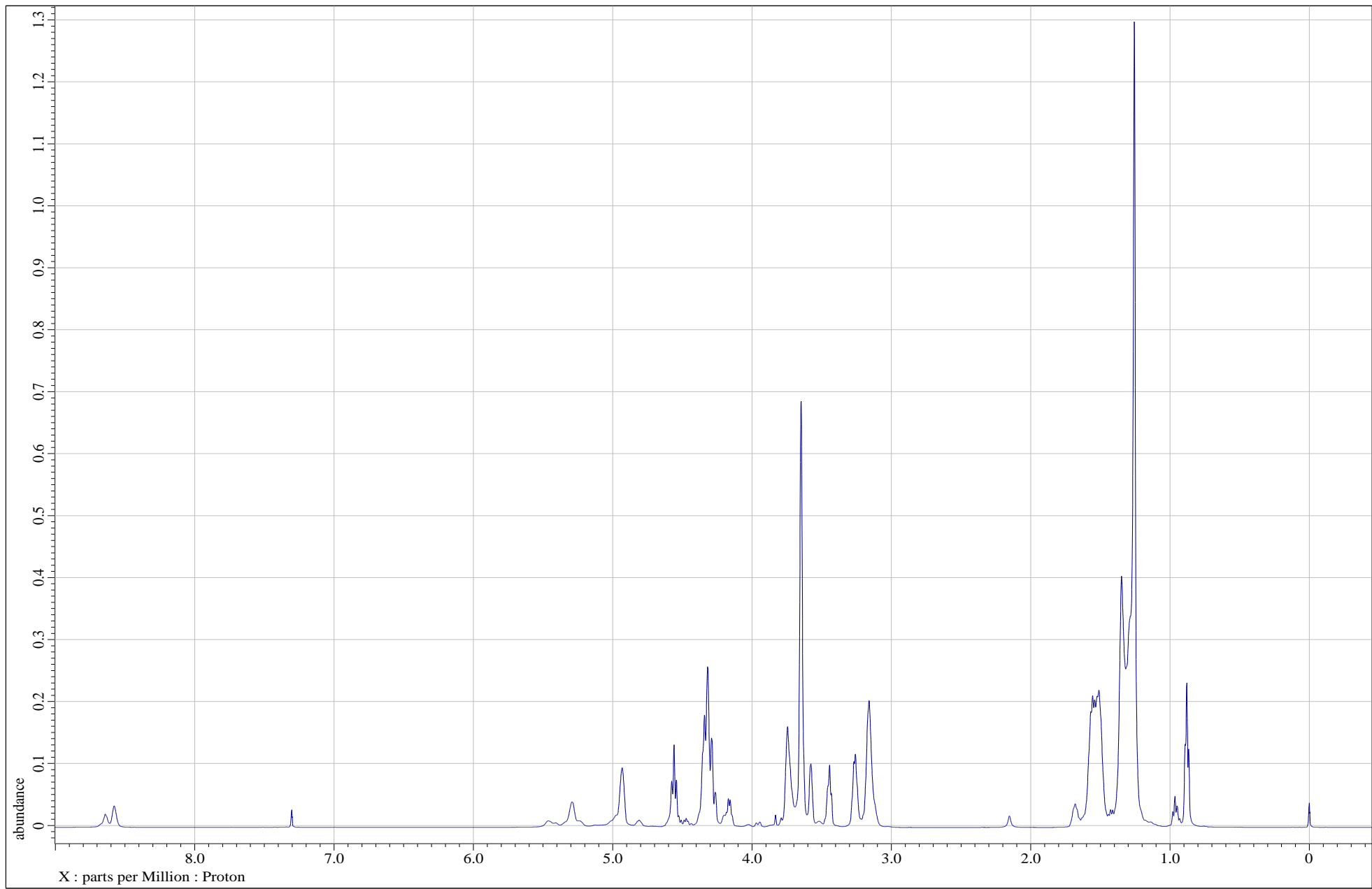
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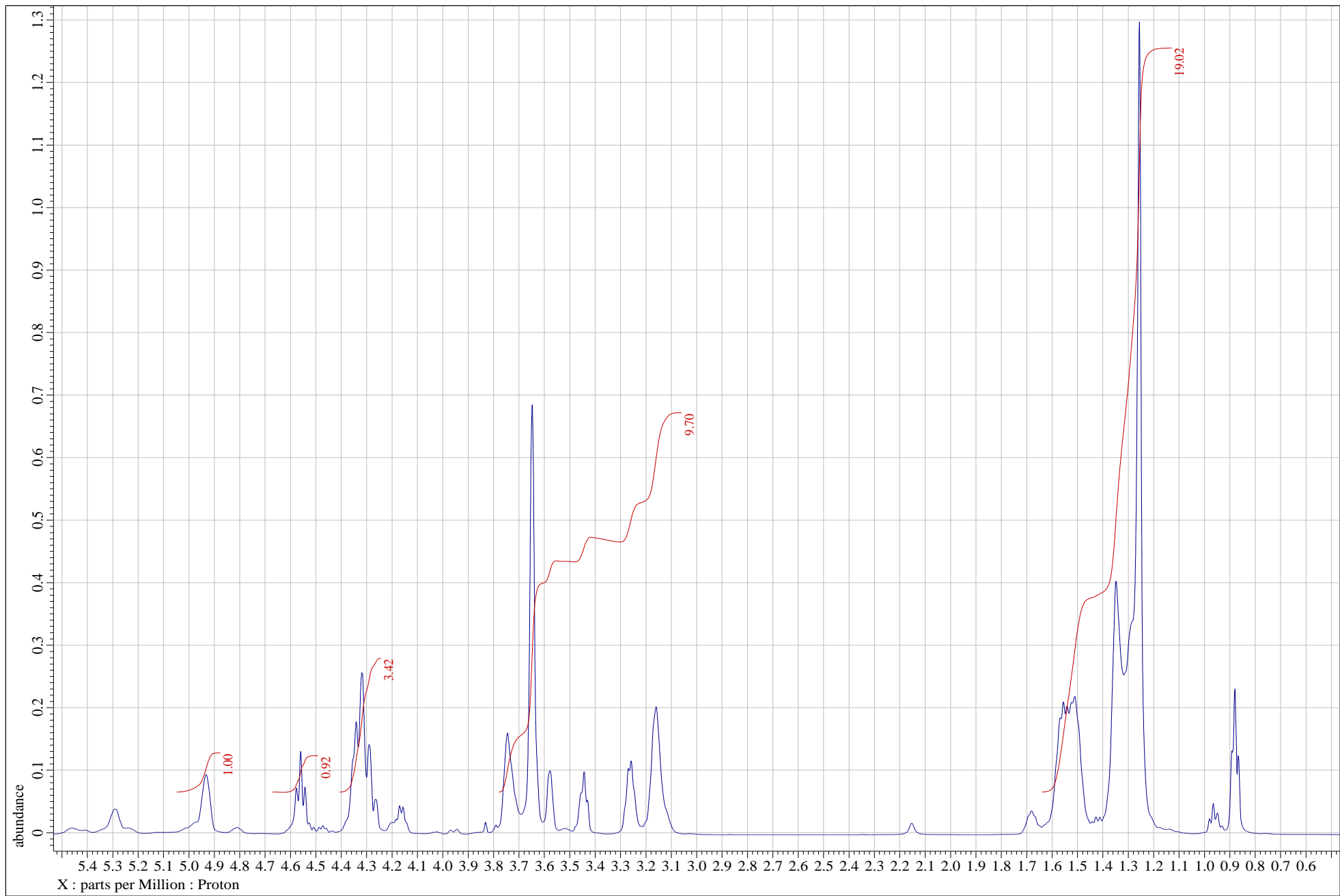
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