Material Science and Engineering with Advanced Research

Analysis and Characterization of Quasi-Prepolymers Obtained from Polyethylene Glycol 1500 and 4, 4´-Diphenylmethane-DiIsocyanate

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Abstract

The quasi-prepolymers were synthesized by using the pre-polymerization method with polyethylene glycol (PEG) 1500 and polymeric 4,4´-diphenylmethano diisocyanate (pMDI) in different molar ratios. The monomers and prepolymers were characterized by means of FTIR, ^{1}H-NMR and ^{13}C-NMR. It was possible to demonstrate that by decreasing the n(NCO)/n(OH) ratio, the average molecular weight of the prepolymers increased. It was also possible to show that by decreasing the prepolymer NCO content, the viscosity of the prepolymers increased. These properties have to be considered when a formulation of final polyurethane (PU) employing the isocyanate prepolymers and other diols is made.
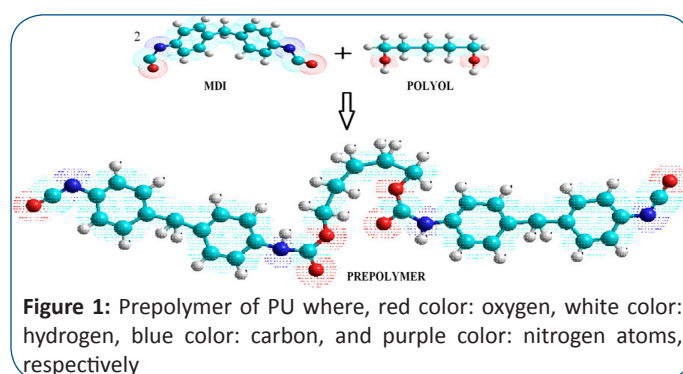
Keywords: PEG, MDI, quasi-prepolymer, FTIR, NMR

Introduction

The industrial use of prepolymers is the basis for producing a wide range of innovative products and for manufacturing general technical parts, high-performance coatings, paints, decorative architectural components, household goods, or sport devices [1]. In the PU technology, prepolymers are also widely used because the final thermal and mechanical properties of the products can be determined and fine-tuned by these systems. Therefore, a good understanding of the mechanism and curing kinetics of urethane reactions are essential to control the properties of the resulting PUs [1-2].

PU prepolymer is a product formed by a reaction between and a diisocyanate. These reactions are so exothermic that they self-destruct; i.e., no orderly polymer structure could be created. The curing agent is either a polyamine or a polyol. It has been discovered that a PU prepolymer cured with a slow-reacting curing agent selected from the group of slow reacting polyamine curing agents or polyfunctional glycols produces a golf ball cover that has good durability and performance. These materials are obtained through the addition of different chain extenders or by varying the prepolymers composition using different polyol structure and functionality, and also changing the NCO content (see Figure 1) [3-4].

Figure 1: Prepolymer of PU where, red color: oxygen, white color: hydrogen, blue color: carbon, and purple color: nitrogen atoms, respectively

PUs have been applied in the medical and pharmaceutical industries since 1970 behind biomaterial such as: prosthesis, microspheres, patch and others [5-7].

PUs are conventionally prepared by a so-called one-shot process [8-10] or by a prepolymer mixing process (or pre-polymerization method) [11-15]. In these processes the ionic centers are incorporated as chain extenders and located among the hard segments. Consequently, the mobility of the ionic segments is limited by the rigidity of the hard segments, and the ionic groups are not well exposed to the particle surfaces, which necessitates more ionic groups to produce a stable dispersion. Very little progress in this area has been reported in scientific literature. The use of prepolymers like an intermediate stage in

the PUs production presents several advantages with relation to the method of a single stage [16].

