UNIVERSITAT ROVIRA I VIRGILI

POLYCARBODIIMIDE SYNTHESIS OPTIMIZATION AND ITS APPLICATION AS POLYMER STABILIZER AGAINST DEGRADATION PROCESSES

ALBERT MORELL GARCIA

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Polycarbodiimide synthesis optimization and its application as polymer stabilizer against degradation processes

Doctoral Thesis

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Cromogenia Units S.A.

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I STATE that the present study, entitled "**Polycarbodiimide synthesis optimization and its application as polymer stabilizer against degradation processes**", presented by Albert Morell Garcia for the award of the degree of Doctor, has been carried out under my supervision at the Department of Nanoscience, materials and chemical engineering of this university.

Tarragona, 04/07/2017

Doctoral Thesis Supervisor

Dr. Francesc Medina Cabello

PREFACE

The present Doctoral Thesis has been carried out under the Industrial Doctorates scholarship promoted by the Generalitat de Catalunya and the Agencia de Gestió d'Ajuts Universitaris i d'Investigació (AGAUR).

This scholarship facilitates the insertion of young students to the industry and allows qualified workers to continue its formation. In addition, this kind of aids, helps the industrial sector to develop new research projects under the academic support of the universities.

In 2013 the project 2013 DI 014 "Polycarbodiimide synthesis optimization and its application as polymer stabilizer against degradation processes" starts as an Industrial Doctorate project from Cromogenia Units S.A. and the Universitat Rovira i Virgili.

Cromogenia Units S.A. decided to improve its product range with the development of carbodiimides. The Universitat Rovira i Virgili has helped with its wide knowledge and equipment to complete this project research and development.

This new stage increases the relationship between industry, universities and technological centers, which are given mutual support in issues such as development, technical trials with specific equipment, production and result evaluation.

A mis padres,

Ramón y María

“La vida es como un fandango; y hay que saberlo bailar”

A mis tíos y primos

A Javier y Teresa

A Pablo y Marina

A Cris

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No quisiera olvidarme de los compañeros del grupo de investigación Catheter, a quienes por motivos de realización de gran parte de la Tesis a más de 100 km de distancia, he visto muy poco. Aun y así siempre que he necesitado cualquier cosa, o resolver cualquier cuestión, me han ayudado en todo lo posible, en especial a Susana Dominguez en la etapa final de impresión de la Tesis. Agradecer también a Núria Joanpere sus rápidas respuestas ante cualquier tipo de duda surgida.

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ABSTRACT

The research of this doctoral thesis is framed in the collaboration between Cromogenia Units S.A. and the Catheter research group of the Chemical Engineering Department from the Rovira I Virgili University.

This thesis is based in the synthesis, characterization and application of polycarbodiimides.

The chemistry of polymers, especially the polymers to be exposed outdoor, requires an extra stability to degradation, principally to hydrolysis and oxidations processes which causes the properties loss of the final product manufactured.

Carbodiimides are used as polymer stabilizers against this kind of degradation processes by reacting the new generated groups and rebuilding the polymer structure.

During this study a research about the carbodiimide reaction conditions, the synthesis process and the reaction mechanism has been carried out in an initial phase of the project. Depending on the initial isocyanate monomer used, the reaction condition needs to be stronger. Differences in the activities to reach close to 85% of carbodiimide conversion are also studied.

Campbell and Monagle first postulated the reaction mechanism of this kind of reactions in 1962. The mechanism indicates the formation of a reaction intermediate before generate the final carbodiimide group. This research work has identified for first time this intermediate by using NMR technique, which demonstrate and confirms the initial mechanism postulated.

A catalyst study has been also performed to study the dependence between the catalyst structure and the activity. Furthermore, MALDI TOF mass spectroscopy has been used for a molecular study. A dependence between the catalyst amount and the final oligomer structure has been observed. Uretonimine branched structures has been identified. Its presence vary depending the catalyst dose used and the temperature applied to the reaction system.

The exclusive use of the phospholene oxides for the conversion of isocyanates to carbodiimides makes the catalyst as a strategic product. For this reason and due

to the monopoly production of certain companies the price of this kind of catalyst is very expensive. In order to optimize the catalyst amount used, an isomerization study has been carried out to increase the catalyst activity.

In the last part of the study, an oligomer functionalization has been done to incorporate the synthetized carbodiimde sample to different polymer matrix. After this incorporation, different accelerated aging tests such as external agents exposition and UV light exposition were performed to study how carbodiimides works as stabilizing agents.

Polycarbodiimides has been tested in polyester based polyurethane and in polypropylene system. In both matrix carbodiimides has shown a resistance improvement against degradation.

The main objective of the industry is to produce different products to solve the customer necessities. For this reason a scaling up study has also been performed. A pilot plant and industrial production has been carried out to check the optimized laboratory process repeatability. Different modifications in the industrial facilities has been done to improve the final production.

RESUMEN

La investigación realizada en esta tesis se ha llevado a cabo con la colaboración entre Cromogenia Units S.A. y el grupo de investigación Catheter del Departamento de Ingeniería Química la Universidad Rovira y Virgili.

Esta tesis se basa en el estudio de la síntesis, la caracterización y la aplicación final de policarbodiimidas.

La química de los polímeros, especialmente la de los polímeros destinados a ser expuestos a la intemperie, requiere una estabilidad extra a la degradación, principalmente a procesos como la hidrólisis y la oxidación que provocan la pérdida de propiedades de la pieza final fabricada.

Las carbodiimidas se usan como productos estabilizantes de polímeros frente a procesos de degradación mediante su reacción frente a los nuevos compuestos generados, reconstruyendo así la estructura del polímero degradado.

Durante la elaboración de este estudio, en una primera etapa del proyecto se han investigado las condiciones de reacción, el proceso de síntesis y el mecanismo de reacción de las carbodiimidas. Dependiendo del monómero isocianato empleado, las condiciones de reacción deben verse modificadas. Se han estudiado también las diferencias de actividad en la reacción de conversión de isocianato a carbodiimida para llegar a alcanzar cerca de un 85% de conversión.

El mecanismo de reacción fue postulado por primera vez por Campbell y Monagle en el 1962. Dicho mecanismo indica la formación de un intermedio de reacción previo a la generación del grupo carbodiimida. Este estudio ha logrado identificar por primera vez dicho intermedio de reacción mediante el uso de RMN, lo cual demuestra y confirma el mecanismo inicial postulado.

Además, también se realizó un estudio del catalizador para estudiar la relación entre la estructura del catalizador y su actividad para la conversión de isocianatos. Mediante el uso de la espectrometría de masas MALDI TOF se realizó un estudio del peso molecular obtenido en los oligómeros preparados. Durante la elaboración de dicho estudio se ha observado una dependencia entre la dosis de catalizador y la estructura final del oligómero sintetizado. Mediante ésta técnica se han podido identificar estructuras ramificadas formando uretoniminas. Su

presencia en las distintas muestras preparadas varía en función de la cantidad de catalizador usada y de la temperatura aplicada al sistema de reacción.

El exclusivo uso de los óxidos de fosfoleno para la conversión de isocianatos en carbodiimidas, hace del catalizador un producto estratégico en el mercado. Debido a esto, y al monopolio que han generado las multinacionales en torno a estos compuestos hacen del catalizador un producto muy caro. Para tratar de optimizar la cantidad de catalizador empleada, se ha realizado un estudio de isomerización para incrementar la actividad del catalizador.

Durante la última parte del estudio se han realizado diferentes funcionalizaciones para poder incorporar las carbodiimidas preparadas a diferentes matrices poliméricas. Después de dicha incorporación las muestras se han sometido a diferentes tests acelerados de envejecimiento como a agentes externos y a la exposición de luz ultravioleta para poder estudiar el comportamiento de las carbodiimidas como agentes estabilizantes.

Las policarbodiimidas han sido probadas en poliuretanos basados en poliéster y en polipropileno. Los resultados obtenidos en ambas matrices poliméricas muestran una mejora de la resistencia a la degradación.

El objetivo principal de la industria es la producción de diferentes productos para satisfacer las necesidades del consumidor. Por este motivo también se ha realizado el proceso de escalado del producto. Se han preparado una prueba piloto y una industrial para comprobar la repetitividad del proceso optimizado a nivel laboratorio. Para la mejora de dicho proceso de escalado industrial se han tenido que realizar diferentes modificaciones para mejorar la obtención del producto final.

RESUM

La investigació que s'ha dut a terme en aquesta tesi ha sigut realitzada en col·laboració entre Cromogenia Units S.A. i el grup d'investigació Catheter del Departament d'Enginyeria Química de la Universitat Rovira i Virgili.

Aquesta tesi està basada en l'estudi de la síntesi, la caracterització i l'aplicació final de les policarbodiimides.

La química dels polímers, especialment la dels polímers destinats a ser exposats a la intempèrie, requereixen una estabilitat extra a la degradació, bàsicament a processos com la hidròlisi i la oxidació que provoquen la pèrdua de propietats de la peça final fabricada.

Les carbodiimides s'utilitzen com a productes estabilitzants de polímers envers els processos de degradació mitjançant la seva reacció amb els nous compostos generats, reconstruint d'aquesta manera la estructura del polímer degradat.

Durant la elaboració d'aquest estudi, en una primera etapa del projecte s'han investigat les condicions de reacció, el procés de síntesis i el mecanisme de reacció de les carbodiimides. Depenent del monòmer isocianat utilitzat, les condicions de reacció s'han de modificar. S'han estudiat també les diferents activitats trobades en la reacció de conversió d'isocianat en carbodiimida per arribar a un grau de conversió proper al 85%.

El mecanisme de reacció va ser postulat per primera vegada per Campbell i Monagle al 1962. Aquest mecanisme indica la formació d'un intermig de reacció previ a la formació del grup carbodiimida. Aquest estudi ha aconseguit identificar per primera vegada aquest intermig de reacció mitjançant RMN, el que demostra i confirma el mecanisme inicial postulat.

A més a més, també s'ha dut a terme un estudi del catalitzador per estudiar la relació entre la seva estructura i la activitat mostrada per a la conversió de isocianats en carbodiimides. Mitjançant l'ús de la espectrometria de masses MALDI TOF s'ha realitzat un estudi del pes molecular obtingut en els oligòmers preparats. Durant la elaboració del estudi s'ha observat una dependència entre la dosi del catalitzador i la estructura final del oligòmer sintetitzat. Mitjançant aquesta tècnica s'han pogut identificar estructures ramificades formant

uretoinimines. La seva presència en les diferents mostres preparades varia en funció de la quantitat de catalitzador emprada i de la temperatura aplicada al sistema de reacció.

El exclusiu ús dels òxids de fosfolè per a la conversió d'isocianats en carbodiimides, fa del catalitzador un producte estratègic en el mercat. Degut a això, i al monopoli generat per les multinacionals envers a aquests productes, fan del catalitzador un producte molt car. Per intentar optimitzar la dosi de catalitzador utilitzada, s'ha realitzat un estudi d'isomerització per incrementar l'activitat del catalitzador.

Durant la última part de l'estudi s'han realitzat diferents funcionalitzacions per poder incorporar les carbodiimides preparades a diferents matrius polimèriques. Després de la seva incorporació les mostres han estat sotmeses a diferents assajos accelerats d'envelliment com és la exposició a agents externs i a la llum ultravioleta, per poder estudiar el comportament de les carbodiimides com agents estabilitzants.

Les policarbodiimides han sigut provades en poliuretà base polièster i en polipropilè. Els resultats obtinguts en ambdues matrius polimèriques han mostrat una millora de la resistència a la degradació.

L'objectiu final de la industria és la producció de diferents productes per satisfer les necessitats del consumidor. Per aquest motiu s'ha realitzat també un procés d'escalat del producte. S'han preparat una proba pilot i una industrial per tal de comprovar la repetibilitat del procés optimitzat a nivell de laboratori. Per la millora del procés d'escalat industrial s'han tingut que realitzar diferents modificacions per millorar la obtenció del producte final.

Chapter 1

Introduction

1 INTRODUCTION

Carbodiimides are a class of organic compounds having the heterocumulene structure R-N=C=N-R, where R could be a multiple kind of substituents like alkyl, aryl, imidoyl or sulfonyl. This kind of products could be considered as a diimide of carbon dioxide and are directly related to isocyanates [1]. Carbodiimides are commonly used in the industry as a polymer stabilizers against hydrolysis and ageing [2].

There was many different synthetic routes to produce carbodiimides, such as starting from ureas, by nitrene rearrangements, from cianamides, but the conversion of isocyanates into this kind of products increases the yield under mild conditions [3].

1.1 CROMOGENIA UNITS S.A.

This doctoral thesis has been carried out in collaboration between Cromogenia Units S.A. and the Universitat Rovira i Virgili through the industrial doctorate fellowship granted by the Generalitat de Catalunya.

Cromogenia Units S.A. is a familiar company created in 1942 and it's dedicated to many different chemical products for leather, textile, paper, detergency, flexible packaging, composites, construction, coatings, water treatment, metalworking, fine chemicals and others. It pertains to the UNITS group, that englobe 5 chemical Spanish companies, Cromogenia Units S.A., Alcover Química S.L., Arteixo Química S.L., Auxicolor S.A. and Quimipiel S.L. It also has manufacturing centers in America (Units Mexico, Units Sudamericana), Europe (Alcover Italiana Units Kimyevi) and Asia (Cromogenia Units Shangai CO) and different commercial offices that has performed the entrance to different global markets (see Figure 1.1), and has increased the total business up to 180 million euros per year.

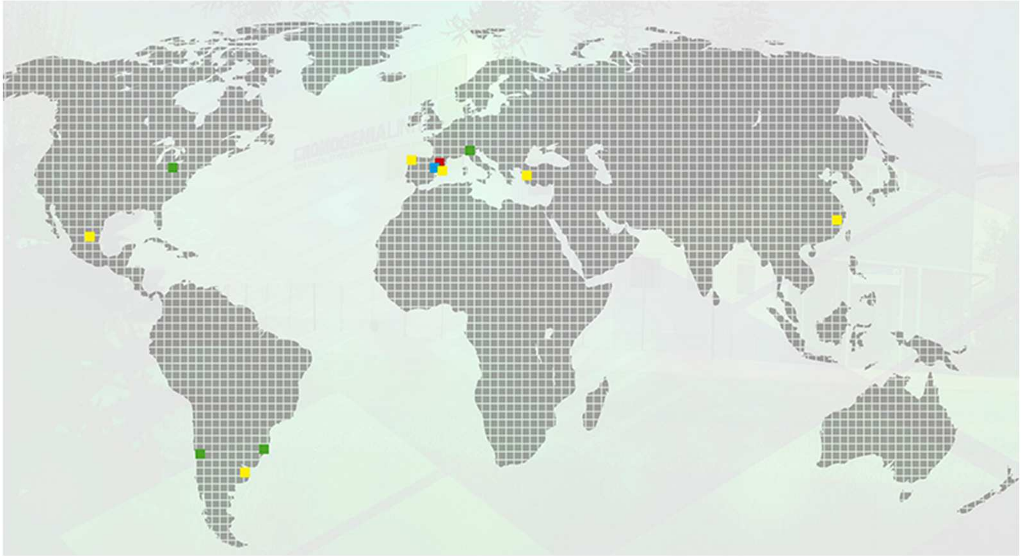


Figure 1.1 Global Cromogenia Units infrastructure [4].

Cromogenia are actually producing around 175 to 200 M tons of goods per year of which the 25-30% correspond to acrylic resins or polymers and polyurethanes production.

Regarding to the most important industry use of carbodiimides, polymer stabilizers, this doctoral PhD can improve some products by the inclusion of carbodiimdes to different polymer structures that Cromogenia Units are producing and can also introduce a new range of specialty products that can increase its business. The use of isocyanates as a starting raw material to produce carbodiimides, makes Cromogenia Units a good potential manufacturer of this kind of products improving its market position obtained over many years of polyurethanes production.

Economical journals and plastic producers, expect a polyurethane increasing global business of more than 4.8% during the next 3 years. The 29% of this market is focused in occidental Europe. A little percentage of this production could be finally sold with incorporated carbodiimide groups.

1.2 SYNTHETIC ROUTES TO OBTAIN CARBODIIMIDES

The first synthesis and characterization of carbodiimides was described by Weith in 1873, but it was first prepared twenty years later by Heinterberger and Zinin [5] by desulfurization of 1,3-disubstituted thioureas.

Carbodiimides can be obtained by using different synthetic routes, depending on the starting raw materials available by using different catalytic systems. The most important ones are described as follows.

1.2.1 Carbodiimide synthesis from thioureas and ureas

The synthesis of carbodiimides by desulfurization of thioureas was the first method used to synthetize it. This method uses yellow mercuric oxide to desulfurize the N,N-disubstituted thiourea [6].

$$RNHCSNHR + HgO \rightarrow RN{=}C{=}NR + HgS + H_2O$$

This process is carried out in solvent media, removing the water produced during the reaction by distillation, shifting the reaction to the products formation. Furthermore, a dehydrating agent as $CaCl_2$ or $MgSO_4$ can be added to the reaction media to improve the yield. Depending on the R substituents presents in the selected thiourea, dialkyl, diaryl, alkylaryl, different heterocyclic carbodiimides are obtained [7].

Salts of Lead, Zinc and other metals can catalyze this synthesis [8]. Chlorine compounds such as $SOCl_2$ or $COCl_2$ can also catalyze this synthesis [9, 10].

Disubstituted ureas, or ureas in general, can be dehydrated to give the corresponding carbodiimide by using phosphorus pentoxide [11], and triphenylphosphine in presence of carbon tetrachloride and trimethylamine [12]. This catalytic system could also be used starting from thioureas.

$$RNHCONHR_1 + CCl_4 + N(CH_2CH_3)_3 \rightarrow RN{=}C{=}N\text{-}R_1$$

1.2.2 Carbodiimide synthesis by Nitrene Rearrangements

The Tiemann rearrangement of amidoximes affords carbodiimides through a nitrene intermediate [7]. Oxadiazolium and tetrazolium salts in presence of triethylamine also prepare the corresponding carbodiimide involving a nitrene intermediate [7, 13].

1.2.3 Carbodiimide synthesis from Cyanamides

Carbodiimides can be obtained from cyanamides, by alkylation processes by using monotritylcyanamide with triphenyl chloride. Photolysis in presence of cyclohexene is described as another method to obtain carbodiimides, but with a very low yield [13].

1.2.4 Carbodiimide synthesis from isocyanates or isothiocyanates

This process, starting from isocyanates and by using a catalytic conversion, is the most commonly used method to obtain carbodiimides at industrial scale. Due to the easily available market of this raw material and because the byproduct obtained is carbon dioxide gas [14].

Campbell and Monagle discovered that cyclic phosphine oxides are excellent catalysts for the conversion of isocyanates to carbodiimides [15].

$$2\ RNCO + R_3PO \rightarrow RN{=}C{=}NR + CO_2 + R_3PO$$

Several metal carbonyls and metal naphtenates are noted to be also a catalyst for this reaction [7, 16].

Carbodiimides can also be obtained from isocyanates via Aza-Wittig reaction and by using phosphoramidates. In the Aza-Wittig reaction, an iminophosphorane reacts with an isocyanate or thioisocyanate to give the carbodiimide. The iminophosphorane could be prepared in situ as an intermediate by using triphenylphosphine and an azide [17].

$$Ph_3P{=}NPh + RN{=}C{=}O \rightarrow PhN{=}C{=}NR + Ph_3P{=}O$$

Starting from phosphoramidate, it reacts with isocyanates in a similar way than iminophosphorane to give the corresponding carbodiimide [18].

1.3 CARBODIIMIDE SYNTHESIS MECHANISM AND CATALYTIC SYSTEM

The reaction mechanism to convert isocyanates to carbodiimides by using phospholene oxides as catalyst was first described theoretically by Campbell and Monagle in 1962 [15]. The expected mechanism scheme described by Campbell and Monagle is shown in Figure 1.2.

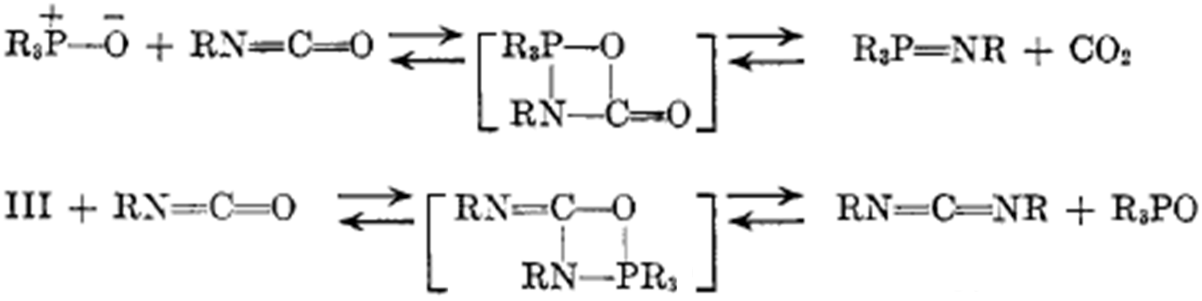


Figure 1.2 Carbodiimide Scheme mechanism starting from isocyanates [15].

Ulrich et al., Monagle and Lyman et al., indicated that the reaction by using phosphine oxides was carried out by a two-step mechanism. They postulated that there are an initial step which is believed to be a nucleophilic attack of the oxygen atom of the polarized phosphorus-oxygen bond in the catalyst on the isocyanate carbonyl. From this first slow step a phosphinimide intermediate and carbon dioxide are formed. This intermediate reacts with a second molecule of isocyanate to both afford the carbodiimide and regenerate the catalyst during the second and fast step of the reaction [15, 19, 20]. This predicted mechanism indicates that any pentavalent phosphorus compound, which has a coordinate covalent bond between phosphorus and oxygen, will catalyze the conversion reaction [3, 13, 15]. The oxides and sulfides of many organic compounds, which contains elements from groups V, and VI of the periodic table, are also effective catalyst. However, the cyclic five membered phosphine oxides are known to be the most successful [19, 21].

The differences on the substituents present in the catalyst affects the catalytic activity and the reaction kinetic. Depending on the substituents present, the polarity of the phosphoryl bond can be modified. Steric hindrance and temperature applied to the reaction system are also very important in the possible mechanism described above. This fact was made apparent by the range of time necessary for complete the conversion to carbodiimide.

Appleman and DeCarlo tested the importance of the phosphoryl group bond polarity by the rate constants for the conversion of phenyl isocyanate to the corresponding carbodiimide. 1-ethyl-3-methyl-3-phospholene and isopropyl methylphosphono-fluoridate were used as catalysts (structures are shown in Figure 1.3). The importance of the steric hindrance was also studied by using these catalyst. The results obtained shown differences between both catalysts in the kinetic orders reaction conversion and also in the carbon dioxide generation rate. The cyclic phosphine has less steric hindrance for approach the phosphorus-oxygen bond, and the alkyl substituents has a minimum electronic effect on its highly polarized linkage. In contrast, the bulky isopropoxy present in the fluorophosphonate makes the approach to the isocyanate difficult and the fluorine substituent depolarize the coordinate bond [22].