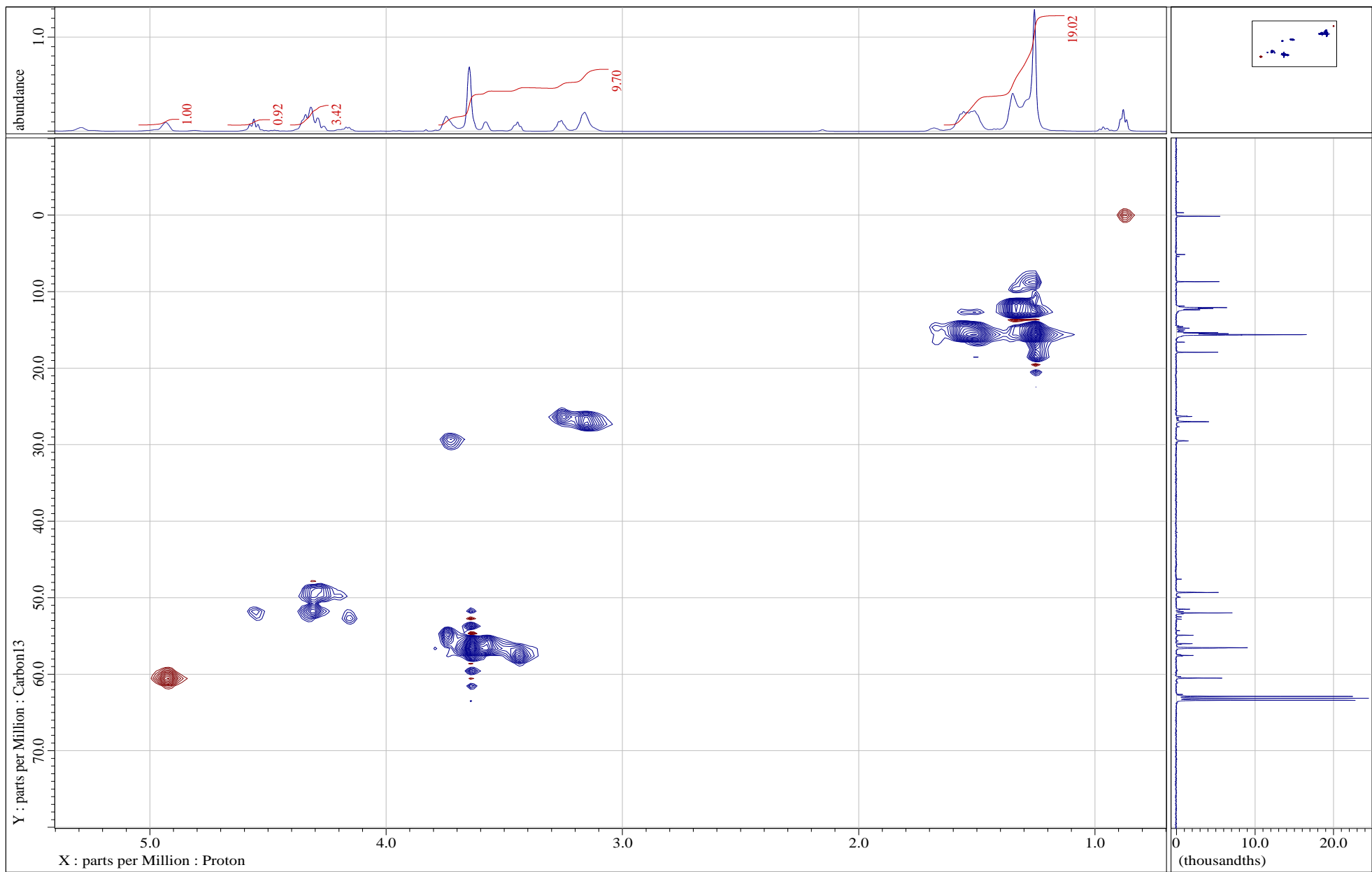
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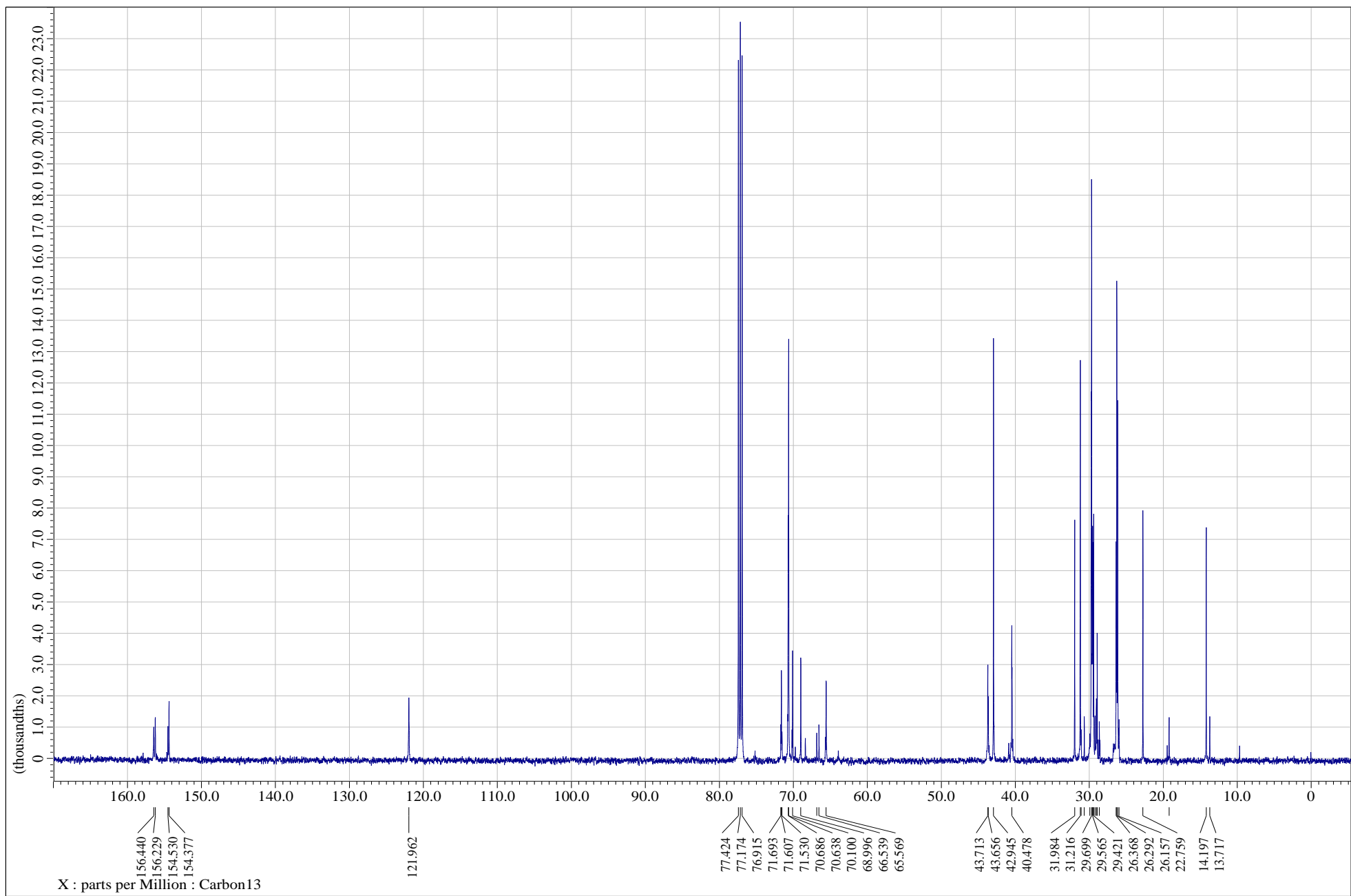