A quasi-prepolymer is not quite a monomeric isocyanate and not quite a full prepolymer. It is in between. It has the characteristics of both and yet some unique properties unto itself. TDI quasi-prepolymers are technically possible to make but are very rarely used in the thermoset castable urethane industry because of obvious health and safety reasons. MDI quasi-prepolymers are overwhelming the ones used in the industry. Typically pure MDI monomer is partially reacted with a glycol or polyol to reduce the NCO content of pure MDI from about 44% down to a range of 12 to 25%. MDI quasi-prepolymers contain both free monomeric MDI and MDI prepolymer. This mixture solves a lot of problems-pure MDI's tendency to dimerize.

Pure MDI tends to be hydrophobic, common glycol chain extenders tend to be hydrophilic and, as such, requires high shear mixing to consistently produce high quality parts.

Most MDI quasi-prepolymers are stable for several months at room temperature, making life a little easier for the processor. Quasi-prepolymers based thermoset cast urethane systems have another great advantage.

The technology enables the use of much cheaper, liquid at room temperature polyols that can be formulated into systems that can be processed at or just above room temperature and require no post curing at elevated temperatures if properly catalyzed. Because these systems can be processed at or near room temperature, a skilled formulator can sneak in a reasonable amount of MOCA or E-300 into the "B" side of a formulation to enhance specific physical properties such as tensile and tear strengths and still have enough gel time pour most parts.

The creation of quasi-prepolymers also reduces the hydrophobic/hydrophilic compatibility problems of many prepolymer systems, making it much easier to get repeatable results under mild mixing conditions. The simple ratios, low processing temperature requirements and component compatibility features makes dispensing machine design and operation very simple and easy.

Quantum mechanical calculations have extensively been used to study the energetics of simple chemical reactions and to understand the electrostatic interactions between compounds. Their application to polymeric systems, until very recently was not available. This was mainly due to very large numbers of atoms in polymeric structures requiring powerful computers and very long computer times.

With advances in both computer and software technology, now it is possible to do quantum mechanical calculations or precise simulations on polymeric systems. In this study we synthesized five different quasi-pre-polymers using PEG (Mw1500) as the macrodiol and p(MDI) as isocyanate. The monomers stoichiometry was changed to prepare quasi-pre-polymers with different percentage of free NCO groups that later can react with other diols to give rise to PUs with different properties. The quasi-prepolymers were characterized by means of FTIR and NMR (^{1}H and ^{13}C) spectroscopy, viscosity and NCO content.

Methods

Geometry optimization

In this work three aspects were considered for selection of geometry optimization method and algorithm: system size, convergence level and force field used. Next a minimization algorithm is chosen to find the potential energy minimum corresponding to the lowest energy structure. Iteration number and convergence level lead optimal structure. The geometry optimization (AM1 method) was calculated by means of the Polak-Ribiere algorithm with a gradient of 0.001 Kcal/(Å mol) in vacuum, 1 spin multiplicity, convergence limit of 0.001, and 1000 iteration limits.

Synthesis of the quasi prepolymers

The synthesis of quasi-prepolymers was carried out using the pre-polymerization method. The quasi-prepolymers were prepared by reacting the pMDI (Desmodur® 44V20L from Bayer) and PEG 1500 (purchased from Aldrich, Portugal) in a 50% w/v solution with dimetylsulfoxide (purchased from Lab – Scan, Portugal and dried over molecular sieves 4 Å) in a three-necked 500mL glass flask, under a dry nitrogen atmosphere. The inert atmosphere was used to avoid the ingress of moisture and the consequent formation of urea bonds during synthesis. The reaction was development with mechanical stirring (400 rpm), at 40 °C and with drop-by-drop addition of polyol for 8h. The synthesis of prepolymers was done in triplicate.

Further syntheses were carried out under identical conditions as described above with the presence of 0.5 mL of the catalyst trietanolamine (Merck,Germany), which was added to each polyol solution that later reacted with the isocyanate [17].

Polymer characterization

The FTIR spectra were obtained with a Nexus Thermo Nicolet spectrometer equipped with attenuated total reflectance (ATR) device. 128 scans with a spectral resolution of 4 cm^{-1} were averaged to give the specimen spectrum from 4000 to 600 cm^{-1}. All FTIR spectra were recorded at ambient temperature. NMR (^{1}H and ^{13}C) spectra were obtained using a BRUKER 300 MHz spectrometer on samples dissolved in CDCl$_3$ at room temperature (the spectra were referred internally using hexamethyldisiloxane, HDMSO, β_H 0.058 and β_C 1.9 relative to tetramethylsilane, TMS) [5, 18].