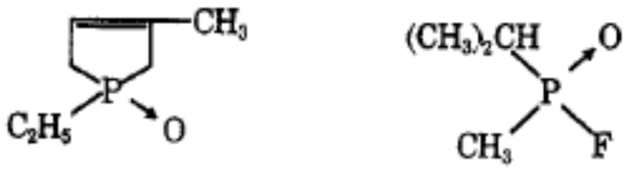
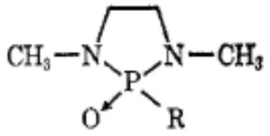


Figure 1.3 Catalysts structures used by Appleman and DeCarlo [22].

Ulrich et al. also studied the effect on the time for complete conversion depending on the different substituents present in the diazophospholidine oxide catalyst. Table 1.1 shows the time needed in minutes to convert o-Tolyl isocyanate into its carbodiimide by using different catalysts between 185 and 250ºC [15, 19].

Table 1.1 Time needed to convert o-Tolyl isocyanate to carbodiimide by using different catalyst [19].

 **R substituent**	**Time for complete conversion (min)**
C_2H_5	20
C_6H_5	68
CH_2Cl	167
OC_2H_5	789
$N(CH_3)_2$	1740

The results show that once more depolarized is the phosphoryl bond and more steric hindrance is applied, more time is needed to carry out the reaction.

Is well known that catalyst and its structure affects to the reaction mechanism. Other studies has been carried out to determine how the isocyanate structure used is another very important factor.

The structure of the isocyanate has a strong influence on the ease of formation of the carbodiimide. In aromatic isocyanates, the electron-withdrawing groups increase the conversion rate. This effect is decreased by using aliphatic isocyanates. These ones reacts more slowly with the phospholene oxides catalysts [3]. This fact was studied by the conversion of different isocyanates to its corresponding carbodiimides by using 2-ethyl-1,3-dimethyl-1,3,2-

diazaphospholidine 2-oxide. The conversion times needed for each isocyanate monomer are shown in Table 1.2 [19, 20].

Table 1.2 Isocyanates conversion time [19].

R-NCO-R substituent	Time for complete conversion (min)	Temperature (ºC)
Phenyl	8	160 – 230
O-Tolyl	20	180 – 250
2,6-diethylphenyl	330	200 – 243
Octadecyl	217	200 – 253
t-Octyl	…	170

Results show that aromatic isocyanates are more reactive than aliphatic ones due to its faster conversion. T-Octyl substituent isocyanate did not react by using this reaction conditions, confirming the theory.

Another important factor that is suggested in this study, is the temperature needed to carry out the conversion. Once the isocyanate has more steric hindrance, more temperature is needed to reach the carbodiimide group.

All the results and studies described above, reaction times, and carbon dioxide generation, are consistent with the proposed mechanism [22].

The postulated two-step mechanism was first confirmed and reported by A.P Gies et al. in 2013. The recent studies also confirms that the phospholene oxide used as catalyst interacts with isocyanates generating a catalyst-attached intermediate in guanidines structures by mass spectrometry [23].

1.4 RAW MATERIALS

Knowing the very importance of the structure of the catalyst as well as the isocyanate starting material is necessary to make a correct selection of both of them. In the following section are reported a brief description of the raw materials used for the isocyanates conversion to carbodiimides by using phospholene oxides as a catalyst.

1.4.1 Isocyanates

Isocyanates are esters of isocyanic acid with the formula R–N=C=O. The first synthesis of an organic isocyanate was reported by A. Wurtz in 1848 [24].

The most efficient and economically attractive synthetic route to obtain isocyanates is treating amines with phosgene (Figure 1.4) [25].

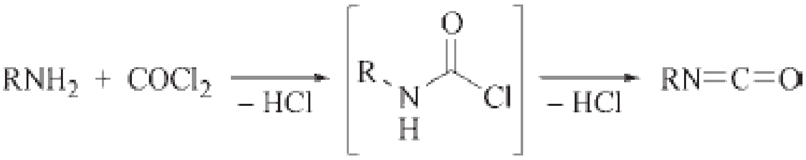
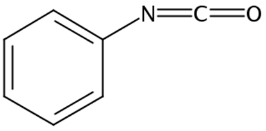
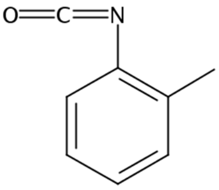
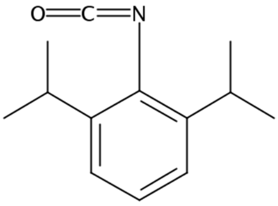
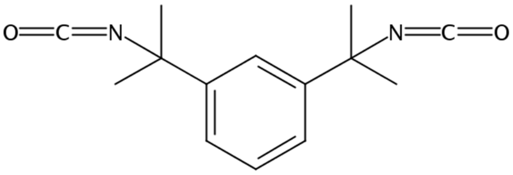
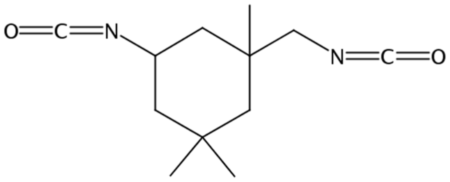
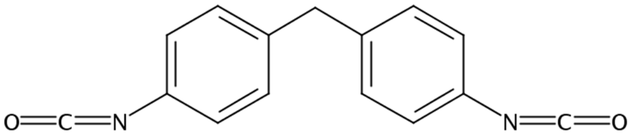


Figure 1.4 scheme of the reaction synthesis of isocyanates [25].

Isocyanates and diisocyanates became commercially important in the 1930s when the polymerization of bifunctional isocyanates and polyols to produce polyurethanes was discovered by O. BAYER and coworkers at the I.G. Farben laboratories in Leverkusen [26]. The most used isocyanates in the carbodiimide industry are listed in Table 1.3.

Table 1.3 Isocyanates and diisocyanates most used in carbodiimide industry.

CHEMICAL STRUCTURE	NAME	CAS NUMBER
	Phenyl isocyanate	103-71-9
	O-Tolyl isocyanate	614-68-6
	Diisopropyl Phenyl Isocyanate	28178-42-9
	Tetramethyl-1,3-Xylene Diisocyanate	2778-42-9

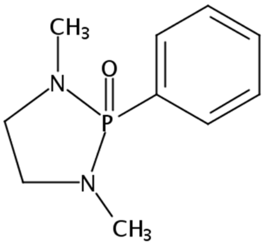
	Isophorone Diisocyanate	4098-71-9
	4,4-Diphenylmethane Diisocyanate	101-68-8

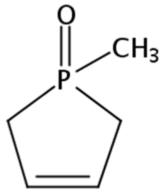
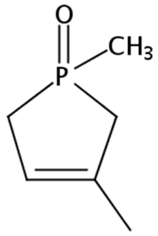
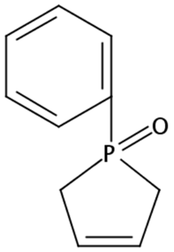
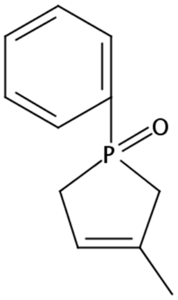
Isocyanates listed in Table 1.3 are the most used in carbodiimide industry [7, 25]. It is possible to differentiate different classes of these raw materials depending on the number of isocyanates groups, and depending on its aromaticity and steric hindrance present on the functional group. It is well known, as described above, that aromatic isocyanates reaches faster conversion reaction and that the steric hindrance produces a more protected carbodiimide group. With aromatic isocyanates, carbodiimidization is extremely fast. When unhindered aromatic isocyanate is used, the reaction occurs also faster, even by using only few ppm of catalyst [27]. It is important to make previous studies in order to select the correct isocyanate to obtain the expected application [7].

1.4.2 Phospholene oxide as catalysts

Concerning to the postulated mechanism described above, there are many catalysts that are able to be used as an isocyanate convertors to carbodiimide. Phosphine oxides and phosphine derivatives shows appreciable catalytic activity, however the most active catalyst studied is the cyclic phosphine oxides [3]. Table 1.4 shows the most used catalyst for carbodiimide synthesis starting from isocyanates.

Table 1.4 Most used catalysts in carbodiimide synthesis from isocyanates.

CHEMICAL STRUCTURE	NAME	CAS NUMBER
	1,3,2-Diazaphospholidine, 1,3-dimethyl-2-phenyl-, 2-oxide	6226-05-7

	1-methyl-3-phospholene-1-oxide	930-38-1
	1,3-methyl-3-phospholene-1-oxide	15450-79-0
	1-phenyl -3-phospholene-1-oxide	5186-73-2
	1-phenyl -3-methyl-3-phospholene-1-oxide	7564-51-4

Phosphor compounds listed in Table 1.4 are described in the prior art as the most common catalysts used to convert isocyanates to carbodiimides [3, 7, 13, 15, 20, 22, 28, 29].

This kind of products are produced as described by McCormack. In this reaction a 1,3-diene and a source of $R2P^+$ are combined to give phospholenium cation. The reaction proceeds via pericyclic 1+4 process. The resulting derivatives can be hydrolyzed to give the desired phosphine oxide (see Figure 1.5) [20, 30].

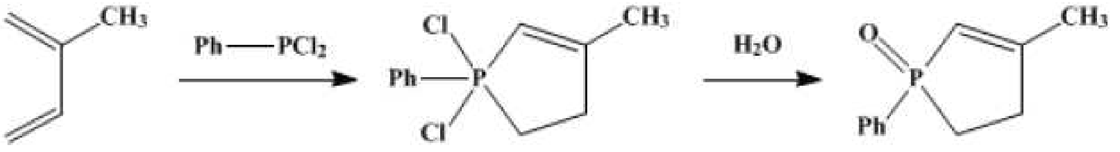


Figure 1.5 Reaction scheme for the synthesis of 1-phenyl-3-methyl-phospholene-1-oxide [30].

If an organo-magnesium reagent is used first with the phosphine, different alkyl or aryl substituents can be added. Depending on the diene and the $R2P^+$ source used, different carbodiimide catalyst are prepared. This kind of synthesis are characterized for its high cost of manufacturing and for the toxicity of the raw materials and intermediates needed [30, 31].

For this reasons, it is important to mention that the commercial price of this kind of specialties, that are much focused to catalyze the conversion of isocyanates to carbodiimides, is very high. There are only few companies able to produce it at industrial scale, and they have the monopoly. Knowing this fact, prices could arrive until more than 1000 euros per kilo if you have an important and a good market place.

The reaction mechanism produces an isomeric mixture of 2-phospholene and 3-phospholene whether the phenylphosphonium is used or the methylphosphium. For this reason, commercial sources of this kind of catalysts are provided as a mixture of both isomers [32, 33].

1.5 POLYMERIC CARBODIIMIDES

The synthesis of carbodiimides starting from an isocyanate produces the carbodiimide dimer. If a polymer or oligomer is required, a diisocyanate is needed to carry out the reaction. This kind of macromolecules which has many carbodiimide units could be obtained from aliphatic and aromatic diiscocyanates. For example, reaction of 4,4-Diphenylmethane Diisocyanate in presence of phospholene oxide catalyst should produce a linear polymer (see Figure 1.6) [7, 19].

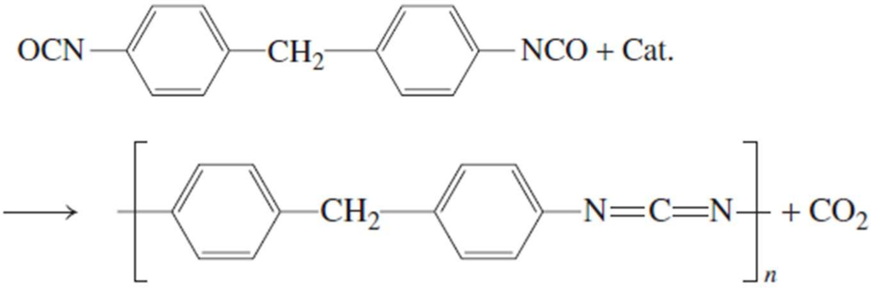


Figure 1.6 Scheme of polycarbodiimide synthesis [19].

In the same manner, polycarbodiimides can be prepared by using highly hindered diisocyanates but stronger reaction condition, like higher temperature, will be required [34].

The oligomers or polymers obtained are considered live polymers due to both isocyanate end groups.

1.5.1 Structures

Once polycarbodiimides are synthetized not only linear chains are obtained. Ulrich et al. suggested that crosslinked polymers are obtained instead. Carbodiimide group can react with an isocyanate group present in the system leading the formation of four membered ring cycloadducts called uretonimine. This kind of structures can continue reacting with another isocyanate or carbodiimide group crosslinking the polymer obtained (see Figure 1.7) [7].

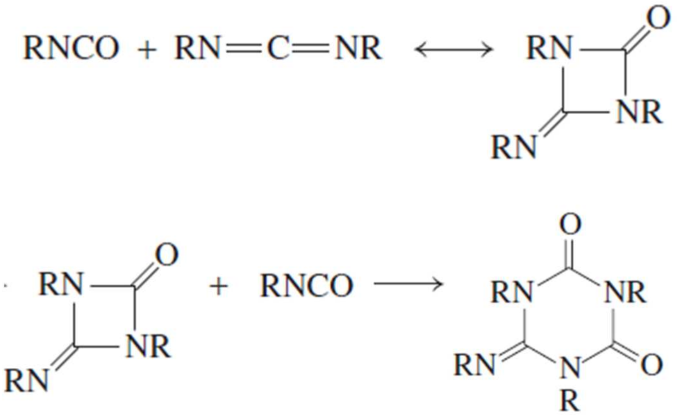


Figure 1.7 Suggested crosslinked structures obtained in polycarbodiimide synthesis [7].

This side reactions could be partially avoided by using highly hindered isocyanates. The extra protection applied on the carbodiimide groups generated makes the approach between both functional groups more difficult, decreasing this byproducts formation.

Carbodiimide group could also polymerize forming polyguanidines by using metal transition catalysts [35] . In this case a helical polymer is produced due to the high steric hindrance present on the carbodiimide substituents. The helical structure has been determined by using ^{15}N NMR technique [36].

1.5.2 Production process and control

The process to convert isocyanates to carbodiimides requires a minimum equipment that allow to get the system stirred and heated. The temperature must be controlled by using a thermometer. Also needs an inert gas sparging and a condenser, both to avoid lose material and let carbon dioxide generated scape from the reaction system [22].

The production procedure consists in heating the reaction mixture which is formed by the isocyanate and the catalyst. This initial raw materials mixture can be polymerized either in bulk, using the own isocyanate as solvent, or in solution media by dimethyl sulfoxide addition [3, 20].

The reaction temperatures depends on the raw materials selected being necessary work between 30 to 200ºC. Using a highly hindrance isocyanate, higher temperatures will be required. The activity of the catalyst used will also modify the required working temperature [27, 34].

The amounts of catalysts described in the prior art are from less than 0.1% to more than 1% respect to the diisocyanate monomer used [3, 20]. In patent ES 2201580 T3 [29] is mentioned the necessity to make previous studies to optimize the correct temperature and catalyst dose once the diisocyanate is selected. The optimizing test has to be focused on the optimum reaction time to obtain the desired oligomer or polymer, with the minimum secondary reactions.

Reaction times needed to finish the conversion are described since a couple of minutes until more than 25 hours. This multiple variety of times depends also on the amount of catalyst, temperature applied and raw materials used. For example, treating 2,6-diisopropylphenyl isocyanate with 0,01% of catalyst dose regarding to the isocyanate monomer, at 170ºC; needs close to 27 hours to reach 0% of isocyanate signal [28]. However, changing all these conditions to 0.8% of catalyst dose and applying 100ºC by using tolylene diisocyanate, only 3 hours are needed to reach a carbodiimide conversion close to 100% [37]. All the results show that a preliminary test has to be done before start production.

Another important factor in polycarbodiimide synthesis is to know when to stop the reaction. In carbodiimide dimer synthesis the reaction ends is easier to be detected. Using a monoisocyante monomer reaction finishes once no isocyanate is detected. In contrast, the use of diisocyantes, which are required to polycarbodiimide synthesis, produces, as described above, polymers or oligomers with double isocyanate end groups. In these cases, the polymerization reaction needs to be finished once the isocyanate content reaches a previously determined value.

The reaction tracking and kinetics needs to be monitored. To study the polymerization reaction, an isocyanate content analysis is the best way to know how the synthesis is going [27]. The decreasing isocyanate content analyzed inform about the carbodiimidization progress. An isocyanate content of 0% signifies a degree of carbodiimidization of 100% [28]. The amount of carbon dioxide generation is another important variable which can give information about the kinetics. A kinetic study was carried out (see Table 1.5) by monitoring the carbon dioxide and carbodiimide generation rate, using three different catalyst doses for the phenyl isocyanate polymerization at 135ºC [22].

Table 1.5 Rate constants for CO_2 evolution and carbodiimide formation from phenyl isocyanate [22].

Catalyst amount (mole/l)	**CO_2 (moles/l. sec)**	**N=C=N (moles/l. sec)**
0.15	1.96	1.98
0.076	0.98	0.93
0.038	0.50	0.45

The study also shows that higher catalyst doses increases the reaction kinetics.

All these parameters can be analyzed by using different titration methods, infrared spectroscopy and gas chromatography.

The end of the reaction should be different depending on the isocyanate used. As described above, the mechanism proposed finally reach a living polymer due to the isocyanates end groups and for the residual catalyst activity. Once more reactive is the isocyanate used lower is the temperature needed to react, and for this reason, in the most reactive cases, are described a carbon dioxide addition at the end of the reaction. This sparging is done at high temperatures with vacuum applying into the reaction system in order to remove the catalyst present [28]. This step is postulated to be not necessary in highly hindered monomers that needs extremely hard reaction conditions to react.

1.6 CARBODIIMIDE CHARACTERIZATION

After the synthesis of any product is necessary to characterize it in order to know if the reaction has gone by the expected way. Carbodiimides and polycarbodiimides also needs of this characterization step.

Exists many different techniques which are very helpfully depending on the analysis we need to do. By this way, Fourier transformed infrared spectroscopy (FTIR) and gas chromatography (GC), as described above, are useful techniques to monitor the reaction and also to identify and quantify the final obtained product.

Nuclear magnetic resonance spectroscopy (NMR) permits understand the structure of the obtained molecule, and in some cases identify what kind of specie has been formed. Yavari et al. studied the different shifts obtained in different carbodiimides by using ^{15}N NMR and ^{13}C NMR. Depending on the substituents present in the carbodiimide structure, different chemical shifts and resonances are obtained [38]. ^{15}N NMR has also been used to identify helical polycarbodiimides structures [36].

Historically, size exclusion chromatography (SEC) and ultraviolet (UV) together to the previously commented infrared spectroscopy and NMR has been used for polymer characterization. However, these classical methods has the disadvantage to be averaging techniques, which provide general information about the average polymer mixture as whole, instead of providing selective information about individual oligomers within the mixture. In contrast, mass spectrometry can be used to obtain more accurate molecular information. For this reason, recently, MALDI TOF mass spectrometry has been used to characterize polycarbodiimides. This technique has been used to identify many different structures of polycarbodiimides and polyguanidines [23].

1.7 CARBODIIMIDE REACTIVITY

Carbodiimide molecule has two centers of reactivity. The central carbon atom is electrophilic and the terminal nitrogen is electron rich. The most important reactions involve nucleophilic attack [39]. As indicated in the structures section, carbodiimides can react with isocyanates to give four-membered ring 2+2 cycloadducts via addition across the CN double bonds of both heterocomulenes.

The cycloadduct formed can react with another isocyanate to give six-membered ring structure. Steric hindrance and electronic effects influence on this kind of products distribution. The more nucleophilic nitrogen in the carbodiimide attacks the electrophilic carbon center in the isocyanate group [40].

Carbodiimide can be used as a monomer in a polymerization reaction [41]. Reuther et al. polymerized carbodiimide monomers using (bistriphenylphosphino) aryl nickel (II) bromide initiators. The reaction occurred in a controlled living polymerization initiated via aryl ligand transfer to the electrophilic center carbon of the carbodiimide (see Figure 1.8). Sequential insertions of the carbodiimide bond into the nickel-nitrogen coordination bond propagates the polymer chain [42].

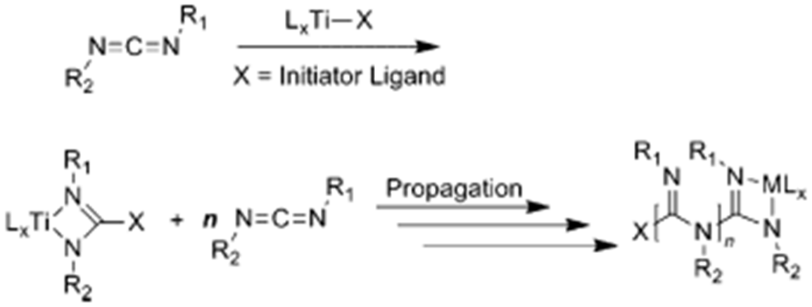


Figure 1.8 Scheme of the carbodiimide group polymerization by using metal catalysts [42].

The hydrolysis of carbodiimides is often used and finally forms the corresponding urea. This reaction is catalyzed by hydroxide ions. In this kind of reaction, the steric hindrance presents initially in the isocyanate and after in the carbodiimide group, affects the reactivity, being more stable in water for the most highly hindrance isocyanates. [34] The NCN group can react with alcohols to yield O-Alkyl-isoureas by using alkoxides or catalyzed by cooper salts. The isourea obtained, as is shown in Figure 1.9, can be used as an in situ alkylating agent. [13, 43]

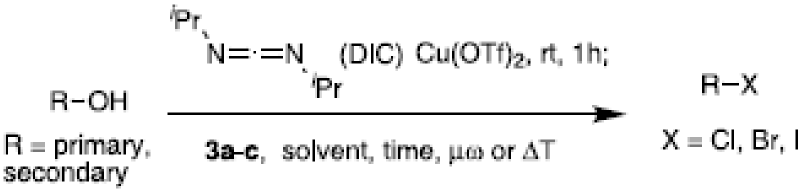


Figure 1.9 Alkylation by in situ formation of Alkyl-isourea from carbodiimide [43].

Reaction with amines to form guanidines in general requires no catalyst, and its polymer has been prepared by the addition of biscarbodiimides with diamines.

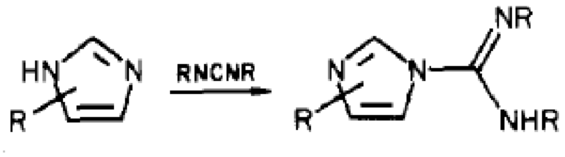


Figure 1.10 Imidazole reaction with carbodiimide.