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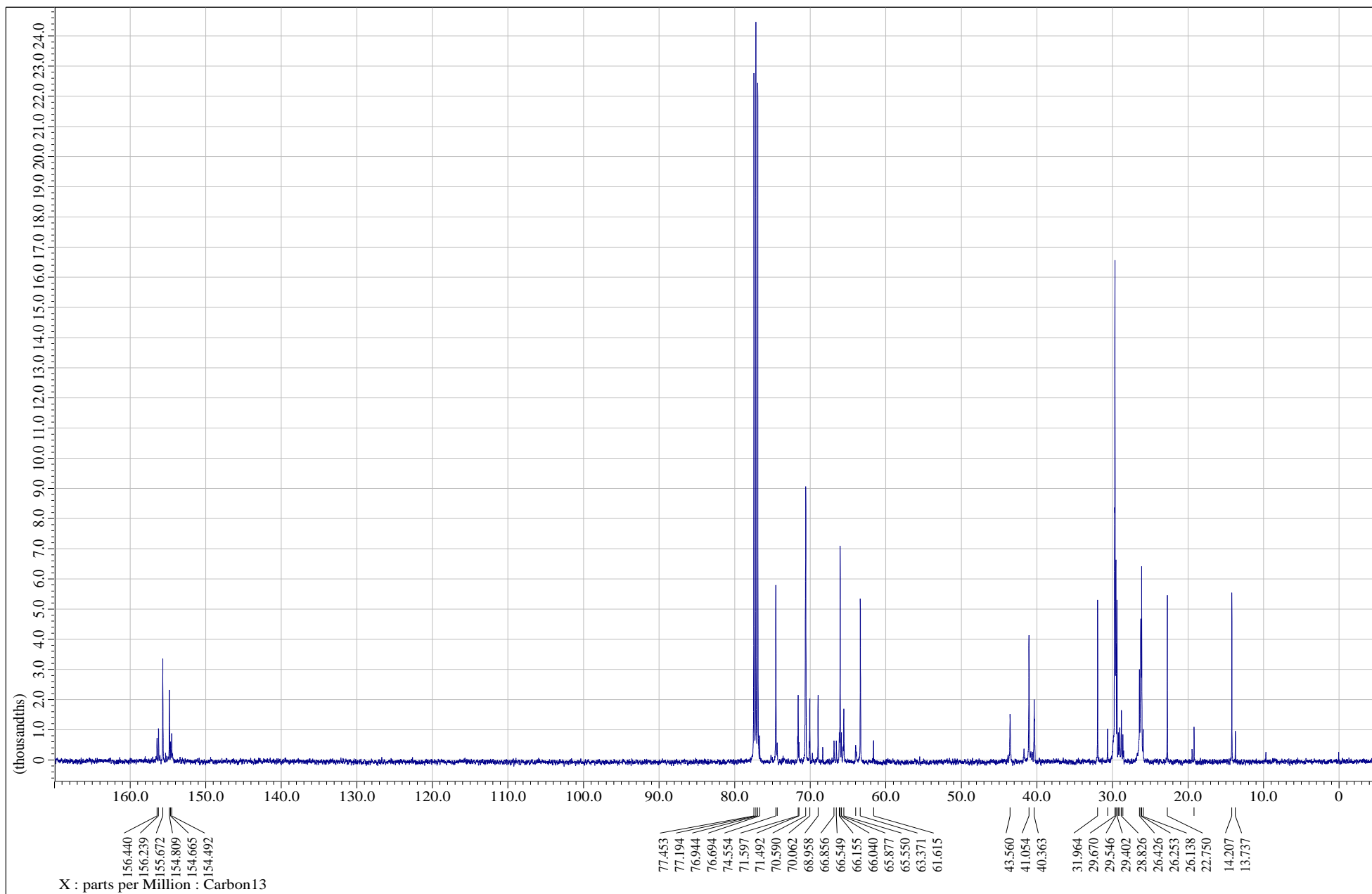
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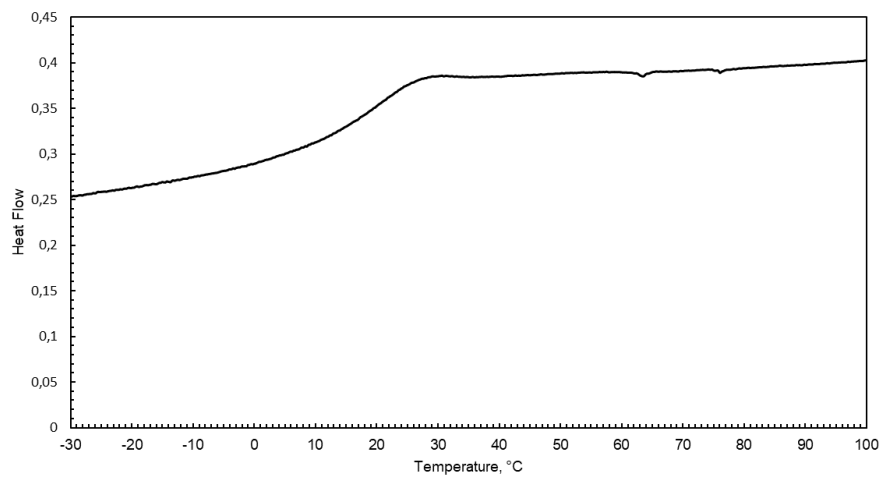