The measurement was made using approximately 10 mg samples. The viscosity measurements of the prepolymers were performed using an ICI Cone and Plate viscometer (ICI, London, LTD) at 25 °C. The measurements took place once the reading has stabilized but without allowing too much time in order to avoid the reaction of the prepolymer with the humidity of the air. The NCO content in the prepolymer was determined by back titration of excess N,N-dibutylamine with standard HCl as described in the European Standard en 1242:1998.

Statistical analysis

The viscosity content and viscosity are expressed as mean ± standard deviation. The confidence interval of NCO content in the study of the influence of the reaction time was obtained by the Statgraphics Puls© (for Windows 5.1, Statistical Graphics. Microsoft Corporation, EUA).

The data were compared using the Student's t-test.

Results

The geometry optimization was used to locate a minimum of energy, on the surface, of the potential energy surface, and

get the balance structure of a molecular system. Using the Hyperchem 8v software, by means of the AM1 method, with the Polak-Ribiere algorithm was possible calculate the Gibbs free energy (ΔG) of different materials (see Table 1), where were observed the negative values obtained shows that the reaction is spontaneous [19].

Table 1: Gibbs free energy (ΔG) for quasi-prepolymer

Properties	MDI	PEG	Quasi-Prepolymer
ΔG (Kcal/mol)	- 3395.882	- 1497.515	- 7794.101
Log P	- 0.04	0.19	1.41

The partition coefficient is a ratio of concentrations of un-ionized compound between the two liquid phases. The logarithm of the ratio of the concentrations of the un-ionized solute in the solvents is called log P. When one of the solvents is water and the other is a non-polar solvent, then the log P value is also known as a measure of lipophilicity. In the chemical and pharmaceutical sciences, the two phases are often restricted to mean two immiscible solvents. In this context, a partition coefficient is the ratio of concentrations of a compound in the two phases of a mixture of two immiscible liquids at equilibrium.
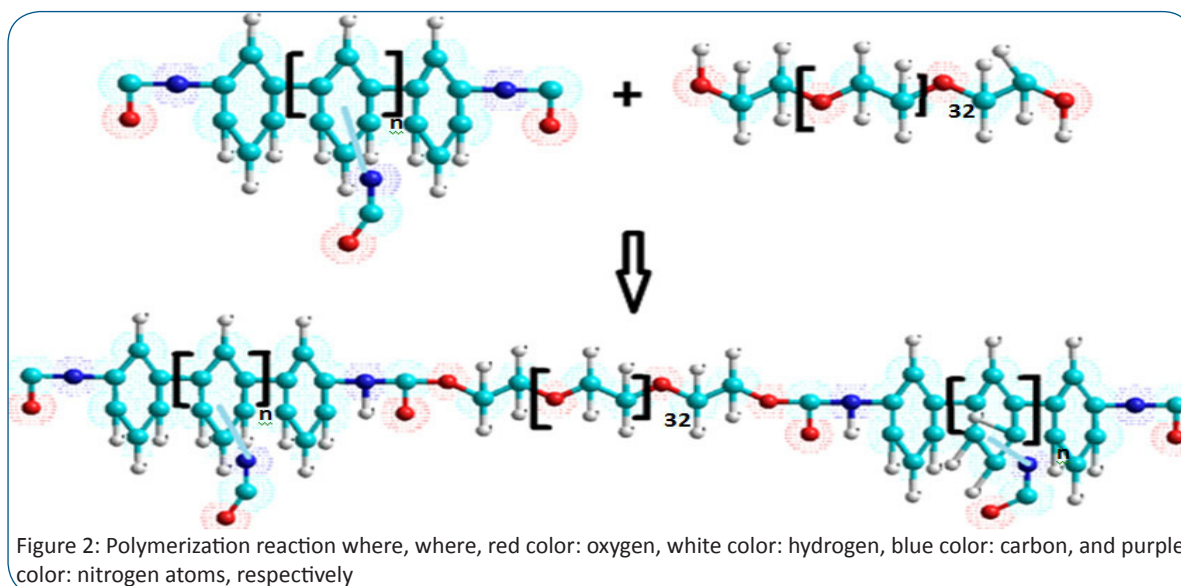
Normally one of the solvents chosen is aqueous while the second is hydrophobic such as 1-octanol. Hence both the partition and distribution coefficient are measures of how hydrophilic or hydrophobic a chemical substance is. Partition coefficients are useful in estimating the distribution of drugs within the body [20-21].