The carbodiimide reactivity are so varied, however, one of the most important reaction that requires the heterocomulene group of carbodiimide, is its reaction with carboxylic acids. The reaction with mono and di carboxylic acids has been extensively investigated due to its application as a precursor for peptide synthesis; it can be used also as an amide precursor. The reaction sequence involves the formation of an O-Acylisourea. This key intermediate can react with amines to give the desired amide and urea. There are side reactions in this mechanism. The O-Acylisourea can react with an additional carboxylic acid to give the acid anhydride. After, it can react further with the amine to give the amide and the urea. However the most undesirable side reaction involves the rearrangement of the O-Acylisourea to the N-Acylurea. This last side reaction can be minimized by using solvents. [13] The mechanism is shown in Figure 1.11.

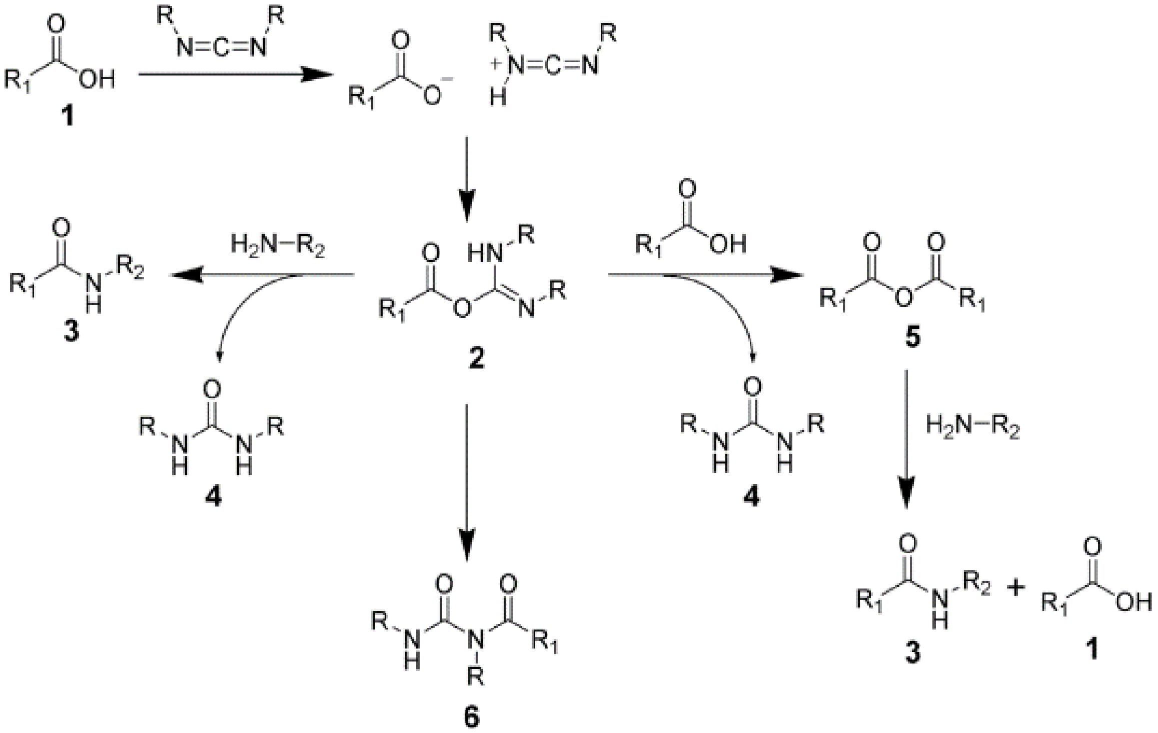


Figure 1.11 Scheme reaction of carboxylic acids with carbodiimides. 1: Carobxylic acid. 2: O-Acylisourea. 3: Amide. 4: Urea. 5: Anhydride. 6: N-Acylurea [44].

Above there are described the most important carbodiimide reactions, however, carbon nucleophiles can form C-C bonds with carbodiimides. This functional group also has a coordinating capacity with metals, preferably iron.

1.8 CARBODIIMIDE APPLICATIONS

Numerous applications for carbodiimides in organic chemistry and in bioorganic chemistry are known.

Due to the rapid reaction of unhindered carbodiimides with water, they are often used as dehydrating agents in water release reactions. Some esterification reactions and the formation of peptides are examples of this carbodiimide application. Dicyclohexylcarbodiimide are usually used because the corresponding urea byproducts are insoluble in most organic solvents and water, and can be easily removed from the system.

The commented 2+2 cycloadduct formation in low concentrations in 4,4-diisocyanatodiphenylmethane (MDI) decrease its melting point, producing a more liquid monomer easier to handle. [45] Carbodiimides also plays a role in the synthesis of H-heterocycles. Sometimes the carbodiimide generation is made in situ which often undergo subsequent cyclisation reactions [17].

The use of carbodiimides as mediators in biological condensation reactions is of considerable importance. Sheehan received the Nobel Price for the first total synthesis of phenoxymethyl penicillin by using dicyclohexylcarbodiimide (DCC) to force the lactam ring closure reaction [46]. Carbodiimide are also used for amide bond formation in the synthesis of some antiviral antibiotic [47].

In some cases, due to its high reactivity with carboxylic acids, carbodiimides are used to determine the number of carboxyl groups present in proteins [48]. Exists many application in the modification of proteins field, like as ATPases inhibitor or as a protein crosslinker. This last use is often used for the mapping of the three dimensional structures in proteins. They are also used as a fixing agent, for example for intestinal glucagon.

Carbodiimides has herbicides and pesticides applications. They are used for the detection of insecticides and herbicides in immunoassays techniques.

Organic and bioorganic chemistry applications has been described above. However, one of the most important applications of carbodiimides is focused in polymer chemistry. Polymers with pendant carbodiimide groups were synthetized and used for solid phase dehydration agent and as a fiber reinforcements for glass fiber compositions. Coating applications uses carbodiimides by crosslinking polyunsaturated carboxylic acids to form oligomeric acylureas.

Oligomeric carbodiimides are very useful stabilizers for ester based polymers, such as polyester, polyester based polyurethanes, polyether, polyether based polyurethanes and polycarbonates. The scavenging of carboxyl groups generated in the hydrolysis of polyesters which can catalyze the polymer hydrolysis is prevented by the reaction of carbodiimides with this carboxylic groups. This application also mediates in the loss of molecular weight by reacting the degraded chains [49]. This oligomeric compounds are non-volatile, resistant to extraction and have good compatibility with the suggested polymers. For example, in a thermoplastic polyurethane, the 2% addition of the carbodiimide stabilizer is sufficient to retain 90% of its properties after nine weeks of immersion in 70ºC water. The unstabilized base polymer completely disintegrates in the test [50]. There are many different tests done by using carbodiimide as stabilizers. In Table 1.6 and Table 1.7 are shown the results of the tensile strength and the elongation after several days at 70 and 100ºC of hydrolyzing ageing test exposition of three different test samples of polyester based polyurethane.

Table 1.6 Tensile strength and elongation after hydrolysis aging test at 70ºC during several days [2].

Exposition days	**SAMPLE A**		**SAMPLE B**		**SAMPLE C**	
	Tensile Strenght (Kg/cm^2)	**Elongation (%)**	**Tensile Strenght (Kg/cm^2)**	**Elongation (%)**	**Tensile Strenght (Kg/cm^2)**	**Elongation (%)**
0	300	540	310	550	340	500
3	174	670	198	640	308	530
7	81	70	186	660	290	545
14	Destroyed		108	685	248	560
21	Destroyed		41	835	190	590

Polyurethane samples were prepared by non carbodiimide incorporation (A), 4% of dicyclohexylcarbodiimide (B) and 4% of triisopropylbenzene polycarbodiimide (C) [2].

Table 1.7 Tensile strength and elongation after hydrolysis aging test at 100ºC during several days. [2]

Exposition days	**SAMPLE A**		**SAMPLE B**		**SAMPLE C**	
	Tensile Strenght (Kg/cm^2)	**Elongation (%)**	**Tensile Strenght (Kg/cm^2)**	**Elongation (%)**	**Tensile Strenght (Kg/cm^2)**	**Elongation (%)**
0	407	550	387	560	436	525
1	141	690	204	585	346	530
2	Destroyed		85	585	250	545
3	Destroyed		34	680	104	630
4	Destroyed		Destroyed		57	695

Most recently other similar tests has been carried out on thermoplastic polyurethanes by the addition of less than 1% of polycarbodiimide diol modified. Results obtained shows an improved resistance in the hydrolysis ageing test [29].

This kind of oligomeric carbodiimide used as stabilizers are actually commercially available under the trade name Stabaxol from Rhein Chemie. Also exists other companies like Nisshinbo, BASF and Stahl that manufacture carbodiimide for these purposes.

1.9 REFERENCES

1. Yranzo, G.I., et al., Formation of Cumulenes, Triple-Bonded, and Related Compounds by Flash Vacuum Thermolysis of Five-Membered Heterocycles. European Journal of Organic Chemistry, 2001. 2001(12): p. 2209-2220.

2. Wolfram, N., et al., Stabilization of polyesters with polycarbodiimide. 1965, Google Patents.

3. Campbell, T.W., Monagle, J.J., and Foldi, V.S., Carbodiimides. I. Conversion of isocyanates to carbodiimides with phospholine oxide catalyst. Journal of the American Chemical Society, 1962. 84(19): p. 3673-3677.

4. http://www.cromogenia.com/.

5. Ulrich, H. and Reymore, H., Chemistry and properties of low density poly (carbodiimide) foams. Journal of cellular plastics, 1985. 21(5): p. 350-357.

6. Weith, W., Ber. Dtsch. Chem. Ges, 1873. 6: p. 1395.

7. Ulrich, H., Chemistry and technology of carbodiimides. 2008: John Wiley & Sons.

8. Sheehan, J.C., Heterocyclic substituted carbodhmides and method of preparation. 1964, Google Patents.

9. Fell, J.B. and Coppola, G.M., A mild and efficient preparation of carbodiimides. Synthetic communications, 1995. 25(1): p. 43-47.

10. Henri, U. and Sayigh, A.A., Process for the preparation of carbodiimides. 1967, Google Patents.

11. Stevens, C.L., Singhal, G.H., and Ash, A.B., Carbodiimides. Dehydration of ureas. The Journal of Organic Chemistry, 1967. 32(9): p. 2895-2895.

12. Lawton, E.L., Preparation of carbodiimides from ureas by dehydration. 1976, Google Patents.

13. Williams, A. and Ibrahim, I.T., Carbodiimide chemistry: recent advances. Chemical Reviews, 1981. 81(6): p. 589-636.

14. Ulrich, H., Chemistry and technology of isocyanates. 1996: Wiley.

15. Monagle, J.J., Carbodiimides. III. Conversion of isocyanates to carbodiimides. Catalyst studies. The Journal of Organic Chemistry, 1962. 27(11): p. 3851-3855.

16. Rahman, A.F. and Nicholas, K.M., Catalytic conversion of isocyanates to carbodiimides by cyclopentadienyl manganese tricarbonyl and cyclopentadienyl iron dicarbonyl dimer. Tetrahedron letters, 2007. 48(34): p. 6002-6004.

17. Molina, P., et al., A New and Efficient Preparation of Cyclic Carbodiimides from Bis (iminophosphoranes) and the System Boc2O/DMAP. The Journal of Organic Chemistry, 1994. 59(24): p. 7306-7315.

18. Wadsworth Jr, W. and Emmons, W., Phosphoramidate Anions. The Preparation of Carbodiimides, Ketenimines, Isocyanates, and Isothiocyanates1. The Journal of Organic Chemistry, 1964. 29(10): p. 2816-2820.

19. Ulrich, H., Tucker, B., and Sayigh, A.A., PN heterocycles. Synthesis and use in the catalytic conversion of isocyanates into carbodiimides. The Journal of Organic Chemistry, 1967. 32(5): p. 1360-1362.

20. Lyman, D.J. and Sadri, N., Polycarbodiimides and their derivatives. Macromolecular Chemistry and Physics, 1963. 67(1): p. 1-9.

21. Neumann, W. and Fisher, P., The Preparation of Carbodiimides from Isocyantes. Angewandte Chemie International Edition, 1962. 1(12): p. 621-625.

22. Appleman, J.O. and DeCarlo, V.J., Conversion of isocyanates into carbodiimides with isopropyl methylphosphonofluoridate as catalyst. Kinetic studies. The Journal of Organic Chemistry, 1967. 32(5): p. 1505-1507.

23. Gies, A.P., et al., MALDI–TOF/TOF CID Study of Polycarbodiimide Branching Reactions. Macromolecules, 2013. 46(19): p. 7616-7637.

24. Wurtz, A., Recherches sur les ethers cyaniques et leurs derives. CR Hebd. Seances. Acad. Sci, 1848. 27: p. 241.

25. Six, C. and Richter, F., Isocyanates, organic, in Ullmann's Encyclopedia of Industrial Chemistry. 2003.

26. Bayer, O., Das Di-Isocyanat-Polyadditionsverfahren (Polyurethane). Angewandte Chemie, 1947. 59(9): p. 257-272.

27. Wagner, K., et al., α, ω-Diisocyanatocarbodiimides,-Polycarbodiimides, and Their Derivatives. Angewandte Chemie International Edition in English, 1981. 20(10): p. 819-830.

28. Scholl, H.-J., Process for the production of organic carbodiimides and their use as stabilizers for plastics. 1994, Google Patents.

29. AKTIENGESELLSHAFT, B., Carbodiimidas y procedimiento para su producción. 2004.

30. McCormack, W.B., 3-methyl-1-phenylphospholene oxide. Organic Synthesis, 1973. 5: p. 787.

31. James, L.W., Manufacture of diarylalkyl phosphine oxides. 1963, Google Patents.

32. Quin, L.D., Gratz, J.P., and Barket, T.P., Structure of diene-phosphonous dihalide addition products and of derived phospholenes and phospholene oxides. The Journal of Organic Chemistry, 1968. 33(3): p. 1034-1041.

33. Yamada, M., et al., Preparation and characterization of novel 4-bromo-3, 4-dimethyl-1-phenyl-2-phospholene 1-oxide and the analogous phosphorus heterocycles or phospha sugars. Bioorganic & medicinal chemistry letters, 2010. 20(19): p. 5943-5946.

34. Hesselmans, L.C.J., Derksen, A.J., and Munneke, J.C., Process for preparation of stable polycarbodiimide dispersions in water, which are free of organic solvents and may be used as crosslinking agent. 2008, Google Patents.

35. Kennemur, J.G. and Novak, B.M., Advances in polycarbodiimide chemistry. Polymer, 2011. 52(8): p. 1693-1710.

36. Budhathoki-Uprety, J., Reuther, J.F., and Novak, B.M., Determining the Regioregularity in Alkyne Polycarbodiimides and Their Orthogonal Modification of Side Chains To Yield Perfectly Alternating Functional Polymers. Macromolecules, 2012. 45(20): p. 8155-8165.

37. Campbell, T.W., Carbodiimide polymers. 1960, Google Patents.

38. Yavari, I. and Roberts, J.D., Nitrogen-15 nuclear magnetic resonance spectroscopy. Carbodiimides. The Journal of Organic Chemistry, 1978. 43(25): p. 4689-4693.

39. Bellucci, M.C. and Volonterio, A., carbodiimides-Mediated Multi component synthesis of Biologically Relevant structures. Organic Chemistry Insights, 2012. 4: p. 1.

40. Ulrich, H., Richter, R., and Tucker, B., [2+ 2] Cycloaddition reactions of unsymmetrically substituted carbodiimides. Journal of heterocyclic chemistry, 1987. 24(4): p. 1121-1123.

41. Budhathoki-Uprety, J., et al., Synthesis of guanidinium functionalized polycarbodiimides and their antibacterial activities. ACS Macro Letters, 2012. 1(3): p. 370-374.

42. Reuther, J.F., et al., Controlled Living Polymerization of Carbodiimides Using Versatile, Air-Stable Nickel (II) Initiators: Facile Incorporation of Helical, Rod-like Materials. Macromolecules, 2014. 47(14): p. 4587-4595.

43. Li, Z., Crosignani, S., and Linclau, B., A mild, phosphine-free method for the conversion of alcohols into halides (Cl, Br, I) via the corresponding O-alkyl isoureas. Tetrahedron letters, 2003. 44(44): p. 8143-8147.

44. Scientific, T.F. https://*www.thermofisher.com/es/es/home/life-science/protein-biology/protein-biology-learning-center/protein-biology-resource-library/pierce-protein-methods/carbodiimide-crosslinker-chemistry.html#*.

45. Alec, O. and Erner, W.E., Compositions of methylenebis (phenyl isocyanate) with trihydrocarbyl phosphates and preparation thereof. 1968, Google Patents.

46. Sheehan, J.C. and Logan, K.R.H., A general synthesis of the penicillins. Journal of the American Chemical Society, 1959. 81(21): p. 5838-5839.

47. Grehn, L. and Ragnarsson, U., Novel efficient total synthesis of antiviral antibiotic distamycin A. The Journal of Organic Chemistry, 1981. 46(17): p. 3492-3497.

48. Horinishi, H., et al., States of Amino Acid Residues in Proteins XV. Ethyl-morpholinylpropyl-carbodiimide for Modification of Carboxyl Groups in Proteins. Journal of biochemistry, 1968. 63(1): p. 41-50.

49. Brown, D.W., Lowry, R.E., and Smith, L.E., Hydrolytic degradation of polyester polyurethanes containing carbodiimides. Macromolecules, 1982. 15(2): p. 453-458.

50. Schollenberger, C.S., Thermoplastic polyurethane elastomers. Handbook of Elastomers. Vol. 11. 1988. 375-409.

Chapter 2

Objectives

2. OBJECTIVES

The present doctoral thesis is framed in the industrial doctorate scholarship. Cromogenia Units S.A. as partner of this project, has the global objective to finally incorporate the polycarbodiimides products generated into a new product brand of the company.

Nevertheless, in addition to the first global objective commented, this doctoral thesis has to be used as a way of knowledge of this kind of products. Once the product is better known, it is easier to know how to solve the different handicaps that will appear during the final product application. For this reason, the main objective is to acquire a better knowledge about how it is synthetized, how it works in the final application and how this final application can be improved.

Different objectives have been designed, which constitute the necessary steps to be done in order to finally achieve all the main aims of the project. The specific objectives are as follows:

- ***Reaction conditions and synthesis process optimization***. The polycarbodiimide synthesis study will constitute a key factor in all the project because is the beginning of the final desired product. A correct understanding of its synthesis mechanism, and the key factors to optimize it are required to select the best method to carry out the process.

- ***Carbodiimide catalyst optimization***. The correct catalyst selection to improve the carbodiimide synthesis and its optimization are important objectives to complete the synthesis of polycarbodiimides.

- ***Characterization of the prepared oligomers.*** The synthesis process optimization requires the final sample characterization, in order to know how the synthesis conditions and process affects to the final carbodiimide sample prepared.

- ***Final application of the prepared carbodiimides***. Carbodiimides are designed to carry out a final function in the market which need to be tested in different polymer systems. The determination of the relation between the final stability results against the synthesis process carried out and to define how carbodiimides works; are the most important objectives.

- ***Industrial production***. Scale up the selected carbodiimide process synthesis is the final objective which also means a correct project development.

Chapter 3

Materials, experimental procedure and techniques

3. MATERIALS, EXPERIMENTAL PROCEDURE AND TECHNIQUES

For the synthesis of carbodiimides from isocyanates, it is essential to make a correct initial selection of the isocyanate to be used as precursor of these products. This initial selection will determine the final result of the application. In this way, and in the most generic possible way, we can differentiate isocyanates monomers between monoisocyanates, and polyisocyanates. By using the first ones we will get dimers, resulting from the reaction between two molecules of isocyanate; while with the latter ones, due to their polyfunctionality, they eventually generate polymers or oligomers. Isocyanates monomers with more than 2 isocyanates groups, finally produce branched polymer. The specific case that includes this study, will require diisocyanates to synthetize lineal polycarbodiimides.

Within each of these two large groups of isocyanates, we can also differentiate between aromatic or aliphatic isocyanate monomers, and within each of those, it is possible to differentiate between monomers which have the isocyanate functional group (R-NCO) more or less hindered or sterically protected.

Depending on the isocyanate used as raw material; the reaction conditions will necessarily be modified to reach the same objective; synthesis of carbodiimides. Reaction conditions are understood, basically as the temperature required for the conversion and the reaction time necessary to reach the required conversion. In addition to these basic reaction conditions, the amount and the type of catalyst used also are key points for the reaction, which modulate the average molecular weight of the polycarbodiimide obtained [1].

For the correct design of the reaction system to carry out the synthesis of carbodiimides, it is necessary to know first the reaction mechanism, as well as the by-products that can be generated. The known reaction mechanism postulated by Campbell and Monagle is shown in Figure 3.1 as a summarized reaction scheme [2].

$$2\ R'\text{-}N{=}C{=}O \xrightarrow[\text{Cat.}]{R_3P{=}O} R'\text{-}N{=}C{=}N\text{-}R' + CO_2$$

Figure 3.1 General reaction scheme for carbodiimide synthesis [2].

3.1 MATERIALS

To carry out the present study different products have been used that can be classified depending on their use. In this way, we can differentiate between the materials used for the preparation and synthesis of the carbodiimide and polycarbodiimide samples, shown in Table 3.1; and the materials used for their production control and characterization, shown in Table 3.2.

Table 3.1 Chemical products used for carbodiimide and polycarbodiimide samples preparation.

PRODUCT	NAME	CAS NUMBER	PURITY	SUPPLIER
Diisopropyl phenyl isocyanate	DIPI	28178-42-9	>98%	Sigma Aldrich
Meta-Tetramethylxylylene Diisocyanate	TMXDI	85902-02-9	>98%	ALLNEX
1-methyl-1-oxo Phospholene	CAT 1	31563-86-7	>98%	CLARIANT
1-phenyl-3-methyl-1-oxo Phospholene	CAT 2	707-61-9 + 7564-51-4	>98%	Sigma Aldrich
Triphenylphosphine oxide	CAT 3	791-28-6	>98%	Sigma Aldrich
2,6-di-terc-buthyl-p-cresol	BHT	128-37-0	>99.8%	OXIRIS
Potassium methylate	MeO K	865-33-8	32%	BASF
Potassium-tert-Butoxide	tBuO K	865-47-4	>98%	Sigma Aldrich
Nitrogen	N_2	7727-37-9	99,99%	LINDE
N-ethyl-2-pirrolidone	NEP	2687-91-4	>99%	Quimidroga
Dimethyl propionic acid	DMPA	4767-03-7	>95%	Perstorp
Triethylamine	TEA	121-44-8	>99.5%	Campi y Jové
Hydrazine		302-01-2	80%	Lanxess
2-Hidroxyethyl Methacrylate	HEMA	868-77-9	>97%	Quimidroga

Dibutyl amine	DBA	111-92-2	>99%	PANREAC
Glycidol		556-52-5	>96%	Sigma Aldrich
Mono Polyethylene glycol	MPEG	9004-74-4	100%	INEOS
Ethoxylated Lauryc alcohol		78330-20-8	100%	BASF
Water	H_2O	7732-18-5	100%	Aquarifer
Sodium Lauryl Benzoate		68411-27-8	>99%	E & V
Dipropylene glycol dimethyl ether	DPGDME	111109-77-4	>99%	UNIVAR

Table 3.2 Chemical products used for process control and characterization of the prepared samples.