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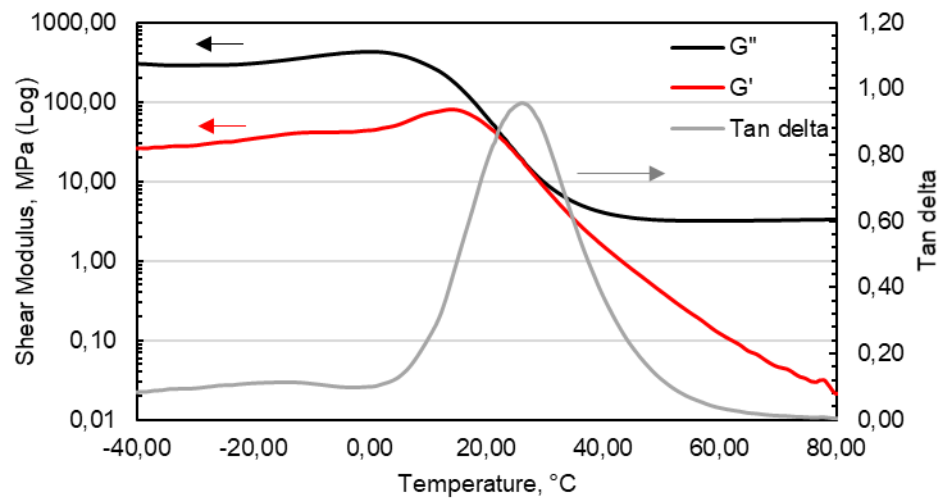
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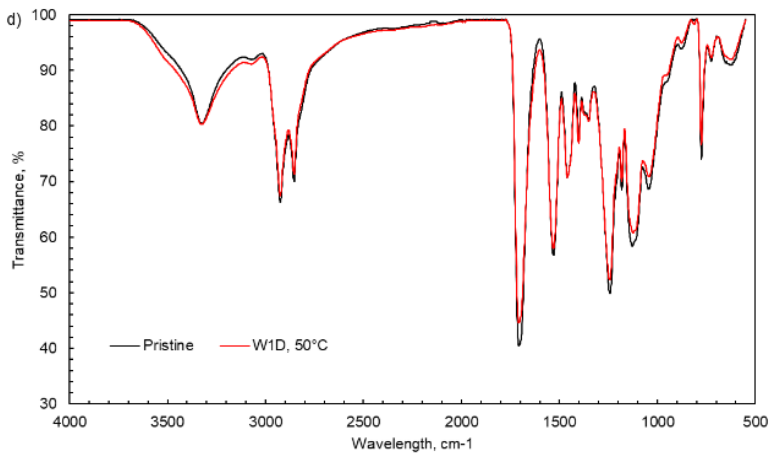