Log P value of quasi-prepolymer calculated was 1.41, and represents the hydrophilic properties of a substance and is considered to be a model for the absorption of molecules into hydrogels. The chemical structures proposed for the prepolymers are given in Figure 2. The formulation, NCO content and viscosity for all prepolymers synthesized are presented in Table 2. All the polymers were obtained in liquid phase and presented an amber color.

Analysis of the viscosity and NCO content

Table 2 shows that the viscosity of the prepolymers decreased as the NCO content increased. These results are agreement with the results of other authors. Decreasing the NCO/OH molar ratio produced an increase in the average molecular weight of the prepolymers and viscosity. These properties have influence in the prepolymers lifetime. Almost all prepolymers remained liquids for five months after the synthesis, maintaining equal viscosity values. Hardening was only observed for the Pre-6 on the seventh day after the synthesis.

Table 2 shows a viscosity of 24 Pa.s for Pre-6, which might indicate that it possesses the highest molecular weight and a highest degree of crosslinker than the rest of the prepolymers. In NCO-range (15% to 16%), a good compromise between viscosity of the material and the reactivity of the system is obtained. Lower NCO-prepolymers have a higher viscosity, but give higher elasticity and slower reactivity. Higher NCO-prepolymers are lower in viscosity, which is good for an effective mix of the two components.


Figure 2: Polymerization reaction where, where, red color: oxygen, white color: hydrogen, blue color: carbon, and purple color: nitrogen atoms, respectively

Table 2: Formulation, isocyanate content and viscosity of the quasi-prepolymers SD: standard derivation

| Prepolymer	p(MDI) (g)	m(PEG) (g)	n(NCO) (mol)	n(OH) (mol)	RATIO (m/m)	%NCO free Average±SD	Viscosity average (Pa.s)±SD
PRE − 6	100	92	0.7380	0.1230	1.1	9.00 ± 0.03	24.0±0.01
PRE − 8	100	69	0.7380	0.0922	1.4	10.0±0.28	10.7±0.01
PRE − 10	100	55	0.7380	0.0738	1.8	13.0±0.55	9.60±0.01
PRE − 12	100	46	0.7380	0.0615	2.2	14.0±0.14	8.30±0.02
PRE − 14	100	39	0.7380	0.0527	2.6	15.0±0.40	5.0±0.01

Influence of the reaction time

Quasi-prepolymers syntheses were carried out from 15 to 480 min, respectively. The NCO content of each quasi prepolymer was analyzed as presented in Figure 3 for the prepolymer 14. On other hand the statistical analysis (Statgraphics Plus©) done over the NCO content, for quasi-prepolymer 14, between 60 and 480 min gave rise to a confidence interval of 15.03±0.37 and 14.86±1.00 respectively. With the time, the percent of isocyanate group (NCO) decrease that is to say that there is more reaction between the glycol and isocyanate, the chains overlaps and possibly increase the molecular weight, however according to the research after 60 min, the reaction behavior is the same as at 480 min.
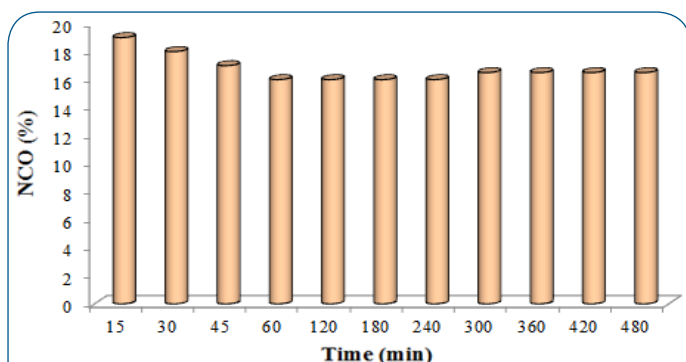
Figure 3: Variation of NCO content with reaction time of the isocyanate quasi-prepolymer