PRODUCT	**NAME**	**CAS NUMBER**	**PURITY**	**SUPPLIER**
Toluene		108-88-3	100%	PANREAC
Dibutylamine	DBA	111-92-2	>99%	PANREAC
Hydrochloric acid 0.5N	HCl	7647-01-0	0.5N	PANREAC
Sodium Hydroxide	NaOH	1310-73-2	50%	PANREAC
Isopropyl alcohol	IPA	67-63-0	99,5%	PANREAC
2,5-Dihydroxybenzoic acid	DHB	490-79-9	>98%	Sigma Aldrich
Dithranol		1143-38-0	>90%	Sigma Aldrich
Tetrahydrofuran	THF	109-99-9	>99.9%	Sigma Aldrich
Sodium Trifluoroacetate	Na TFA	2923-18-4	>98%	Sigma Aldrich
Bruker Peptide Calibration standard				BRUKER
Deuterated Chloroform	$CDCl_3$	865-49-6	>99.5%	Sigma Aldrich
Dioxane		123-91-1	>99.5%	PANREAC
Oxalic acid		144-62-7	>99%	Sigma Aldrich

Potassium hydroxide 0.5N	KOH	1310-58-3	0.5N	PANREAC
N,N-Dicyclohexylcarbodiimide	DCC	538-75-0	>99%	Sigma Aldrich

3.2 PROCEDURES FOR SAMPLE PREPARATIONS

This section describes the set of procedures followed for the preparation of the sample to its evaluation in the final application. In this work 2 different types of procedures are shown:

- Process for the synthesis of carbodiimides and carbodiimide oligomers.
- Procedure for the inclusion of carbodiimides in polymers and its specimen test preparation process.

3.2.1 Process for the synthesis of carbodiimides and carbodiimide oligomers

The reaction procedure for carrying out the conversion of isocyanates to carbodiimides is set forth below.

Once the reaction to be studied is known, and knowing the most important reaction conditions; the design of the reaction system must ensure the control of these conditions and the correct development of the reaction. A reaction system equipped with stirring, temperature control, inert gas (nitrogen) inlet, gas outlet (nitrogen and carbon dioxide generated) and a heating system have been designed for this purpose. The scheme of the proposed reaction assembly is shown in Figure 3.2; being:

1. Stirrer motor
2. Stirrer
3. Temperature probe
4. Nitrogen sparger
5. 5 neck glass reactor
6. Temperature controller
7. Dry Nitrogen bottle
8. Electric mantle
9. Gas outlet
10. Scrubber
11. Sample outlet

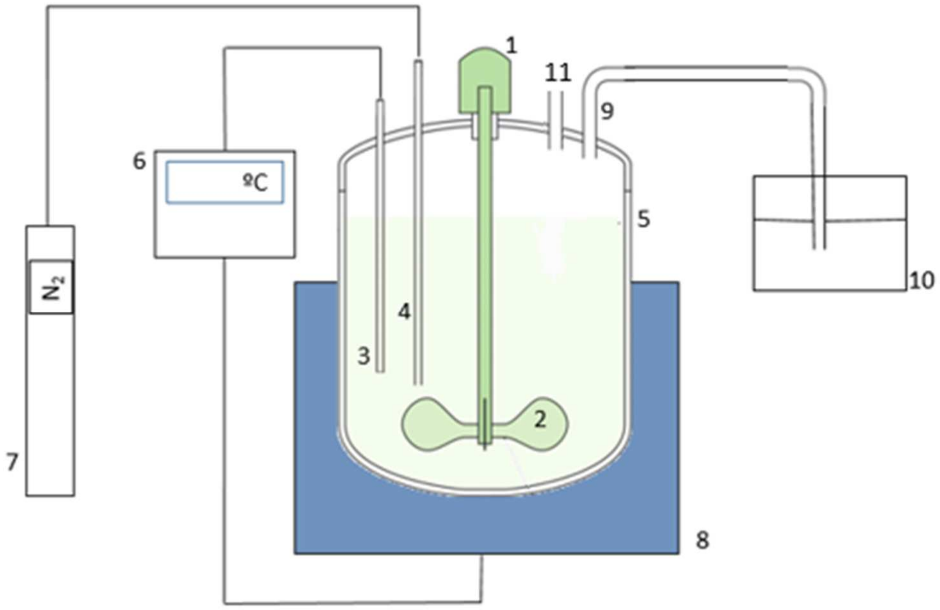


Figure 3.2 Reaction assembly scheme.

A picture of the real assembly used for this purpose is shown below (Figure 3.3).

Figure 3.3 Real reaction assembly used for carbodiimide synthesis.

To carry out the reaction under study, the isocyanate monomer must be charged initially into the reactor, with the required amount of the commercial catalyst and the antioxidant additive. The amount of catalyst used in the present study ranged from 0.15% to 0.4% (w/w) regarding to the total monomer charged.

Depending on the sample prepared, alkali is also added first to the catalyst, and the resulting mixture is charged into the reaction system.

Once the raw materials involved are charged, the system is heated between 120 and 180°C depending on the isocyanate monomer used.

The heating system chosen to reach the required high temperatures consists of an electric heating mantle connected to the temperature controller which is connected to the temperature probe which is in direct contact with the reaction mixture.

Throughout the process, the system must be kept stirred and sparged by using dry nitrogen [3]. The introduction of dry nitrogen is necessary to remove the carbon dioxide that is generated during the reaction. These gases are expelled from the system and collected in a scrubber in which there is an aqueous solution of sodium hydroxide that retain the CO_2 as Sodium carbonate.

Nitrogen used must be dry because any presence of moisture can reacts with the isocyanate group generating amine, which also reacts with the isocyanate group to generate urea [4].

The usual conversion time varies depending on the isocyanate monomer chosen for that purpose; being necessary about 12 hours for the case of non-hindered isocyanates and between 20 and 26 hours for hindered isocyanates. The amount of catalyst added and the use of alkali also modifies the reaction time.

Once the reaction is finished vacuum is applied during 30 minutes to distill out the rests of unreacted isocyanate monomer and catalyst.

Taking into account the proposed mechanism, the activity of the used catalyst becomes important because it is the only element that interacts directly with the isocyanate monomer to carry out the desired reaction.

3.2.2 Procedure for the inclusion of carbodiimides in polymers

The procedures for the preparation of the different samples or polymers in which a certain amount of carbodiimide is incorporated to evaluate the effects of such addition are described below. We differentiate 2 different procedures depending on the polymer to be doped:

- Preparation process of water based polyurethanes.
- Process for the preparation of acrylic polymers.

3.2.2.1 Preparation process of doped water based polyurethanes and its specimen test preparation

For the preparation of water based polyurethane samples which are subsequently tested for evaluation of the improvement properties provided by the carbodiimides, it is necessary to apply the following procedure:

1. A diol (which may be of different origin) and a small amount of dimethylolpropionic acid (DMPA) are charged in a reactor equipped with stirrer, temperature control probe, inlet for raw materials and a condenser. The reaction mixture is diluted with N-EthylPyrrolidone (NEP) to facilitate the stirring and is heated to 70ºC.
2. The Diisocyanate is then added, with or without the carbodiimide oligomer, and the reaction mixture is heated up to 80ºC.
3. Once the isocyanate content has reached the expected value, the mixture is cooled to 70ºC and Triethylamine is added (amount necessary to neutralize the acid previously added).
4. Once the acid is neutralized, the mixture is cooled to 25ºC and the obtained polymer is dispersed at 40% in water.
5. Finally, hydrazine is added as a chain extender to react the free isocyanate.

Once the doped polymer is prepared, test specimens are prepared as follows in order to study the stability of the prepared doped water based polyurethane samples:

1. 30ml of prepared water based polyurethane solution are poured into a mold (see Figure 3.4).
2. The mold and sample are dried for 24 hours at room temperature.
3. Finally the test specimen is unmolded and a polyurethane (PU) film of about 0.5 mm thickness is obtained and ready to be tested.

Figure 3.4 Mold used to prepare polyurethane films

3.2.2.2 Preparation process of acrylic system doped polymers and its specimen test preparation

For the evaluation of the application of carbodiimides in acrylic systems, polypropylene specimens have been prepared by extrusion and injection techniques. The combination of these two techniques has been employed to aid in the mixing of the two components in a first extrusion phase, and subsequently to inject the mixture obtained into the molds of the final specimens. Similar preparation process has been used before to test this kind of application [1]. The extrusion and injection conditions for the preparation of the test specimens are detailed below in Table 3.3 and Table 3.4.

Extrusion step was performed with a Brabender TSE20 twin screw extruder, and the final injection of the specimens was carried out by using a 110 ton locking force injector, Battenfeld TM110.

Table 3.3 Extrusion conditions for the polypropylene specimen test preparation.

VARIABLE	VALUE
Temperature profiles (ºC)	200 – 220 – 240 – 240 – 220 – 200
Extrusion speed (rpm)	80
Torque (Nm)	9.5 - 10

Table 3.4 Injection conditions for the polypropylene specimen test preparation.

VARIABLE	VALUE
Temperature profiles (ºC)	200 – 190 – 190 - 180
Injection pressure (bar)	900
Compaction pressure (bar)	600
Compaction time (s)	12

3.3 ANALYTICAL METHODS

This section describes the analytical methods used to carry out the analysis and control of the syntheses performed. To carry out the kinetic monitoring of the reaction, basically the total CO_2 generated and the isocyanate content present in the system has been determined [5]. Carbodiimide content present in the final sample has been also determined. All the analytical methods used in this thesis are detailed as follows.

3.3.1 CO_2 determination

During the carbodiimide synthesis reaction, CO_2 is evolved. This CO_2 is removed from the system by using nitrogen as gas sparging. The amount of CO_2 generated during the reaction can be determined by its quantification in the scrubber solution or by the difference of weight in the reactor. The total amount produced is very helpfully to understand the kinetic of the reaction.

3.3.1.1 CO_2 determination by the scrubber solution analysis

The generated gas is removed from the system using nitrogen as gas carrier and is introduced in the scrubber, where the CO_2 reacts with a solution of sodium hydroxide forming sodium carbonate.

$$2NaOH\ (aq) + CO_2\ (g) \rightarrow Na_2CO_3\ (aq) + H2O\ (l)$$

The amount of CO_2 retained in the scrubber is calculated from the final amount of calcium carbonate generated by the addition of calcium chloride to the scrubber solution. This is because the interaction of the sodium carbonate previously generated with an excess of calcium chloride generates a precipitate of calcium carbonate and sodium chloride that is soluble, according to the reaction:

$$NaCO_3 + CaCl_2 \rightarrow CaCO_3\ (s) + 2NaCl\ (aq)$$

The measurement of the amount of calcium carbonate generated, recovered by filtration, allows us the quantification of the amount of CO_2 retained in the scrubber; which comes from the carbodiimide synthesis; by using the following equation:

$$\mathrm{g\ CO_2\ total} = \frac{\mathrm{W}\, x\ 44}{100}$$

Being:

W, the amount in grams of calcium carbonate generated.

44, the molecular weight of carbon dioxide.

100, the molecular weight of calcium carbonate.

3.3.1.2 CO_2 determination by reactor weight difference

The determination of the amount of CO_2 generated during the reaction can also be performed by reactor weight difference. Knowing the initial weight of the reactor and the amount of monomer and catalyst added, the generated CO_2 is calculated by subtracting the initial weight with the final weight once the reaction is finished.

Is important to measure the final weight before applying vacuum. In this last process step, the monomer residues are removed which can falsify the final obtained result. The result is obtained by applying the following equation:

$$\text{g } CO_2 = (\text{Initial reactor weight} + \text{charged reagents}) - \text{Final reactor weight}$$

This calculation is easy to perform at laboratory scale. Furthermore, for industrial scale production there are very accurate sensors to measure the reactor weight that can help to get this measurement.

3.3.2 Isocyanate (NCO) content determination

The synthesis of carbodiimides is based on the conversion of two isocyanate groups to generate the desired carbodiimide functional group. While the reaction proceeds, the amount of isocyanate present in the system (R-NCO) decreases. The control of this value is used to study the reaction kinetic.

The determination of the isocyanate content is based on a back-titration (ASTM D2572-97), for this reason a blank test should be made. 0.1 to 3 g of sample are dissolved in Toluene. The amount of sample required increases once the reaction is closer to the end. For a correct sample dissolution the mixture may be heated [6]. In the case of polycarbodiimides synthesis the heating step is more necessary once the reaction approaches to the end of the reaction because the sample has a higher molecular weight.

Once the sample is dissolved, 25 ml of a 0.5N solution of Dibutylamine in toluene is added. The mixture is stirred for 5 minutes to ensure the correct reaction of the Dibutylamine added with the isocyanate present in the sample.

Finally, the excess of Dibutylamine non-reacted is titrated using a 0.5N hydrochloric acid solution.

The difference on the hydrochloric acid solution volumes used between the blank and the sample, can be used to calculate the amount of isocyanate present in our sample by following the next equation:

$$\%\mathrm{NCO} = \frac{(\mathrm{Vb} - \mathrm{V})\, x\, 0.5\, x\, \mathrm{f}\, x\, 42}{1000\, x\, \mathrm{W}}\, x\, 100$$

Being:

Vb; the hydrochloride acid solution used for the blank titration.

V; the hydrochloride acid solution used for the sample titration.

f; the normality factor of the hydrochloride acid solution used.

W; the sample weight.

3.3.3 Carbodiimide (NCN) content determination

The high reactivity of the carbodiimide group with carboxylic acids is well known. For this reason Oxalic acid is used to perform a back titration with potassium hydroxide to quantify the carbodiimide group [7]. The process is detailed below:

0.4 to 0.6 grams of sample are weighted and introduced into a 250 ml balloon.

100 ml of dioxane are added and the mixture is stirred with a magnetic stirrer until obtain a homogeneous solution. The mixture can be heated to facilitate the dissolution.

0.5 to 0.6 grams of oxalic acid is added to the solution. The purity of the oxalic acid must be determined to obtain a more accurate result.

A condenser is placed on the balloon to avoid loss of Dioxane and the mixture is heated at around 110ºC while stirring for 2 hours.

After this reaction time the resulting solution is titrated with a solution of 0.5N of potassium hydroxide, using phenolphthalein as indicator.

The final result is expressed as the weight percent of carbodiimide and is found using the following equations:

$$Oxalic\ acid\ initial\ moles = \frac{Wacid\ x\ 100}{f\ x\ 90.03}$$

$$unreacted\ Oxalic\ Acid\ moles = \frac{V\ x\ 0.5}{1000\ x\ 2}$$

$$\%NCN = \frac{(\text{initial Oxalic moles} - \text{unreacted oxalic moles})\ x\ 40}{W}\ x\ 100\ \text{-}\ \%NCO$$

Being;

Wacid; the oxalic acid weight.

f; the factor or purity of the oxalic acid used.

V; the KOH volume used in the titration.

W; the sample weight used.

3.3.4 Color Gardner determination

The determination of the color appearance of the samples prepared has been performed by using the color Gardner scale. This common used method covers the measurement of the color of liquids by means comparison with arbitrarily numbered glass standards. The standards are defined in the ASTM D-1544-04 [8].

3.4 TECHNIQUES AND EQUIPMENT

Characterization of the catalysts and raw materials used, as well as the final samples obtained, has been performed by using the following techniques and equipment:

Matrix-assisted laser desorption / ionization with time-of-flight detector (MALDI TOF) mass spectroscopy by using an UltraFlexExtrem spectrometer from Bruker.

Fourier Transformed Infrared Spectrometry (FTIR) by using a Perkin Elmer Spectrum ONE and a Shimadzu spectrometer.

Nuclear magnetic resonance (NMR) by using a VARIAN NMP System 400 equipment.

Scanning electron microscopy (SEM), was carried out using a Zeiss Evo MA 25 equipment.

For the final evaluation of the samples prepared, different equipments have been used for the study of the mechanical properties, as well as their resistance to the chemical degradation at superficial and molecular levels.

3.4.1 Techniques for carbodiimide samples preparation and characterization

In this section, all the techniques used to monitor the carbodiimide reaction synthesis as well as for the raw materials and samples characterization are described.

3.4.1.1 MALDI TOF mass spectrometry

MALDI-TOF mass spectrometry is the abbreviation for Matrix-Assisted Laser Desorption/ionization (MALDI) Time Of Flight (TOF) analyzer. This is a soft ionization technique, used in mass spectrometry, which allows the analysis of biomolecules and large organic molecules.

In this kind of spectrometry, the organic matrix selected is very important because it works as a transmitter, transferring the energy necessary for the ionization from the laser to the molecules of the sample that is studied. The sample-matrix mixture must to be crystallized to ensure an optimum spectrum resolution. Therefore, depending on the sample, the use of one type of matrix or another, affects the ionization of the same, and consequently affects the correct spectrum registration.

Depending on the physicochemical characteristics of the sample, sometimes is necessary to incorporate a dopant into the Matrix-Sample mixture. The dopant, which are usually salts of sodium, silver or potassium acetates; is added to improve adducts formation process. This process is necessary in samples that have not a strong tendency to lose or gain electrons [9]. The experience with different types of product families is what leads us to prove their suitability in each case and for each type of sample. The process can be summarized as follows.

The sample is mixed with the matrix on a metal surface (metal board). After solvent evaporation, a crystal is obtained. When a dopant is required, the sample is pre-mixed with the selected ones. Then, the crystal is irradiated with the laser under high vacuum conditions. This irradiated energy is absorbed by the matrix and transferred to the sample in form of excitation energy which causes the transfer of protons or ions from the dopant (in cases that are required). Generally mono-charged species (ionization) are obtained, which are volatilized and sent to the detector. The lighter ions experience greater acceleration moving faster and arriving earlier at the detector. Finally the specific “footprint” or chemical profile of the analyzed sample is generated in the detector.

Each commercial MALDI-TOF mass spectrometry system recommends its own protocols for sample preparation.

In this thesis, the MALDI-TOF mass spectrometry measurements were performed with the UltraFlexExtrem (Bruker GmbH) spectrometer. The spectra were acquired through the Flex Control program, in the reflection method in the mass range from 700 to 3500 Da.

Each series of measurements are preceded by a calibration with a standard provided by Bruker, which contains a mixture of known proteins. In this study, the "Bruker Peptide Calibration Standard", which contains peptides with masses between 1000 and 3500 Da, has been used.

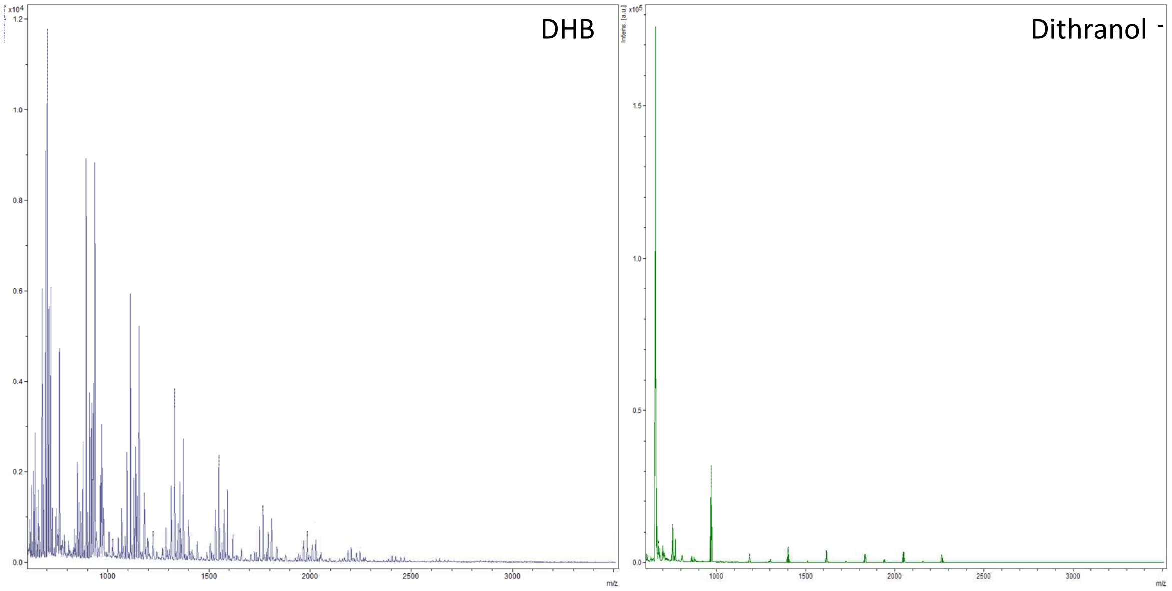
For the processing of the spectra, the flexAnalysis program has been used.

Previously MALDI TOF mass spectrometry studies

An optimization of the analysis, has been previously carried out to determine the most appropriate matrix for the samples which needs to be studied. Carbodiimide oligomers as well as the isocyanate groups are not easily ionized, for this reason sodium trifluoroacetate was used as a dopant.

Initially, and according to the prior art [10], we tested the use of two very common matrices, 2,5-dihydroxybenzoic acid (DHB) and Dithranol.

In Figure 3.5 the spectra obtained using the different matrices selected with two carbodiimide samples are shown.