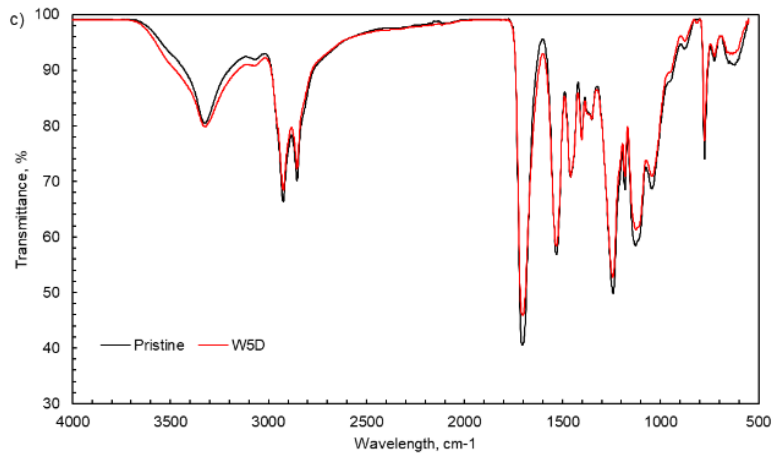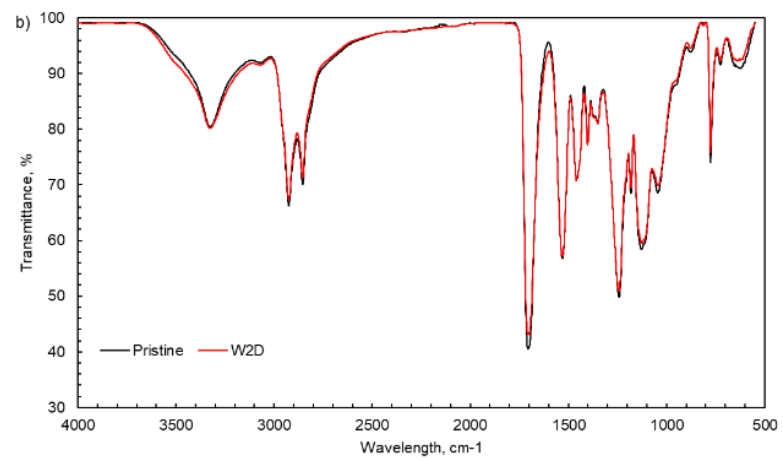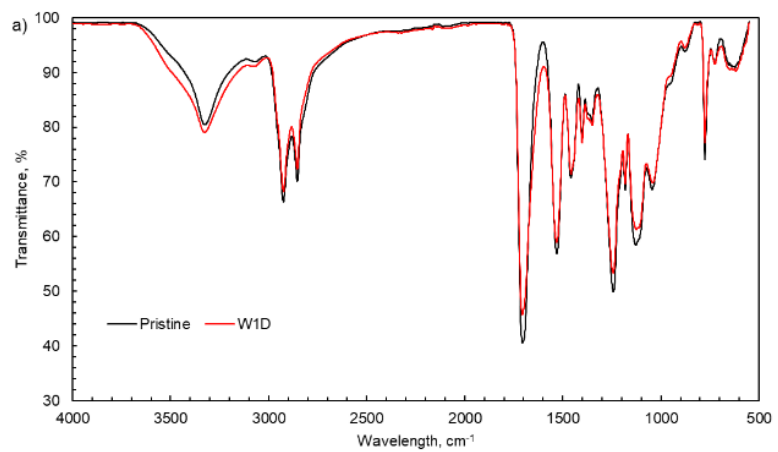
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