The resultant p value of 0.5406 with Student's value of 0.6681 is higher than 0.05 then the null hypothesis is true for the studied group with 95% of confidence level. At shorter times (15, 30 and 45 min) higher values of NCO content for all the isocyanate quasi-prepolymers were obtained and decreased slightly as the reaction proceeded. This result revealed that the NCO content is similar when one considered either 60 or 480 min of reaction time. Figure 4 shows the same behavior, where it can be observed that not considerable difference existed in the NCO content determined at 60 or 480 min for all quasi-prepolymers (8, 10, 12 and 14). For this reason, an hour was selected as the reaction time of syntheses.
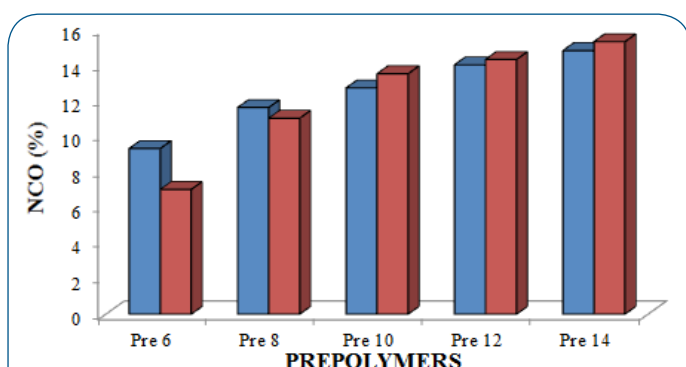
Figure 4: Influence of the reaction time on the NCO content (■ 60 in and ■ 480 min, respectively)

Influence of the presence of the catalyst in the reaction medium

The influence of the catalyst analyzed in the synthesis process based on the NCO content, for one hour of reaction time, is presented in Table 3. It can be seen that the presence of the catalyst does not change the NCO content, since similar values were obtained for both groups of reactions.

Table 3: Influences of the presence of the catalyst in the NCO content of the isocyanate quasi-prepolymers SD: standard derivation

Prepolymer	%NCO average with trietanolamine±SD	%NCO average without trietanolamine±SD
PRE – 6	8.99±0.03	8.90±0.20
PRE – 8	11.08±0.03	12.05±0.05
PRE – 10	12.10±0.56	12.00±0.66
PRE – 12	14.60±0.15	14.50±0.53
PRE – 14	15.40±0.60	14.80±0.10