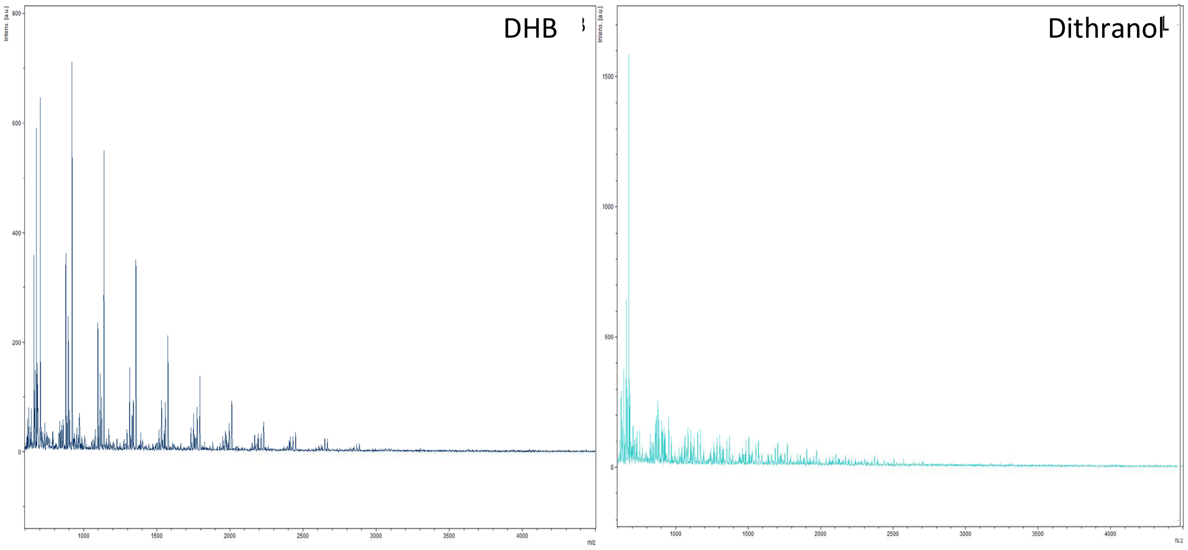


Figure 3.5 MALDI TOF mass spectra of polycarbodiimides using DHB and Dithranol as matrices

As can be observed, the matrix that allows a better sample ionization of the polycarbodiimide samples, and therefore finally gets a more accurate spectrum registration, is the DHB. Consequently, the use of DHB as a matrix and NaTFA as a dopant is used as the analytical medium for polycarbodiimides MALDI TOF analysis. The solvent used for the dissolution of all components is Tetrahydrofuran (THF). With all these data the following sample preparation protocol is established for the analysis of polycarbodiimides by MALDI-TOF mass spectrometry:

Preparation of the matrix, consisting of a solution of 27 mg of DHB per milliliter of THF.

Preparation of the dopant, consisting of a solution of 10 mg of NaTFA per milliliter of THF.

Preparation of the sample, consisting of a solution of 2 mg per 60 microliters of THF.

Once all the solutions have been prepared, the Dopant: Sample mixture is prepared in a volume ratio of 1:1 respectively, and crystallized on the MALDI plate. The prepared Matrix solution is then crystallized above it. The MALDI plate used is a standard ground steel plate from Bruker.

3.4.1.2 Fourier Transformed infrared spectrometry (FTIR)

Infrared spectroscopy, or IR, is the branch of spectroscopy that studies the behavior of molecules when they absorb electromagnetic radiation from the infrared region. It is a very versatile technique, because it allows to study practically any sample, regardless of the state in which it is.

The IR region of the electromagnetic spectrum is between 12800-10 cm^{-1}, and can be divided into three different zones: near IR (NIR): 12800-4000 cm^{-1}, medium IR: 4000-400 cm^{-1} and far IR: 400-10 cm^{-1}; being in the medium IR where the major part of the traditional analytical applications are given.

All actual IR equipments incorporates the Fourier transformed analysis system (FTIR). By using this system the conventional IR spectra are obtained.

In the medium infrared zone a functional group frequency zone is distinguished, where the absorption bands can be assigned to vibration units which only depends on the functional group that produce the absorption and not on the complete structure of the molecule. In this way it is possible to know the presence or not of a certain functional groups, and even if the corresponding calibration is performed, it can be quantified. This strategy is very useful for reaction monitoring where the disappearance of an absorption band, or the appearing of a new one of a different functional group has to be observed.

This technique has been used to carry out several determinations. For the specific case of reaction monitoring and control of the samples prepared, a Perkin Elmer Spectrum ONE FTIR equipment has been used. For the correct characterization, it was necessary to identify the characteristic absorption bands of the Isocyanate (R-NCO) and carbodiimide (R-NCN-R) groups because they are the main functional groups involved in the preparation of the studied samples. The mentioned absorption bands appear around 2300 cm^{-1} and at 2200 cm^{-1} respectively.

In addition, FTIR technique has also been used for the analysis of samples tested in degradation assays. A Shimadzu FTIR spectrometer was also used to record the spectra for this type of test. To observe the degradation suffered by the materials, is necessary focuses on the absorption band about 1700-1750 cm^{-1} that is assigned to the carbonyl group [11]. Is also necessary to study the absorption bands of hydroxyl, carboxyl and amine groups.

Previously FTIR spectrometry studies

To perform the determination of the carbodiimide content through the FTIR spectrum, a calibration of the equipment with a carbodiimide standard sample was performed. This calibration was performed by using N, N-Dicyclohexylcarbodiimide (DCC) as standard which only has one carbodiimide group equivalent per mole of product. By diluting the standard in different proportions using toluene as solvent, and recording the area of the absorption band of this functional group, a useful and efficient calibration method has been developed for the quantification of this functional group in the prepared samples.

The FTIR spectra recorded for this purpose, as well as the concentrations used, are shown in Figure 3.6 and Table 3.5 which are shown below.

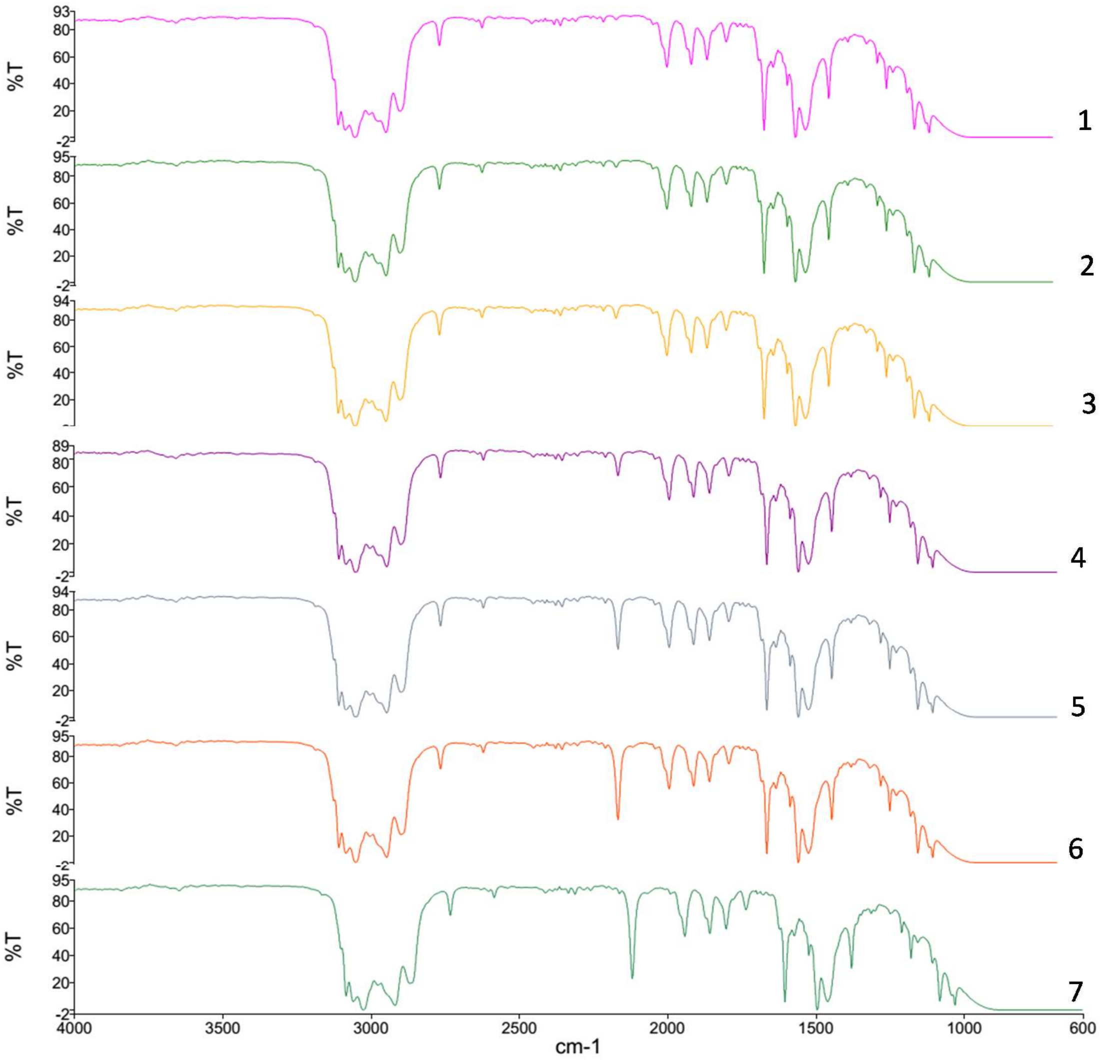


Figure 3.6 FTIR spectra of carbodiimide standard samples 1 to 7.

The following table shows the carbodiimide content present in each standard samples prepared to carry out the calibration.

Table 3.5 Carbodiimide standards concentrations used for calibration.

SAMPLE	CARBODIIMIDE CONTENT (mg/l)
1	41
2	83
3	165
4	332
5	828
6	1620
7	2025

As is observed in Figure 3.6, the band appearing at 2120 - 2150 cm^{-1}, corresponding to the carbodiimide functional group (-N=C=N-) [11], increases its area as the concentration of this group increases in the analyzed pattern. By using the areas obtained, the calibration of this functional group is elaborated. The obtained calibration curve is shown in Figure 3.7.

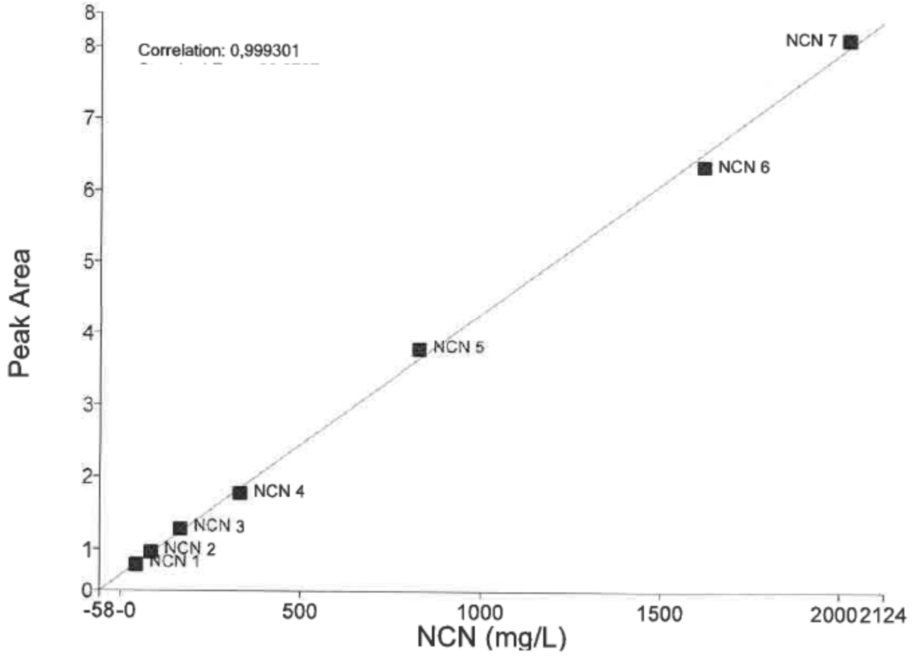


Figure 3.7 Calibration curve for the carbodiimide content determination by FTIR.

The different pattern concentration versus its areas values representation, responds to a linear behavior; so the carbodiimide content can be determined by using FTIR technique. Samples required to be analyzed has to be diluted in toluene and the carbodiimide band area interpolated in the obtained calibration curve.

3.4.1.3 Nuclear Magnetic Resonance spectroscopy (NMR)

Nuclear Magnetic Resonance (NMR) spectroscopy is a technique mainly used for the molecular structures elucidation.

The technique is based on the application of a magnetic field which is absorbed by the atomic nucleus. The exact frequency of absorption of each nucleus depends on its chemical environment, for this reason, NMR technique can be used to determine the structure of the molecule where they are.

To use this technique is necessary that the nucleus under study has a magnetic moment different than zero. For this reason, the most important nucleus studied by this technique are ^{1}H, ^{13}C, ^{15}N, ^{31}P and ^{19}F.

The intensity of the recorded signal depends on the active isotope abundance which is susceptible to interaction. The concentration of that one in the sample determines the final intensity [11, 12].

To carry out the present study, a VARIAN NMR System 400 equipment has been used. The nucleus studied have been the ^{1}H, ^{13}C and ^{31}P.

3.4.2 Equipment, instruments and procedures for final application test

The equipment used for the application evaluation of the samples prepared are described below. Aging tests and mechanical properties as well as microscopy technique has been used to evaluate the possible improvement in the resistance of the new materials.

3.4.2.1 Resistance Test to Climate Cycles

The resistance test to climatic cycles was carried out by using a climatic chamber GRETAGMACBETH SPECTRALIGHT III according to standard PV 1200 [13]. The tested materials have been subjected to environmental cycle stressing by means of cycling temperature and moisture, in order to reproduce the degradative evolution that the sample would experience with the aging time. The susceptibility to cracks, deformation and separation of the composite material has been also evaluated. Test conditions are described in Table 3.6 and Figure 3.8.

Table 3.6 Environmental cycle test conditions.

ENVIRONMENTAL CYCLE	**VALUE**
Cycle conditions	60 min to reach 80ºC±2ºC and 80%±5%R.H.
	240 min at 80ºC±2ºC and 80%±5%R.H.
	120 min to reach -40ºC±2ºC
	240 min at -40ºC±2ºC
	60 min to reach 23ºC±2ºC and 30%±5%R.H.
Number of cycles	14

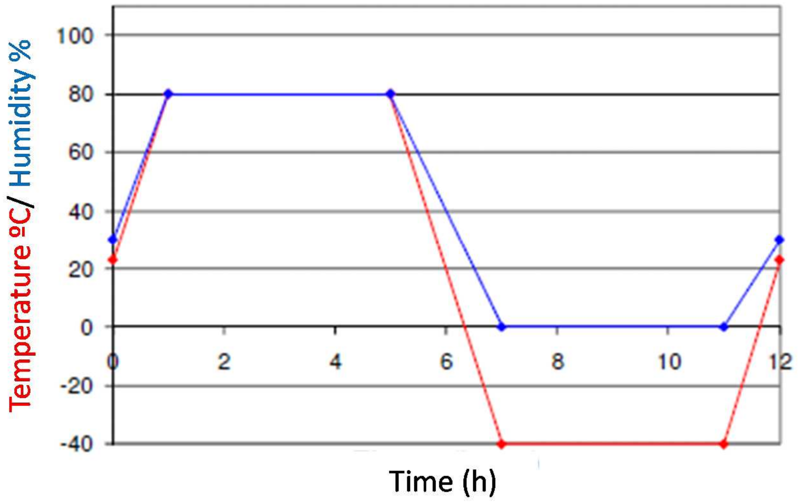


Figure 3.8 Environmental cycle test conditions.

3.4.2.2 Accelerated exposure to external agents

The resistance of the new compounds to the action of UV radiation with the variations of temperature and humidity has been evaluated using Xenotest under the ASTM standard D 2565 [14]. This test allows an accelerated analysis of the effects of external agents on a material after a long time of exposure under real conditions. The equipment used has been an ATLAS Weather-ometer CI 3000 + DCS with artificial light camera. The conditions applied were as follows:

Table 3.7 Accelerated exposure to external agents test conditions.

VARIABLE	VALUE
Temperature	120 min at 70ºC±2ºC 60 min at 38ºC±2ºC
Humidity	50-90%±2%
Radiation	0.55-65W/m^2 (340nm)
Irradiation cycle	120 min light 60 min dark
Water spray	20 min spraying 100 min drying
Exposure time	200 – 1000 h

The exposure time was between 200 to 1000 hours depending on the tested sample. More resistance sample require more exposure time to be degraded.

3.4.2.3 UV light test resistance

The evaluation of the degradation resistance of the new compounds by UV exposure has been carried out according to ISO 4892 [15]. This standard specifies methods for exposing test specimens to fluorescent UV radiation and heat in a designed apparatus in order to reproduce the effects of aging that occurs when the materials are exposed to sunlight. The specimens are exposed to fluorescent UV lamps under controlled environmental conditions.

The equipment used to carry out this test has been an aging camera UV light model Atlas UV FLUORESCENT under the conditions described in Table 3.8.

Table 3.8 UV light resistance test conditions.

VARIABLE	VALUE
UV light	UV A
Temperature	8h at 60ºC±3ºC 4h at 50ºC±3ºC
Radiation	8 h 0.77 W/m^2 (340nm) 4 h un-radiated
Exposure time	1000 h

3.4.2.4 Mechanical properties

The mechanical properties of the final samples prepared has been performed to evaluate the material resistance after applying different degradation tests. Tensile strength and elongation have been determined. In Table 3.9 are shown the different standards followed for each determination.

Table 3.9 Standards used for the mechanical properties determination.

PROPERTY	STANDARD
Tensile strength	ISO 527 [16]
Elongation	ISO 527

3.4.2.5 Leather fastness test

This method has the main objective to determine the leather surface behavior against rub cycles. A leather fabric treated with a coating, is exposed to rub cycles until the specimen test is degraded. The test is carried out by using a plunger with 0.5 kg of weight connected to a rotor. The rotor has a frequency of 40 movements per minutes pressing the leather specimen. The assay has been performed by using a Rub fastness tester VESLIC under the standard IUF-450 [17].

3.4.2.6 Thermal properties (DSC)

The thermal properties of the compounds studied has been performed by using a DSC Q20 kit TA Instrument. Differential Scanning Calorimetry (DSC) is intended to show the material characteristic thermal transitions and the enthalpies associated with these transitions. This information allows us to detect possible variations of glass transition, crystallization and fusion processes.

3.4.2.7 Surface analysis (SEM)

The scanning electron microscope (SEM) is an instrument capable of offering a wide range of information from the surface of the studied sample. Its operation is based on sweeping an electron beam over a desired size area (augments) while a monitor displays the information we have selected. Depending on the required analysis exists different detectors [18] .

In the study a Zeiss Evo MA 25 microscope equipped with a secondary electron detector was used to perform it. The electron beam has been used at 5 kV at 13 mm as working distance. The recorded micrographs have been taken at 50 µm.

3.5 REFERENCES

1. AKTIENGESELLSHAFT, B., Carbodiimidas y procedimiento para su producción. 2004.

2. Monagle, J.J., Carbodiimides. III. Conversion of isocyanates to carbodiimides. Catalyst studies. The Journal of Organic Chemistry, 1962. 27(11): p. 3851-3855.

3. Campbell, T.W., Monagle, J.J., and Foldi, V.S., Carbodiimides. I. Conversion of isocyanates to carbodiimides with phospholine oxide catalyst. Journal of the American Chemical Society, 1962. 84(19): p. 3673-3677.

4. Ulrich, H., Chemistry and technology of isocyanates. 1996: Wiley.

5. Scholl, H.-J., Process for the production of organic carbodiimides and their use as stabilizers for plastics. 1994, Google Patents.

6. ASTM, Standard Test Method for Isocyanate Groups in Urethane Materials or Prepolymers. 2010.

7. Adam, W. and Yany, F., Determination of polymer-supported carbodiimides. Analytical Chemistry, 1977. 49(4): p. 676-676.

8. ASTM, Standard Test Method for Color Transparent Liquids (Gardner Color Scale).

9. Pieles, U., et al., Matrix-assisted laser desorption ionization time-of-flight mas spectrometry: a powerful tool for the mass and sequence analysis of natural and modified oligonucleotides. Nucleic acids research, 1993. 21(14): p. 3191-3196.

10. Gies, A.P., et al., MALDI–TOF/TOF CID Study of Polycarbodiimide Branching Reactions. Macromolecules, 2013. 46(19): p. 7616-7637.

11. Pretsch, E., Determinación estructural de compuestos orgánicos. 2002: Elsevier España.

12. Carrington, A. and McLachlan, A.D., Introduction to magnetic resonance. 1967.

13. Volkswagen, Testing of resistance to environmental cycle test. 2004.

14. ASTM, Standard practice for Xenon-Arc exposure of plastics intended for outdoor applications. 2008.

15. ISO, U., Métodos de exposición de plasticos a fuentes luminosas de laboratorio.

16. AENOR, UNE-EN ISO 527-1:2012 Plásticos. Determinación de las propiedades en tracción. 2012.

17. IUF, 450 (1987).“Colour fastness of leather to dry and wet rubbing”, in J. Soc. Leath. Tech. Ch. p. 24.

18. Artieda, C., Desarrollo y optimización de nuevos componentes lubricante y ligante para el procesado de aceros PM, in Material science. 2017.

Chapter 4

Reaction conditions optimization and synthesis mechanism study

4. REACTION CONDITIONS OPTIMIZATION AND SYNTHESIS MECHANISM STUDY

Carbodiimides can be obtained from a wide variety of sources depending on the starting raw materials selected [1]. Cromogenia units is a usual isocyanate customer, due to its polyurethane production plant, and for this reason this doctoral thesis work has been focused in the study of the conversion of isocyanates to carbodiimides by using phosphorus oxides as catalyst. Furthermore, this synthetic route has been achieved as one of the most important due to the raw materials involved and the byproducts generated, which are easy removable from the system [2].

The most used catalysts to carry out this conversion are the phospholene oxides [3]. This kind of products has the disadvantage to be extremely expensive. The high cost present in the actual market for this kind of catalysts are caused for the specific application that they have (carbodiimide synthesis) and for the low number of industrial producers. One of the main objective of this study is the research of new catalysts or the optimization of the actual ones in order to reduce the extremely high cost.

Before starting carbodiimide synthesis is necessary to optimize the reaction conditions, understood as the chemical-physical variables that modify the reaction kinetics [4]. This chapter takes as main variables the reaction temperature and the catalyst used. There are other variables like the isocyanate monomer used, that will be also studied in this section. Moreover, a mechanism study was also performed by using NMR technique.

4.1 REACTION TEMPERATURE AND CATALYST OPTIMIZATION

The first variable to be optimized is the catalyst. There are different phosphor compounds that could be able to be used as catalyst for the conversion of isocyanates to carbodiimides, however, they have different catalyst activities that needs to be previously studied. For this reason, different synthesis were initially carried out by using 1-methyl-1-oxo phospholene (CAT 1), 1-phenyl-1-oxo phospholene (CAT 2) and triphenylphosphine oxide (CAT 3) in order to study the differences on its catalytic activity. CAT 1 and CAT 2 catalysts were selected because are the most common industrial phospholene oxides available; CAT 3 was selected for its similar phosphor characteristics and because is a very common product in organic chemistry.

All the selected catalyst has similar chemical characteristics; phosphor (V) oxides, but also has different substituents which can causes differences in the phosphoryl bond polarity. Figure 4.1 shows the chemical structures of the catalyst. Both CAT 1 and CAT 2 are supplied as an isomer mixture between 2-phospholene oxide and 3-phospholene oxide due to its synthetic route [5].