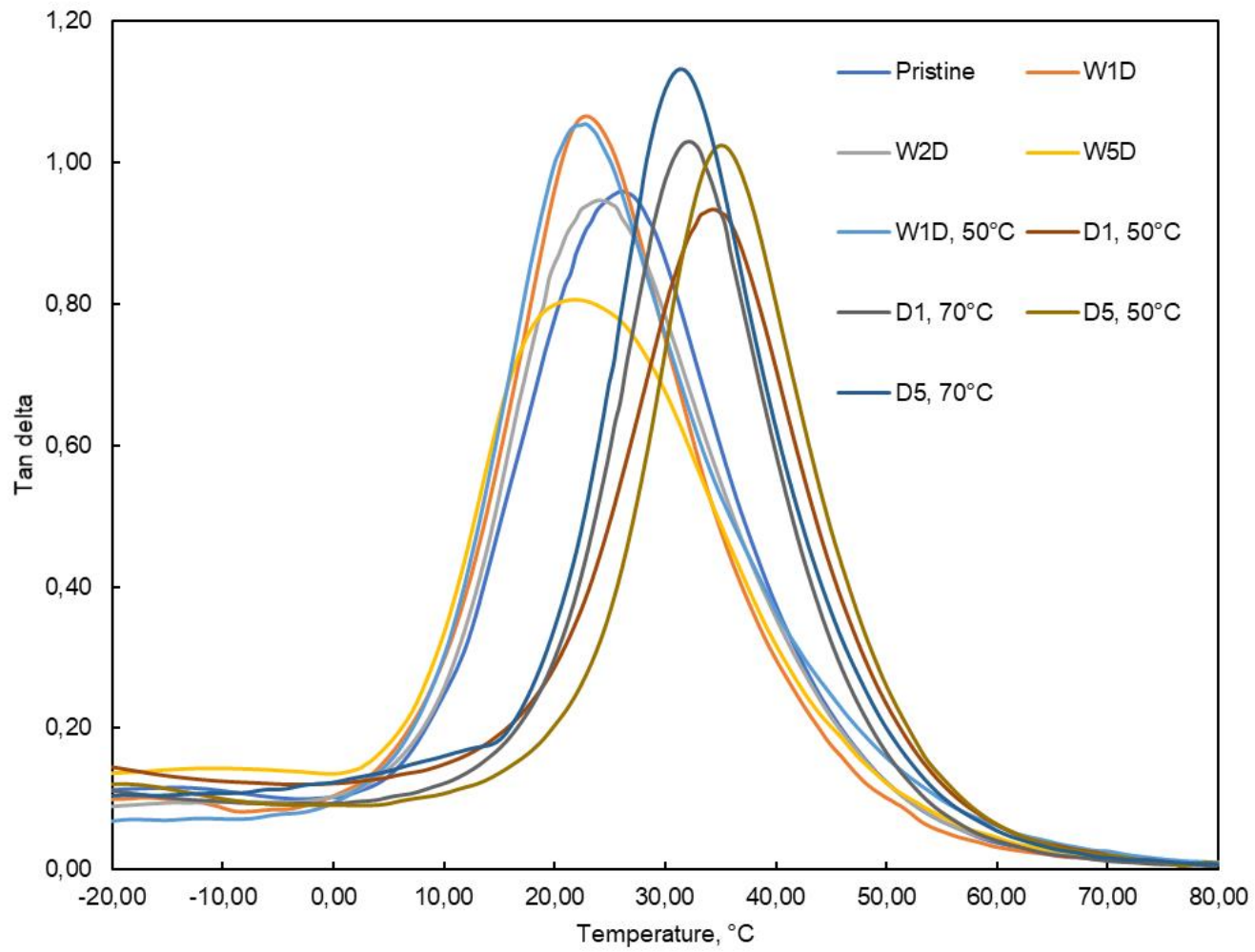
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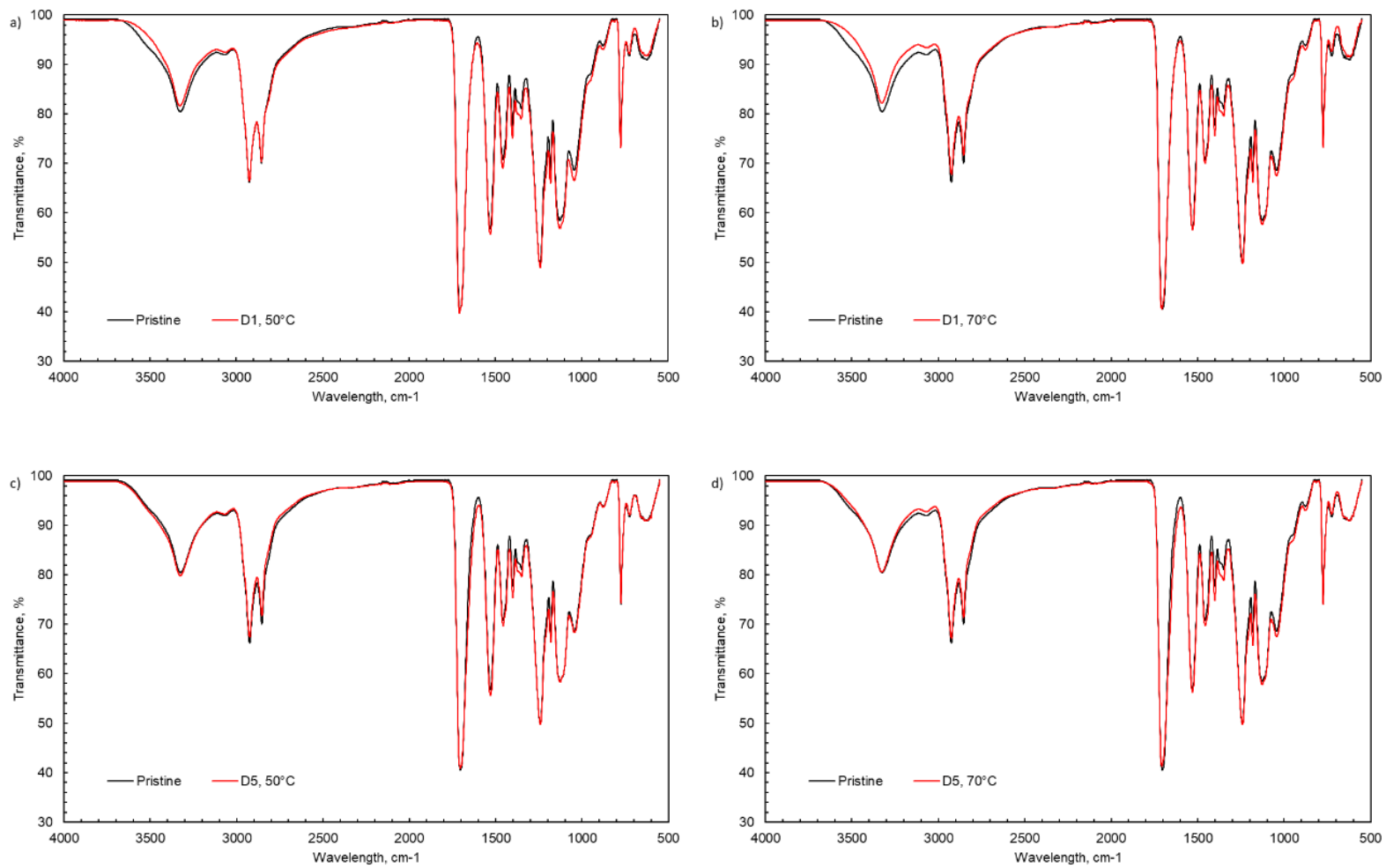
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Table ESI 1. Description of the starting materials and amounts used in the synthesis of cyclic carbonate ended prepolymer and PU/PHU