FTIR analysis

All quasi-prepolymers show a similar FTIR spectrum, for example, Figure 5 confirms the spectrum of quasi-prepolymer 14. The presence of a weak band to 3326 cm^{-1} corresponding to the stretching vibrations of NH groups is observed. The strong band to 2265–2260 cm^{-1} confirmed the existence of free NCO groups in the quasi-prepolymer. The band from 1716 to 1712 cm^{-1} was attributed to the stretching vibration of C=O bond [21] characteristic of urethane group, due to the deformation of the NH bond and C–N stretching vibration. The peak about 1600 cm^{-1} corresponds to C=C stretching in the aromatic ring. Two peaks at 1012 and 1510 cm^{-1} arise from symmetric and asymmetric stretching vibrations of N–C–N, respectively, corresponding to the reactions of the NCO groups with the NH groups [5]. This behavior has been reported previously for PUs [15].
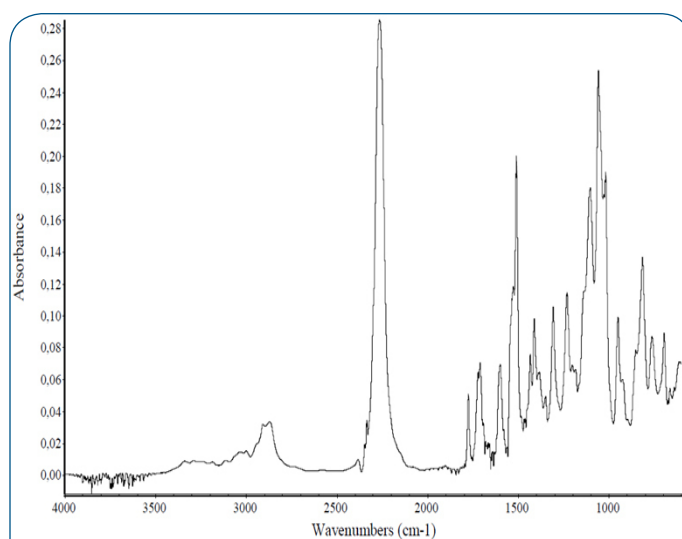
Figure 5: FTIR-ATR mode spectra of the quasi-prepolymer 14

NMR analysis

The interpretations of the quasi-prepolymers NMR spectra were based on a simplified polymer structure presented in Figure 1. We did not consider other more complex molecules that arise from the fact the materials used in the polymer synthesis are polymeric. It is important to mention that this assignment is not precise but only an approximation in agreement with the spectra obtained. Figure 6 shows the quasi prepolymer 8 spectrum and the protons from 3.5 to 3.8 ppm were assigned to the CH$_2$ group.

The sign at 3.8 ppm was attributed to the protons that are between aromatic rings. The protons of the aromatic rings were assigned
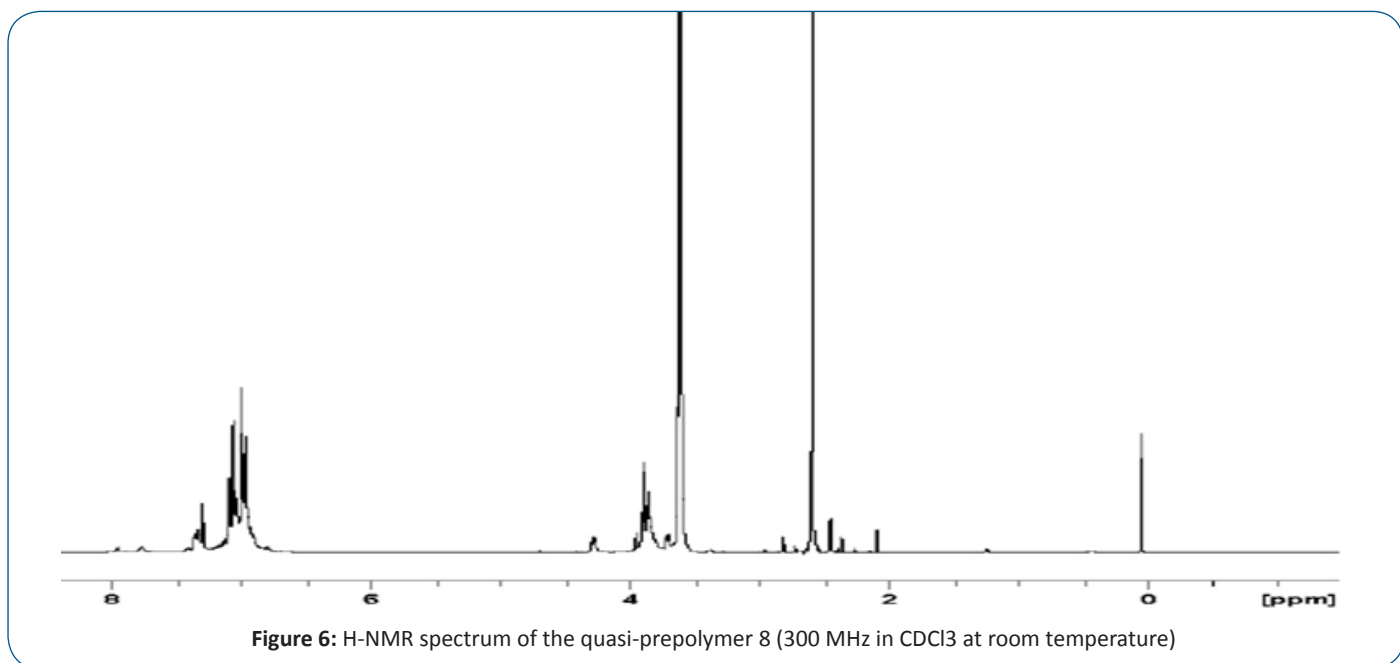
Figure 6: H-NMR spectrum of the quasi-prepolymer 8 (300 MHz in CDCl3 at room temperature)