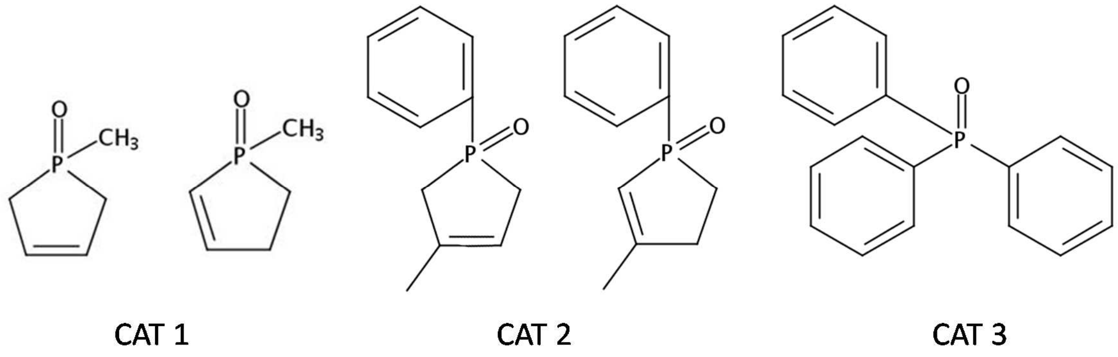


Figure 4.1 Chemical structures of the catalysts.

Besides the structural differences observed between catalysts, there are also differences in the costs of them. CAT 1 and CAT 2 can have a price higher than 1000 euros/ Kilo , even if you have a very good market position, if not, the price could be more than the double. Contrary, CAT 3 has lower price because is a common side product of many useful reactions in organic synthesis involving triphenylphosphine, including Wittig, Staudinger and Mitsunobu reactions [6]. At industrial scale is important to find the better ratio between cost and yield of the final obtained product. For this reason is another variable that needs to be study.

In this study, an optimization of different parameters such as the reaction temperature and the catalyst activity for the isocyanate conversion to carbodiimide, has been carried out. The procedure uses 0.15% by weight of catalyst regarding to the monomer [3] and sparge nitrogen at 0.5 l/min in the reaction system during all the process to remove the generated CO_2. Other variables like temperature applied to the system, catalyst and isocyanate monomer used is studied in this section.

The steric hindrance present in the isocyanate functional group is an important variable to be noted. Also is well known that aromatic isocyanates reacts faster than the aliphatic ones [7]. In this thesis DIPI and TMXDI will be used as isocyanate monomers. Both monomers have differences in the steric hindrance, in the number of isocyanate reactive groups and how this functional groups are connected to the aryl substituent with its consequent aromaticity changes, being DIPI a monoisocyanate and TMXDI a diisocyanate. The number of reactive groups only produces differences in the final product obtained, not in the reactivity, being a carbodiimide dimer in the first case and a polycarbodiimide in the second one. In order to study the catalyst activity, the number of functional groups present does not represent another variable. The chemical structures of the used monomers are shown in Figure 4.2.

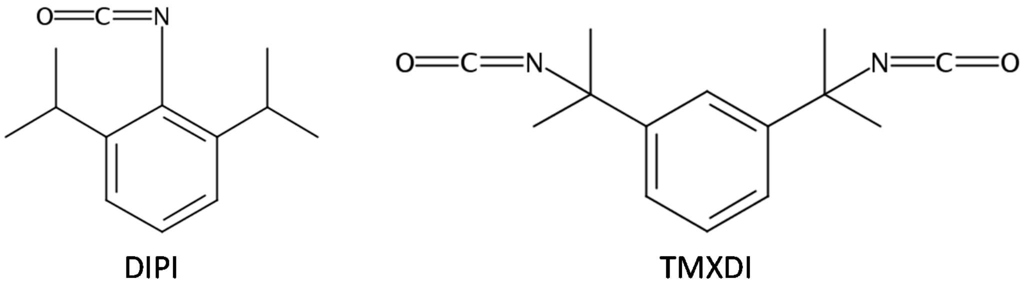


Figure 4.2 Chemical structures of the isocyanate monomers used.

TMXDI and DIPI were selected for its high steric hindrance properties. Is well known that carbodiimides used as polymer stabilizers requires this kind of chemical structure to improve the final application [8]. In order to study the kinetics differences between a highly hindered monomer and an aryl isocyanate and to optimize the reaction conditions, different initial preparations were carried out.

For the correct reaction kinetics evaluation, the isocyanate content present in the system was determined by using the standard ASTM D2572-97 described in section 3.3.2. The obtained values give us information about the kinetics regarding to each catalyst used and the temperature applied.

Furthermore, both the total CO_2 amount generated during the reaction and the final carbodiimide content were evaluated (see section 3.3.1 and 3.3.3), and FTIR spectra was registered to verify that the synthesis was carried out as expected.

4.1.1 DIPI optimization study

In this section the reactions done to optimize the synthesis process by using DIPI as monomer are detailed. The process has been carried out at 100ºC and 120ºC by using the catalysts described in Figure 4.1. Figure 4.3 shows the DIPI isocyanate content regarding the reaction time for each catalyst used at 100ºC and 120ºC.

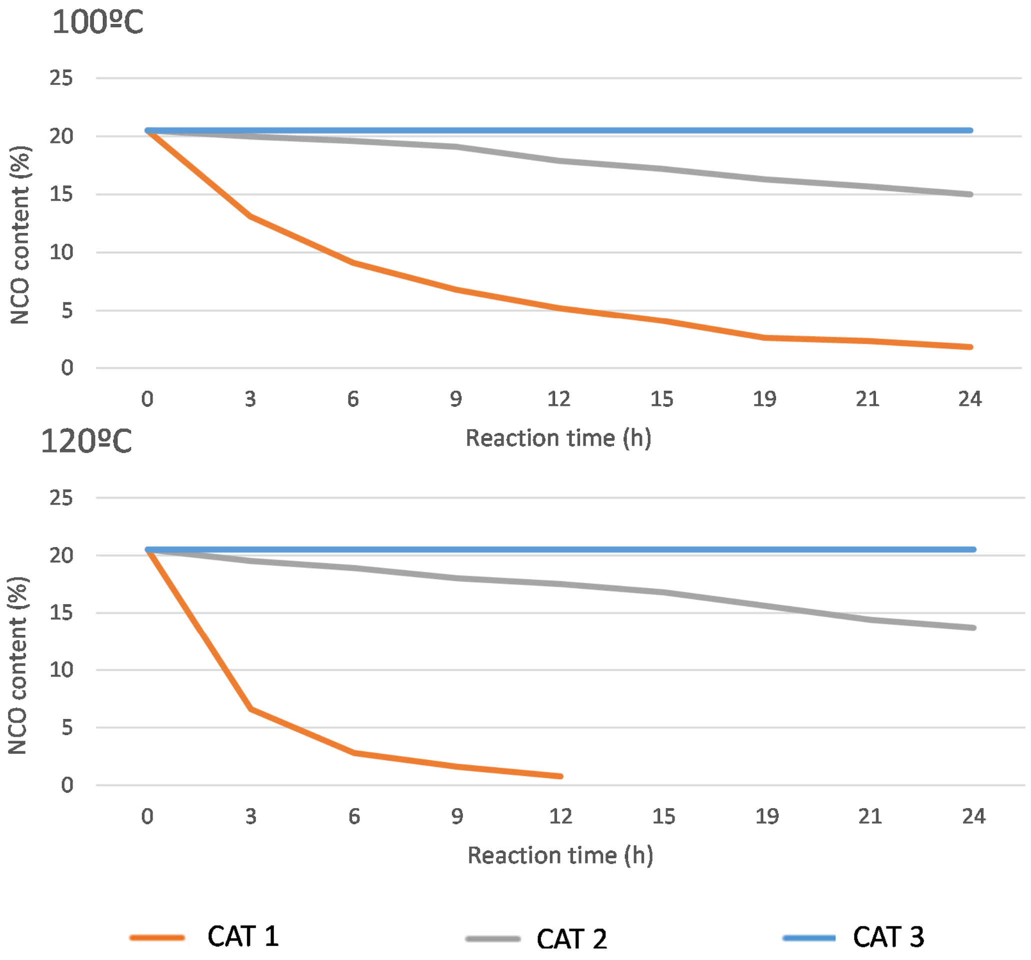


Figure 4.3 NCO content evolution during the preparation of carbodiimide dimer by using DIPI as monomer and 0.15% of catalyst at 100ºC and 120ºC.

Observing the registered values is noted that by using similar dose of commercial catalyst, CAT 1 and CAT 2 can carry out the carbodiimide conversion, contrarily, CAT 3 has not practically activity. CAT 1 is the most effective catalyst tested even at 100ºC and 120ºC, reacting all the isocyanates groups in 12 hours, while CAT 2 shows a 33% conversion by using the double reaction time (24h). Once temperature is increased, the reaction rate is also increased.

CAT 3 is not able to carry out the reaction at the tested temperatures and remains inert in the reaction system maintaining the isocyanate content constant al 20.5% being 20.6% the theoretical value for DIPI monomer.

Knowing the chemical structures of the catalysts and the reaction mechanism for this kind of conversion, the isocyanate group acts as an electrophilic group. For this reason, phenyl substituent present in CAT 2 and CAT 3 produces a higher electron-withdrawing inductive effect compared against CAT 1, over the phosphoryl bond of the catalyst [9] (Figure 4.4), causing a nucleophilic reduction activity of the phosphoryl bond, decreasing the carbodiimide conversion activity due to a low phosphor attack activity to start the reaction. This facts is demonstrated by observing the registered kinetics of the different catalysts.

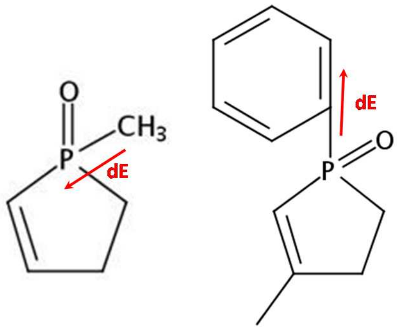


Figure 4.4 Phosphoryl group polarity depending on the substituents.

The phenyl substituents present in CAT 2 and CAT 3 also increases the steric hindrance in comparison with CAT 1. This fact affects to the catalyst-isocyanate approach and its nucleophilic activity. For CAT 3, steric hindrance is higher than in CAT 2, and both this situation and the more depolarized phosphoryl group explains its practically no catalytic activity to carry out the conversion of DIPI to the corresponding carbodiimide dimer. However, triphenylphosphine oxide can carry out this kind of conversion by using total un-hindered aryl-isocyanates monomers. Triphenylphosphine Arsine oxide is also more active [10]. This fact exposes that a perfect equilibrium between the catalyst activity (understood as the polarity of the phosphoryl group), the catalyst steric hindrance, the isocyanate activity (understood as the electrophilic activity) and its steric hindrance are required to carry out this conversion.

In order to check if the conversion has been carried out as expected, it means if carbodiimide group has been formed, FTIR spectra of the samples prepared with CAT 1 at 120ºC compared with the DIPI monomer sample has been performed. The results are shown in Figure 4.5.

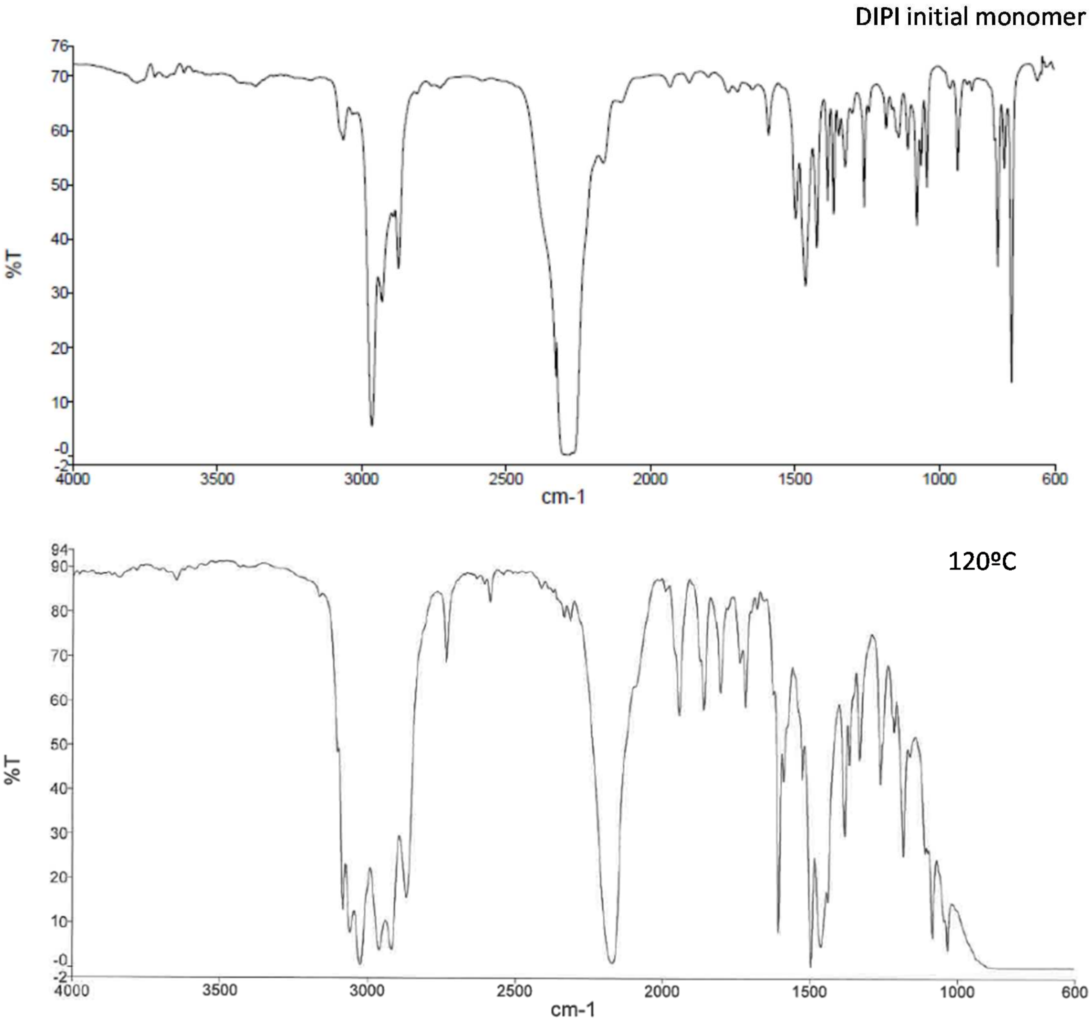


Figure 4.5 FTIR spectra of DIPI monomer and its carbodiimide dimer prepared at 120ºC by using 0.15% of CAT 1 as catalyst.

In the initial DIPI monomer, FTIR registered an intense absorption band at 2310 cm^{-1}. This band is assigned to the isocyanate group [11]. Once the monomer reacts in the presence of CAT 1 at 120ºC, the NCO band disappears to generate a new absorption band at 2120 cm^{-1}, which corresponds to the carbodiimide (-N=C=N-) generated group [12]. The signals present at 2800-3000 cm^{-1} correspond to the C-H aromatic stretching. In the carbodiimide sample FTIR spectrum, a more intense absorption band is observed at 1590 cm^{-1} which is assigned to the stretching C=N absorption band. Also appears three characteristic absorption bands at 1700-2000 cm^{-1} which corresponds to the toluene used to dilute the sample.

In the case of using DIPI as precursor monomer, due to its mono-isocyanate characteristics, the NCO content is completely reacted at the end of the reaction. For this reason the initial absorption band of this functional group completely disappears.

In the same way, using DIPI as monomer only carbodiimide dimers are obtained, being 11% of NCN content the theoretical value for this product which is very close to the obtained experimental NCN content, 10.7% by using the FTIR calibration method. In Figure 4.6 the chemical structure of the carbodiimide dimer obtained starting from DIPI monomer is shown.

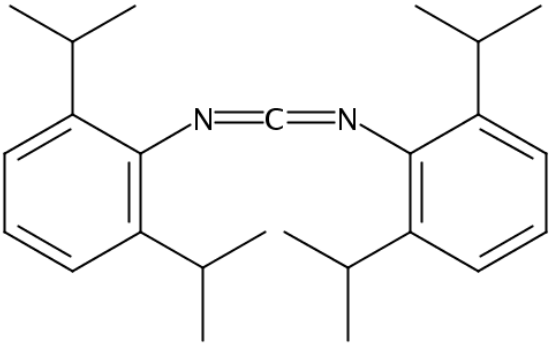


Figure 4.6 Carbodiimide dimer structure obtained by using DIPI as monomer.

Analyzing all the data obtained, 120ºC has been stablished as the optimum temperature for the DIPI conversion to its carbodiimide dimer by using CAT 1 as catalyst, because an interesting reduction in the reaction time has been achieved compared with the reaction at 100ºC.

4.1.2 TMXDI optimization study

Any change in the reaction system requires modification in the reaction conditions. In the same way as for the DIPI monomer, the same optimization study of the reaction conditions was carried out for the TMXDI monomer use. In this case, knowing the reactivity of the catalysts used in section 4.1.1, and the importance of the reaction temperature, an optimization of the reaction temperature was performed for CAT 1. In order to be able to compare with the study carried out on DIPI monomer, 0.15% of catalyst regarding to the monomer was used. Figure 4.8 shows the reduction of the isocyanate content group of the TMXDI monomer regarding the reaction time needed to reach a value closer to 5%, for different temperatures tested (120, 150 and 180ºC).

Using TMXDI as precursor monomer finally forms polycarbodiimides. This oligomer structures has double terminal isocyanates groups. A value of 5% is determined as the reaction end point. This value means 85.5% conversion yield and it is necessary to maintain the oligomer functionality for further applications. The carbodiimide oligomer structure obtained starting from TMXDI monomer is shown in Figure 4.7.

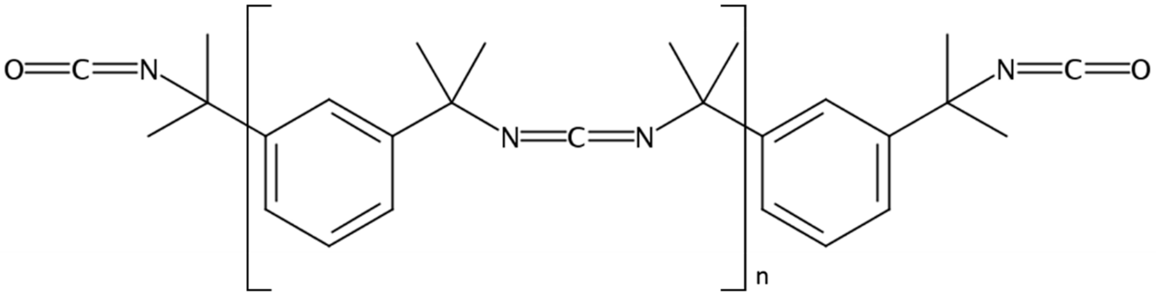


Figure 4.7 Carbodiimide oligomer structure using TMXDI as isocyanate monomer.

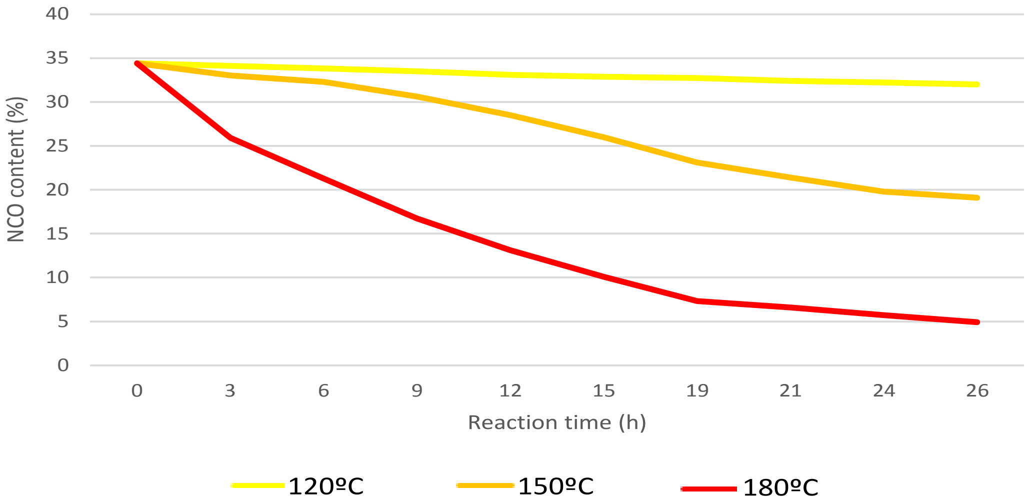


Figure 4.8 Reaction kinetics of the TMXDI conversion to polycarbodiimide at 120, 150 and 180ºC by using 0.15% of CAT 1 as catalyst.

The optimization study has been started by using 120ºC as reaction temperature which was the optimized temperature for DIPI conversion. This starting process by using the same dose of CAT 1 (0.15%) at 120ºC, shows a very slow reaction kinetic, reaching only a 10% conversion in 26 hours. By using this temperature a large reaction time would be necessary to reach the desired 5% final NCO content. This situation is caused for the highly hindrance effect present in the TMXDI monomer, and for its less aryl aromaticity which makes it less reactive.

For this reason different temperatures were tested. Increasing temperature until 150ºC, a faster kinetic is observed, achieving a 45% of conversion in 26 hours. Although the reaction rate is higher than for the experiments performed at 120ºC, an increase in the reaction temperature up to 180ºC reached 5% of final NCO content in 26 hours.

This study has demonstrate that the steric hindrance present in the TMXDI monomer decreases the conversion reaction at the same reaction conditions (temperature and catalyst dose) with respect to DIPI monomer. The difference in the electron withdrawing for DIPI and TMXDI isocyanate groups can also explain the differences in the reaction rate. For this reason, the reaction conditions for TMXDI conversion needs to be more extreme, being necessary increasing the temperature until 180ºC to reach similar reaction rate.

In order to corroborate that the most active catalyst by using TMXDI is CAT 1, a synthesis trial were carried out by using CAT 1, CAT 2 and CAT 3 to convert TMXDI to its carbodiimide oligomer at the optimized CAT 1 temperature (180ºC) by using the same catalyst dose (0.15%).

Figure 4.9 shows the isocyanate content reduction regarding the reaction time and the catalyst used for the TMXDI conversion at 180ºC.