Starting materials

	Molecular weight, g/mol	Equivalent weight, g/mol	Functionality
Tolonate X FLO 100	682	341	2
Jeffsol GC	118	118	1
Lupasol PR 8515	2000	119	16.8

CC prepolymer synthesis

	Amount of isocyanate prepolymer, g	Added Glyserol carbonate, g
CC prepolymer	200	74.5

Added catalyst 0.3 wt.%

Equimolar considerations

	Amount, g	Amount in moles	Equivalent amount in moles
Lupasol PR 8515	74.46	0.037	0.631
GC added amount in prepolymer in total batch	74.50	0.631	0.631

The equimolar calculation is based on added glyserol carbonate assuming no side reactions

Typical PU/PHU synthesis

	Amount, g
Lupasol PR 8515	74.46
CC prepolymer (NCO/OH 0.93)	274.5

Table ESI 2. Used test cycles

Treatment name	Temperature	Used cycle	Amount of cycles	Post treatment prior mechanical testing
Pristine	-	-	-	Stabilized at 23 °C 50% RH for 24 hours
W1W	23°C	96 hours in water	1	Measured as wet
W1D	23°C	96 hours in water	1	Drying 50 °C for 24 hours, stabilized at 23 °C 50% RH for 24 hours
W2D	23°C	96 hours in water	2	Drying 50 °C for 24 hours, stabilized at 23 °C 50% RH for 24 hours
W5D	23°C	96 hours in water	5	Drying 50 °C for 24 hours, stabilized at 23 °C 50% RH for 24 hours
W1D, 50°C	50°C	96 hours in water	1	Drying 50 °C for 24 hours, stabilized at 23 °C 50% RH for 24 hours
D1, 50°C	50°C	Dry	1	Stabilized at 23 °C 50% RH for 24 hours
D1, 70°C	70°C	Dry	1	Stabilized at 23 °C 50% RH for 24 hours
D5, 50°C	50°C	Dry	5	Stabilized at 23 °C 50% RH for 24 hours
D5, 70°C	70°C	Dry	5	Stabilized at 23 °C 50% RH for 24 hours

Table ESI 3. Measurements in water uptake tests

Time, hours	3	24	96	168	336	504	672	Total mass change after test
Water Uptake %, 23C	13	27	27	27	28	29	29	0
STD of water uptake	0.1	0.2	0.2	0.1	0.1	0.0	0.1	0.1
Water Uptake %, 50C	17	24	28	31	42	60	399	-20
STD of water uptake	2.0	0.3	0.4	1.6	2.2	2.2	18.8	2.1
Water Uptake %, 70C	20	27	277					
STD of water uptake	0.2	0.2	7.4					

Table ESI 4. Mechanical testing after test cycles

	Pristine	W1W	W1D	W2D	W5D	W1D, 50°C	D1, 50°C	D1, 70°C	D5, 50°C	D5, 70°C
Tensile strength	2.1	0.9	3.0	2.7	2.6	2.7	3.0	3.1	3.3	2.5
Standard deviation	0.1	0.1	0.3	0.1	0.3	0.1	0.4	0.1	0.4	0.3
Elongation	26.6	7.3	40.4	39.7	40.6	39.7	29.1	38.1	34.8	39.3
Standard deviation	2.3	1.0	2.8	2.2	4.4	3.9	5.6	1.1	4.3	6.0
Lap shear	7.2	3.4	4.1	1.8	0.0	1.8	10.2	13.1	12.6	11.1
Standard deviation	1.1	0.1	0.2	0.2	0.0	0.6	1.0	0.8	1.9	1.9
Gel content in THF	99.1		99.0	99.4	99.1	97.2	99.6	99.6	99.6	99.6
Standard deviation	0.13		0.1	0.7	0.2	0.3	0.1	0.1	0.7	0.4
Tg measured from DMA	25.6		23.0	24.0	22.0	22.2	34.3	31.9	35.1	31.2