to the signals from 6.9 to 7.2 ppm finally the peaks from 7.9 to 8 ppm were assigned to the protons of amines groups present in the quasi prepolymers. This assign is very important because it confirms the reaction between the hydroxyl groups of the PEG1500 and the isocyanate groups of the pMDI.

The ^{13}C-NMR spectrum, which is presented in Figure 7, confirms the proposed structure for prepolymer 8 (Table 1). The methylene signs in the region 40.6–41.6 ppm were assigned to the pMDI structure, also, the region from 64 to 70.4 ppm were attributed to carbons of PEG structure. The aromatic area, from 118–139 ppm, increased the complexity 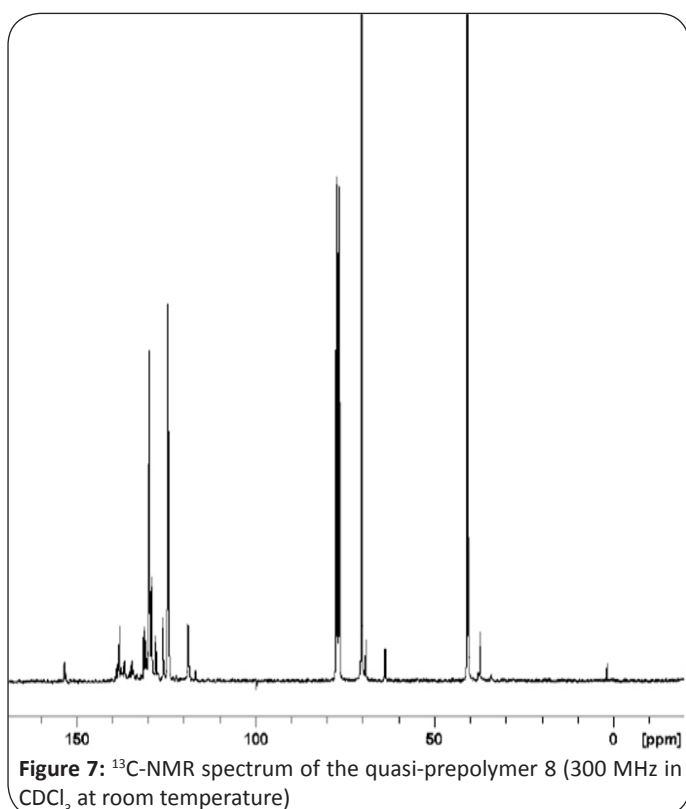of quasi-prepolymer due to symmetry loss of aromatic protons when is compared with pMDI. Finally, two signs at 127 and 153 ppm were detected and assigned to the carbonyl.

Conclusions

It was possible to prepare quasi-prepolymers based in PEG 1500 and MDI, varying the NCO content (4 ratios). The NCO/viscosity ratio was inversely proportional. Using FTIR it was possible to detect the characteristic bands of the quasi-prepolymers formation. Also, the ^{1}HNMR and ^{13}C-NMR analyses confirmed that the reaction between pMDI and PEG 1500.

Acknowledgements

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Figure 7: ^{13}C-NMR spectrum of the quasi-prepolymer 8 (300 MHz in CDCl$_3$ at room temperature)

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