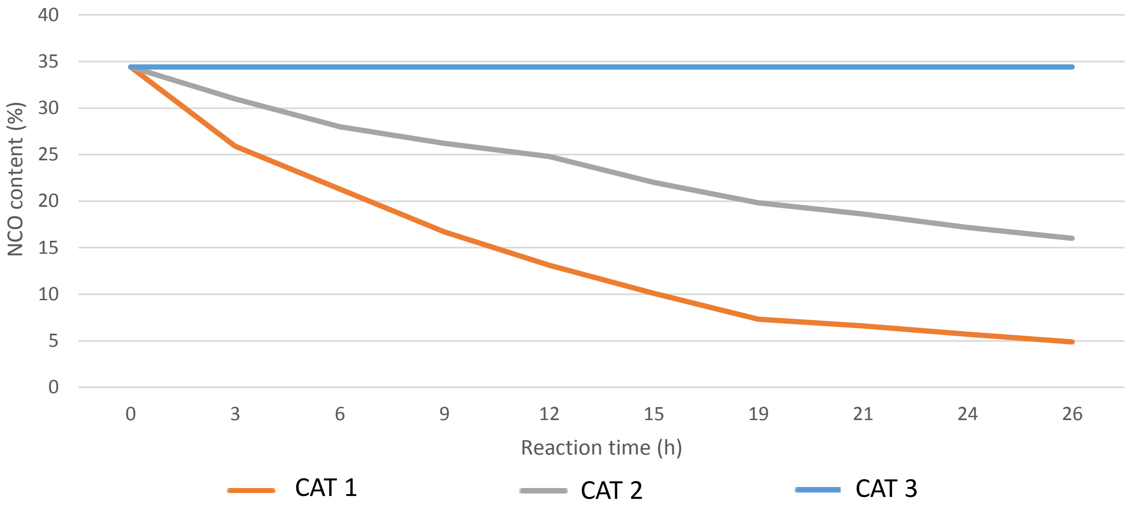


Figure 4.9 NCO content evolution during the preparation of carbodiimide oligomer by using TMXDI as monomer and 0.15% of catalyst at 180ºC.

The reaction synthesis process used to convert TMXDI monomer into its carbodiimide oligomer shows again that the most active catalyst for this purpose is the CAT 1.

Similar pattern than for DIPI study has been observed using the TMXDI monomer. CAT 3 maintains invariable the NCO content at 34.4%, being the same value the theoretical NCO content for the initial monomer. Regarding to CAT 2, higher reactivity than for the DIPI study is observed, reaching near 50% of conversion in similar reaction time. This increase in the catalytic activity is favoured by the increase of the reaction temperature applied. However, the most active catalyst in all cases has been CAT 1.

In this second study carried out at higher reaction temperature, can be noticed that the low reactivity observed by the different catalysts is mainly due to the different polarities present in the phosphoryl bond. This is demonstrated by obtaining similar conversion by using less reactive isocyanate monomer even at higher temperatures. CAT 2 yields a conversion of 53% in 26 hours at 180ºC, whereas at 120ºC yields a conversion of 33% by using a less reactive and highly hindered isocyanate. Steric hindrance present in the catalysts affects the reaction rate, but is not the main reason.

Isocyanate group present in DIPI structure is more active due to its aryl structure. This fact and the less hindered structure explain the softer condition required for its conversion.

In Figure 4.10 is shown the FTIR spectra of the initial TMXDI monomer and its corresponding carbodiimide oligomer prepared at 180ºC by using CAT 1.

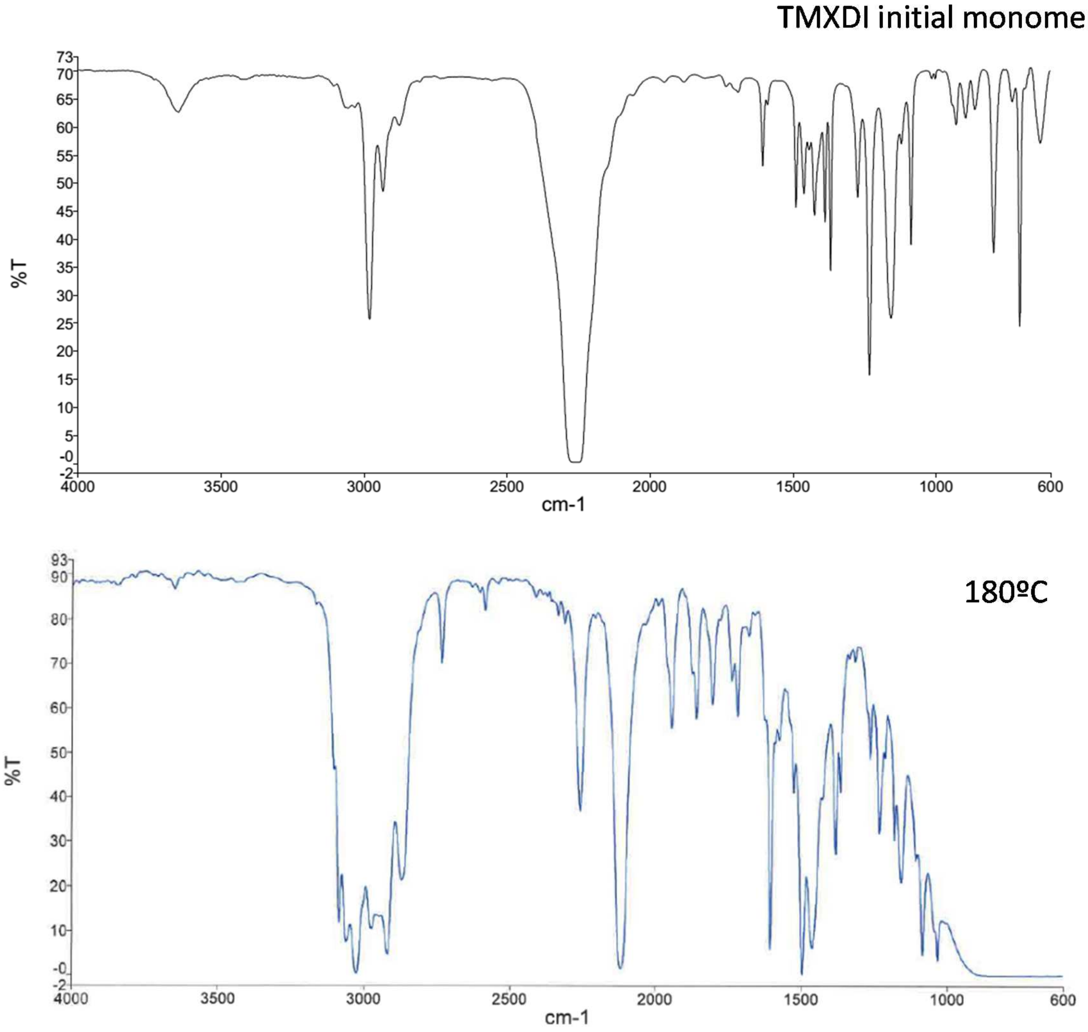


Figure 4.10 FTIR spectra of TMXDI monomer and its carbodiimide oligomer prepared at 180ºC by using 0.15% of CAT 1 as catalyst.

From the observation of the infrared spectra, similar conclusion as for the DIPI monomer are obtained. The initial monomer FTIR clearly shows an intense signal at 2240cm^{-1} which corresponds to the isocyanate group absorption band [11].

Once the TXMDI is converted to carbodiimide at 180ºC, the initial absorption band appearing at 2240cm^{-1} decreases and a new signal is observed at 2130cm^{-1} which corresponds to the carbodiimide group absorption band. In the case of the TMXDI monomer, the isocyanate group signal is still present at the end of the reaction because an oligomer with 2 terminal isocyanate groups (~ 5% NCO content) is required.

By using TMXDI as monomer, due to its similar structure, similar absorption bands are obtained at 2800-3000 cm^{-1}. The bands corresponding to the solvent, toluene, are also observed at 1700-2000 cm^{-1} region.

The carbodiimide content for this sample prepared at 180ºC is 15.1% that has been determined by FTIR. In this synthesis case, contrary from mono-isocyanate study, there is not a theoretical value for the NCN content, its value depends on the final molecular weight of the oligomer formed.

From these experiments, a reaction temperature of 180ºC has been stablished as the optimum reaction temperature for the oligomer carbodiimide synthesis starting from TMXDI monomer by using CAT 1 catalyst.

4.1.3 Optimized samples analysis

The FTIR analysis has been a useful technique to know if the reaction synthesis has been carried out in the correct way. However, the NCN content and the CO_2 analysis are also important values in the quality control process of the samples.

In Table 4.1 and Table 4.2 are detailed the amount of CO_2 generated determined both by scrubber solution analysis and by reactor weight. The NCN content determined both by FTIR calibration and by titration using oxalic acid are also shown.

The experimental values obtained are compared to the theoretical ones. Theoretical values for CO_2 amounts are calculated knowing that one mole of CO_2 and one mole of NCN are generated for each two isocyanate moles reacted. For the TMXDI study the calculation has been done for a 85% isocyanate conversion (because the end of the reaction is considered when a 5% NCO content is reached), whereas for DIPI study a total conversion has been used for the calculation, due to its isocyanate completely reaction.

NCN content results are expressed as weight percentage regarding the total final sample amount and the generated amount of CO_2 are expressed as weight percentage regarding the initial monomer amount charged into the reaction system.

Table 4.1 Theoretical, FTIR and titrated NCN content of the samples prepared with the optimized catalyst and temperature process.

Monomer	Temperature (ºC)	NCO (%)	NCN (%) theoretical	NCN (%) FTIR	NCN (%) Titration
DIPI	Initial	20.7	0	0	0
DIPI	120	0	11.1	10.7	10.9
TMXDI	Initial	34.4	0	0	0
TMXDI	180	5.1	16.4	15.1	15.6

Table 4.2 Theoretical, scrubber analysis and reactor weight CO_2 content of the samples prepared with the optimized catalyst and temperature process.

Monomer	Temperature (ºC)	NCO (%)	CO_2 (%) theoretical	CO_2 (%) scrubber	CO_2 (%) reactor weight
DIPI	Initial	20.7	0	0	0
DIPI	120	0	10.8	6.8	11.2
TMXDI	Initial	34.4	0	0	0
TMXDI	180	5.1	15.3	11.5	14.5

Analysing the obtained results, it is important to note that the correlation between the NCN content value obtained by FTIR analysis and by titration method are very similar, having 96 to 98% of concordance. These values are also very close to the theoretical NCN value in the DIPI dimer sample. Nevertheless, comparing the theoretical TXMDI carbodiimide content more difference is observed.

The differences between the experimental NCN content obtained and the expected one for the TMXDI carbodiimide oligomer sample are caused by incorrect calculation. The theoretical NCN content has been calculated for one linear oligomeric chain with two terminal NCO groups formation, as the structure shown in Figure 4.7. A polymerization reaction is characterized for obtaining a molecular weight distribution depending on the different molecular weights chains formed. The Gaussian chain distribution obtained is the cause of the observed differences.

From Table 4.2 it can also be observed that carrying out the conversion at the optimum temperature (120ºC for DIPI monomer and 180ºC for TMXDI monomer) the CO_2 amount analysed by weight difference are close to theoretical one, which has been calculated 1 mole of CO_2 for each two isocyanates moles reacted.

The CO_2 determination by the scrubber solution analysis do not shows the real CO_2 amount generated. The differences obtained are caused for the gas loss from the gasket and during the sample taken. Likewise, the theoretical CO_2 amount generated during the TMXDI conversion contains the same calculation mistake than for the NCN content calculation.

For a more accurate theoretical values calculation in carbodiimide oligomer samples, the molecular weight average and oligomer chains distribution analysis are required.

Observing the differences obtained in the CO_2 analysis, the reactor weight determination method has been stablished as the most accurate method for this purpose.

Due to the high reaction temperatures required for the conversions, it is not safe to leave the reaction system unattended. This fact, and the long reaction time required to reach the desired conversion yield, makes indispensable to stop the reaction. For this reason, the reaction process was tested at room temperature (25ºC), by using 0.15% CAT 1 and both DIPI and TMXDI as isocyanate monomers (Figure 4.11).

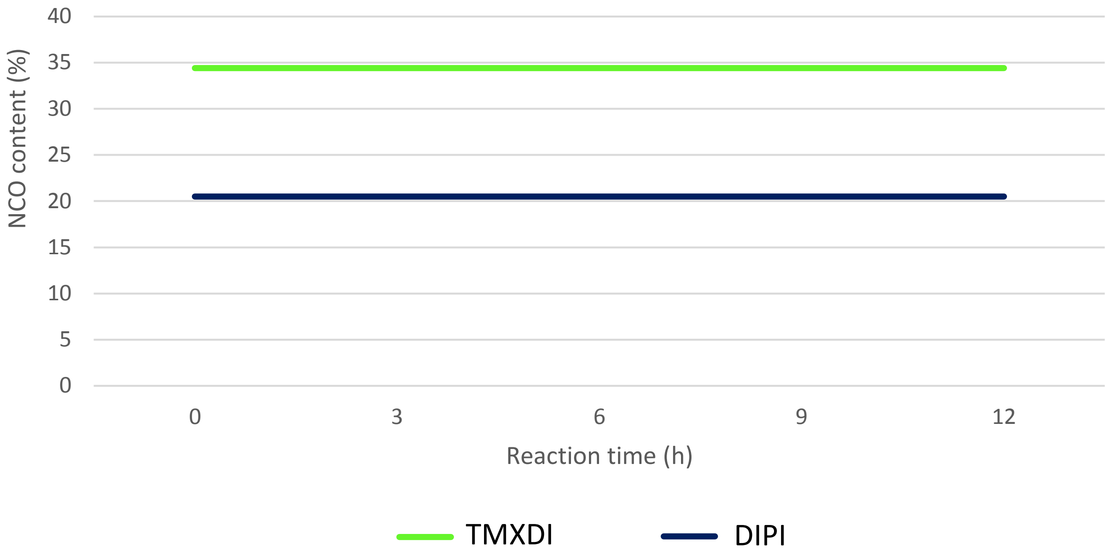


Figure 4.11 NCO content evolution during the isocyanate conversion to carbodiimide by using 0.15% of CAT 1 at 25ºC.

This last study shows that CAT 1 is not active to carry out the conversion to carbodiimide at room temperature by using DIPI and TMXDI as precursors of isocyanate monomers. This fact allows to stop the reaction under nitrogen atmosphere overnight, and restart the reaction the following day. This is possible due to the monomer structures (Figure 4.2), related to the presence of methyl and isopropyl groups. Other monomers can react at low temperatures making impossible to stop the reaction system overnight, for example, P-tolyl isocyanate can converts into carbodiimide dimer at room temperature by using phospholene oxide as catalyst [3]. This study corroborates that depending on the isocyanate monomer used, different reaction conditions are required, being more extreme once the isocyanate group are highly hindered and less reactive.

4.2 SYNTHESIS MECHANISM STUDY

Once conversion reaction temperatures has been studied, is necessary to know how this conversion is carried out by studying and demonstrating the postulated synthesis mechanism.

The postulated isocyanate conversion to carbodiimide mechanism [10, 13] describes the catalyst as one reagent in the reaction system with a directly interaction with the main functional group, the isocyanate. This interaction creates new bonds to finally form the desired carbodiimide functional group, carbon dioxide and the catalyst recuperation.

In Figure 4.12 is detailed the theoretical synthesis mechanism which describes the formation of a reaction intermediate before generation the final carbodiimide group.

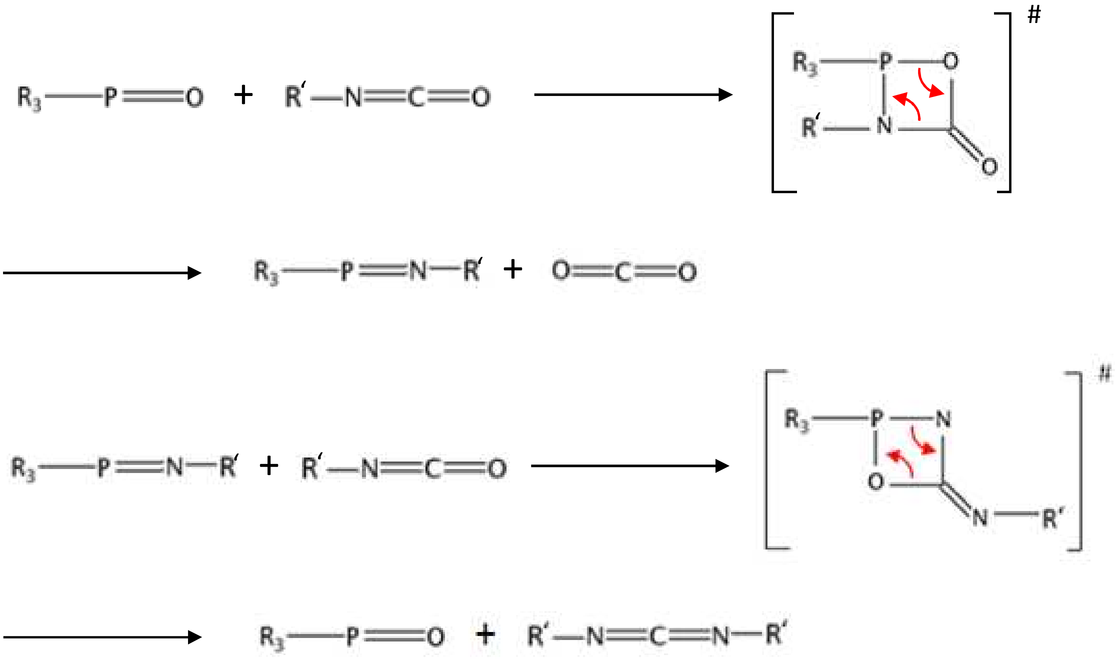


Figure 4.12 isocyanate conversion to carbodiimide synthesis mechanism.

The mechanism detailed in Figure 4.12 can be summarized as is shown in Figure 4.13.

$$2\ R'\text{-}N{=}C{=}O \xrightarrow[\text{Cat.}]{R_3P{=}O} R'\text{-}N{=}C{=}N\text{-}R' + CO_2$$

Figure 4.13 Scheme of the isocyanate conversion to carbodiimide reaction.

The demonstration of the commented reaction mechanism has been performed by the identification of the reaction intermediate where the catalyst participates. The study was carried out by NMR technique, following ^{1}H, ^{13}C and ^{31}P. Furthermore, it is also important to identify the main functional groups involved in the reaction mechanism, before, during and at the end of the reaction. These functional groups are the isocyanate group (R-NCO), initially present in the monomer, and the carbodiimide group (R-NCN-R) which is formed due to the interaction between two isocyanate groups with the phosphorus oxide (V) catalyst.

Initially, the NMR spectra of both the monomer and the catalyst were recorded using $CDCl_3$ as solvent and their structures were identified.

Diisopropylphenyl isocyanate (DIPI) has been used as the monomer for the study of the reaction mechanism because of its easier conversion reaction to carbodiimide, even at lower reaction temperature (100-120ºC). Besides, the carbodiimide dimer formation simplifies the NMR spectra interpretation. CAT 1 has been used as catalyst, because it is the most efficient catalyst tested under the reaction conditions.

4.2.1 NMR initial studies

To characterize the isocyanate monomer as well as the catalyst used, the NMR technique has been performed.

4.2.1.1 DIPI monomer NMR study

For the initial NMR characterization of the monomer, ^{1}H and ^{13}C NMR spectra were recorded at room temperature using deuterated chloroform ($CDCl_3$) as solvent. The structure of DIPI monomer used to carry out this study using both ^{1}H NMR and ^{13}C NMR, is shown in Figure 4.14.

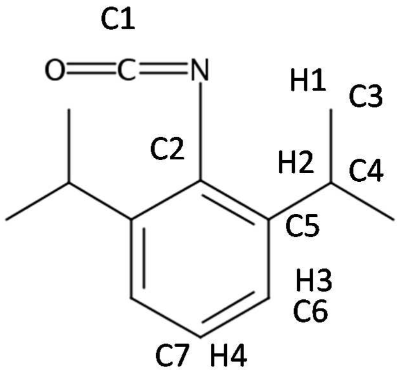


Figure 4.14 Structure of DIPI monomer with both ^{1}H NMR and ^{13}C NMR with the expected signals detailed.

Observing the structure of DIPI monomer, we differentiate, depending on their chemical environment, 4 proton nucleus capable to have signal in ^{1}H NMR. Methyl protons (*H1*), the proton of the isopropyl (*H2*), the protons located in alpha position to the isopropyls (*H3*), and the proton located in Beta position to the isopropyls (*H4*).

Likewise, regarding to the carbon nucleus, 7 nucleus that theoretically should have their own signal in ^{13}C NMR can be observed. The carbon of the isocyanate group (*C1*), methyl carbons which are equivalents (*C3*), isopropyl carbon (*C4*), and 4 carbon signals of the aromatic ring (*C2, C5, C6* and *C7*).

The NMR spectra recorded for the DIPI monomer are shown below.

In Figure 4.15 the ^{1}H NMR spectrum of the DIPI monomer is shown.

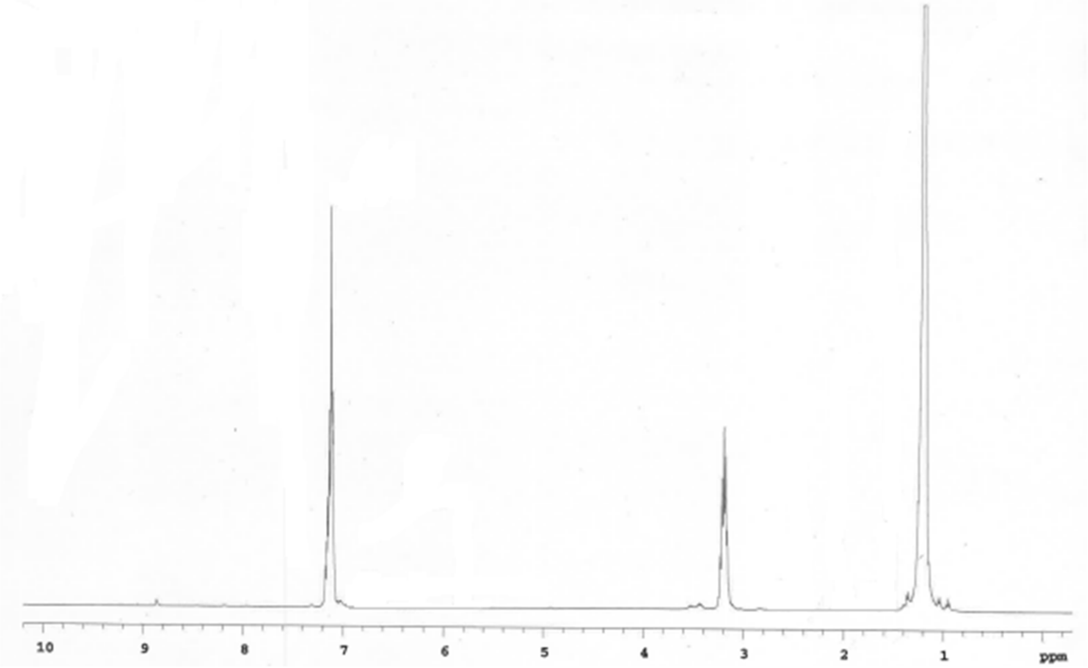


Figure 4.15 DIPI monomer ^{1}H NMR spectra.

In the DIPI ^{1}H NMR spectrum, the signal corresponding to the methyl protons of the isopropyl (*H1*) can be clearly identified, forming a single singlet at 1.2 ppm. The signal at 3.2 ppm can be assigned to the proton of the isopropyl group (*H2*); and the signal at 7.1 ppm to the aromatic protons (*H3* and *H4*), which have very similar displacements; 7.13 ppm and 7.18 ppm respectively. At 7.2 ppm, the signal corresponding to $CDCl_3$ is overlapped by the signal of the aromatic protons of the monomer [11, 14].

In Figure 4.16 the ^{13}C NMR spectrum of the DIPI monomer is shown.

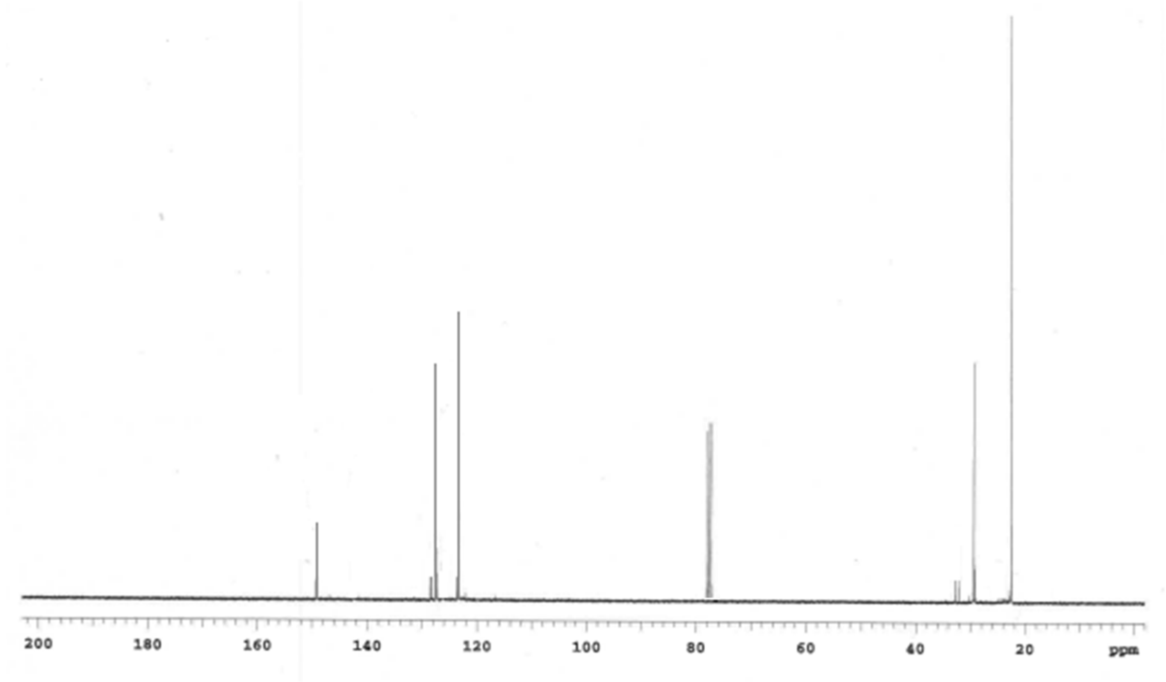


Figure 4.16 DIPI monomer ^{13}C NMR spectra.

In this spectrum, methyl carbon signals (*C3*) can be identified by forming a single singlet about 22 ppm. The singlet that appears about 30 ppm can be assigned to the isopropyl carbon (*C4*). Signal at 123 ppm correspond to the carbon of the isocyanate group (*C1*), and over 127-128 ppm, we find two more signals generated by the aromatic protons (*C6* and *C7*) located in meta and para position regarding to the isocyanate group, being the most displaced signal (128 ppm) the carbon closest to said functional group (*C6*). Slightly more displaced to these ones, another signal is observed at 129.5 ppm, which is assigned to the carbon in alpha position to the isocyanate group (*C2*, 133 ppm theoretical displacement). The signal observed at 149 ppm is attributed to the carbon in alpha position to the isopropyl group (*C5*) [11, 14].

The signal corresponding to $CDCl_3$ appears at 78.5 ppm.

Analysing the spectra obtained and their interpretations, a correct and complete characterization of the DIPI monomer has been done.

4.2.1.2 Catalyst NMR study

Once the isocyanate monomer used was initially characterized, the catalyst used to carry out the conversion is characterized separately and independently from the reaction system. Due to its high activity against the isocyanate monomers used, CAT 1 was used to carry out this conversion.

For the initial characterization of the catalyst, ^{1}H, ^{13}C and ^{31}P NMR spectra were performed at room temperature by using $CDCl_3$ as solvent.

The catalyst (CAT 1) is supplied by a commercial source and is composed by a mixture of two isomers (2 and 3 phospholene oxide). Is important to note it because this fact generates more NMR signals in the spectra due to the presence of more nucleus with different chemical environments.

In Figure 4.17 the structures of the two isomers present in the commercial mixture are shown with both ^{1}H NMR and ^{13}C NMR expected signal numbers detailed.

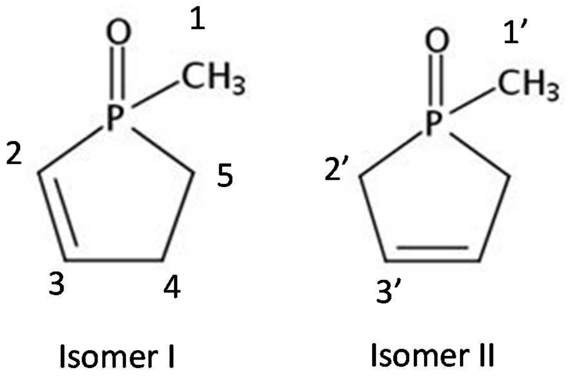


Figure 4.17 Structure of CAT 1 isomers with both ^{1}H NMR and ^{13}C NMR expected signal numbers detailed.

Observing the structures of the isomers present in the commercial CAT 1 mixture, 5 proton and 5 carbon signals are expected for isomer I, whereas for isomer II, due to its greater symmetry, only 3 proton and 3 carbon signals are susceptible to have their own signal by ^{1}H or ^{13}C NMR respectively.

To complete the catalyst characterization, ^{31}P NMR spectrum has also been performed. The two different chemical environments that presents each phosphor nucleus in each isomer should give two distinct signals. Registration of the ^{31}P NMR spectrum was performed using a H_3PO_4 as reference capillary.

The ^{1}H, ^{13}C and ^{31}P spectra recorded for the commercial CAT 1 used are shown in Figure 4.18 and Figure 4.19.

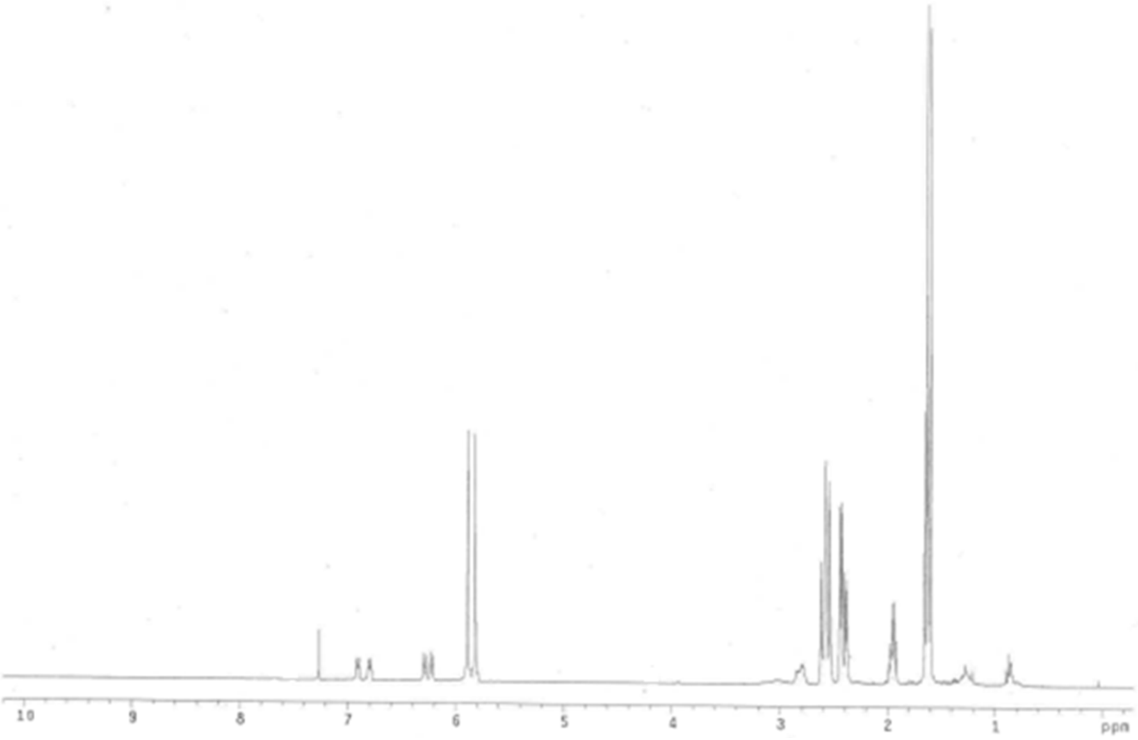


Figure 4.18 ^{1}H NMR spectra of CAT 1.

In the ^{1}H NMR spectrum, the signals of the two isomers present in the commercial mixture are observed. The first signals at 1.5 ppm corresponds to the methyl signals (*1* and *1'*) which have different chemical environments in both isomers, and generate two different but very close signals. Each signal is apparently a doublet, due to the coupling produced with the phosphorus core.

Signal observed at 1.9 ppm can be assigned to protons *4*. The signal is a multiplet due to its coupling with proton *3* and 5. Proton *5* signal appears at 2.4 ppm and is another multiplet resulting from the coupling of proton *4* and the phosphor nucleus. This is also the reason of it higher ppm.

The multiplet observed at 2.6 ppm is identified as the proton *2′* signal, which are equivalents and couple with proton *3′* and the phosphor nucleus.

At 5.8 ppm a doublet is observed which corresponds to the proton *3′* coupled with the phosphor nucleus.

The doublet of doublets appeared at 6.2 and 6.8 ppm are the proton *2* and *3* signals respectively. These signals are doublet due to its self-coupling and doublet of doublets for its coupling with the phosphor nucleus. The proton *2* signal appears at higher ppm (6.8 ppm) because it is closer to the phosphor nucleus.

The signal at 7.2 ppm is due to the $CDCl_3$ solvent [11, 12].

Figure 4.19 shows the ^{13}C NMR spectrum of CAT 1.

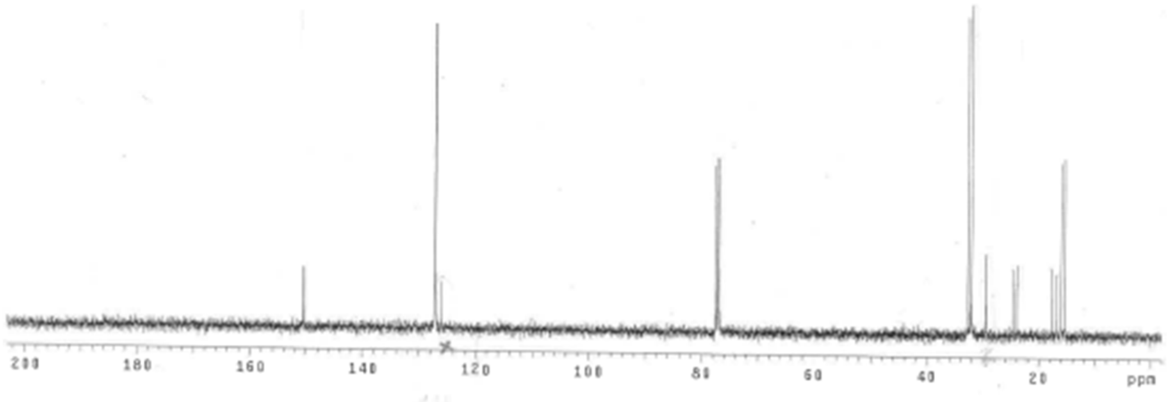


Figure 4.19 ^{13}C NMR spectra of CAT 1.

The ^{13}C NMR spectrum performed, also allows to identify the two isomers present in the commercial CAT 1 mixture.

The doublets present in the 15 and 17 ppm signals can be assigned to carbons *1* and *1'*. The signal are doublets due to its phosphor coupling. At 24 ppm, another doublet is observed, which corresponds to carbon *5* coupled with the phosphor nucleus. Carbon *4* is identified with the single signal at 29 ppm. In this case is a single signal because carbon *4* do not has phosphor coupling.

Signal at 32 ppm is a doublet, which corresponds to carbon *2'* signal, which are equivalent nucleus and has phosphor coupling.

Carbon *3* is assigned to 127 ppm signal, and slightly more displaced, at 128 ppm, are shown the carbon *3'* signal. The ppm difference between them are caused by the unsaturation present between carbons *3'*, which are equivalents. Carbon 2 signal appears at 150 ppm due to the unsaturation and the presence of the phosphor nucleus.

Multiplet signal at 79 ppm corresponds to the solvent used, $CDCl_3$ [11, 12].

The ^{31}P NMR has also been recorded for catalyst characterization. The ^{31}P NMR spectrum of CAT 1 is shown inFigure 4.20.

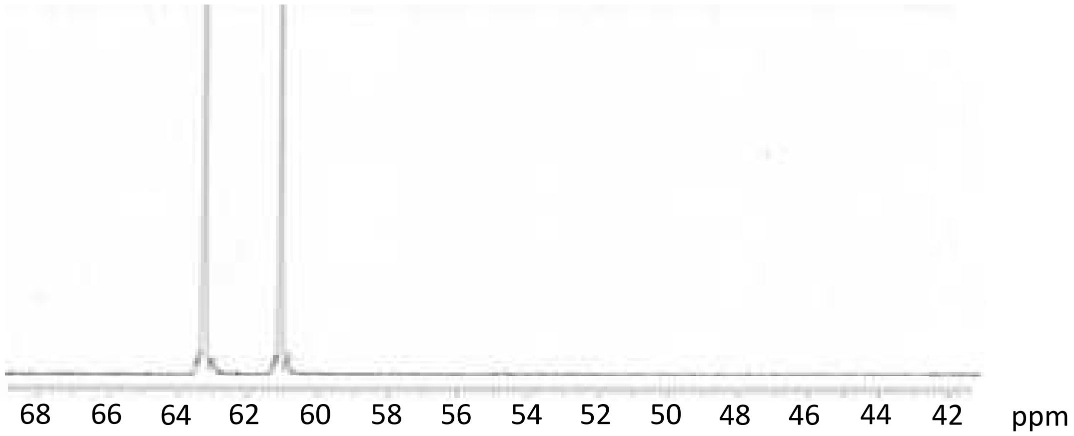


Figure 4.20 CAT 1 ^{31}P NMR spectra.

In the figure two different phosphorus signals are clearly observed which correspond to the two different chemical environments that this nucleus has in the two different isomers of the catalyst. The most displaced signal, at 63.42 ppm, corresponds to the isomer I, which is the isomer with the unsaturation near to the phosphorus nucleus. The signal at 61.37 ppm is assigned to the isomer II which has the unsaturation farthest from the nucleus under study. Both isomers are clearly identified, even having similar chemical structure [12, 15, 16].

4.2.2 Reaction system NMR study

Once all components of the reaction system, both isocyanate monomer and catalyst, have been characterized separately, the conversion reaction of isocyanates to carbodiimide has been also followed by NMR technique. The objective of this study is to identify the new functional groups that are generated during the reaction, as well as the reaction intermediate in which the catalyst is present.

In this study, in order to maintain the ratio between monomer and catalyst in the NMR tube as similar as possible to the ratio present in the original reaction system (0.15% of catalyst regarding to the monomer weight); DIPI monomer was used as solvent. CAT 1 is added to DIPI monomer in a similar ratio than used experimentally.

For the reaction monitoring, the ^{13}C and ^{31}P spectra of the reaction mixture are performed after 30 minutes at 100ºC. This temperature allows the conversion to carbodiimide from DIPI monomer as described in previous sections. The ^{1}H NMR of the mixture has not been performed because the chemical environment of these nucleus is not excessively modified during the reaction.

By performing the ^{13}C NMR it is expected to find new signals corresponding to the formation of new functional groups like carbodiimide group (-NCN-). Also, the ^{31}P NMR can give us valuable information of the reaction intermediates.

In order to carry out this study, the NMR tube charged with the DIPI monomer and the correct amount of CAT 1, is immersed in a thermostated oil bath at 100ºC during 30 minutes. During this reaction time, is noted an effervescence in the tube, which indicates that carbon dioxide has been formed during the isocyanate conversion to carbodiimide. To check if the reaction has been carried out as expected, and to identify the new compounds formed and the reaction intermediate which finally demonstrate the postulated mechanism, the ^{13}C and the ^{31}P NMR of the reaction mixture has been performed after 30 minutes of reaction at 100ºC.

In Figure 4.21 is shown the ^{13}C NMR spectrum of the reaction mixture of DIPI and CAT 1 after 30 minutes of reaction at 100ºC.

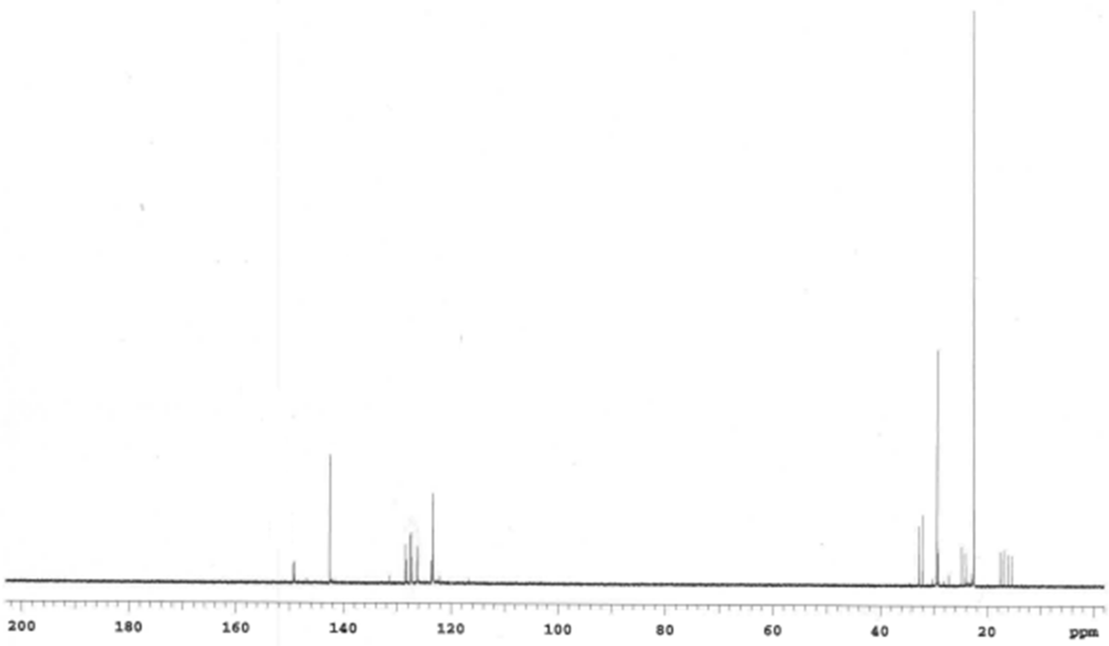


Figure 4.21 ^{13}C NMR spectra of the reaction mixture after 30 minutes of reaction at 100ºC.

Comparing the ^{13}C NMR spectrum registered and the initial NMR study, new signals has been registered after the reaction. The signal at 143 ppm is assigned to the carbodiimide carbon. After 30 minutes of reaction the conversion is not finished, and the isocyanate carbon signal is still present, that can be seen at 123 ppm.

In order to make a more accurate assignation of the new generated signals, in Figure 4.22 is shown the ^{13}C NMR spectrum amplified in the range of 120 – 160 ppm.

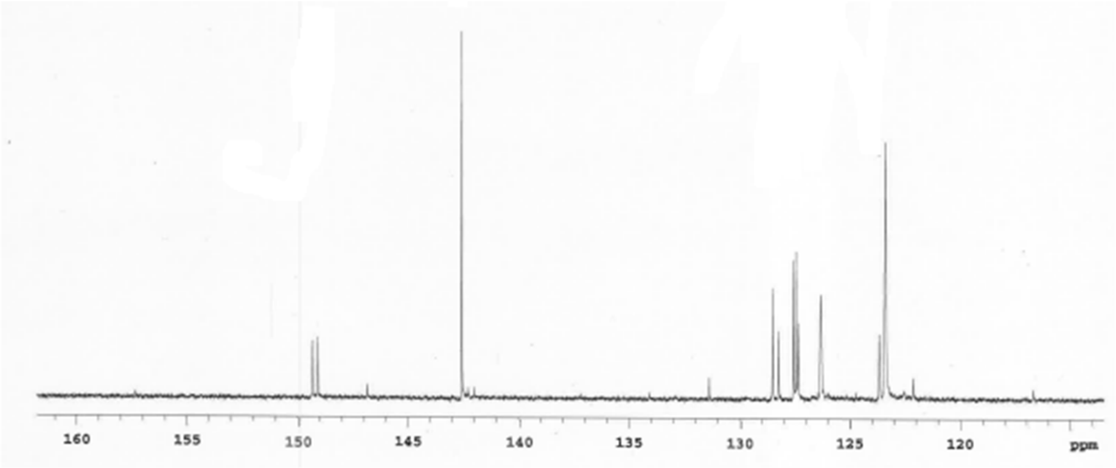


Figure 4.22 ^{13}C NMR amplified spectrum of the reaction mixture after 30 minutes of reaction at 100ºC.

Once the reaction starts, CO_2 is generated which explains the effervescence observed in the tube. Moreover, the new signal appeared at 126 ppm correspond to the diluted CO_2 that remains in the reaction mixture.

Signals at 127 ppm, are assigned to the aromatic carbons situated in meta and para position to the isocyanate group, and to the carbons situated in meta and para position to the carbodiimide group which also have similar ppm. Signals corresponding to the catalyst are also present at 128 ppm, which corresponds to the carbons *3* and *3'*. A new signal is also observed at 131 ppm and corresponds to the new carbon 2 which is in alpha position to the new carbodiimide group formed.

At 150 ppm both the carbon in alpha position to the isopropyl group of the isocyanate (C5) and the unsaturated carbon 2 of the catalyst are also identified [11].

After ^{13}C NMR, the ^{31}P NMR was performed. The obtained spectrum after 30 minutes of reaction at 100 ºC is shown in Figure 4.23.

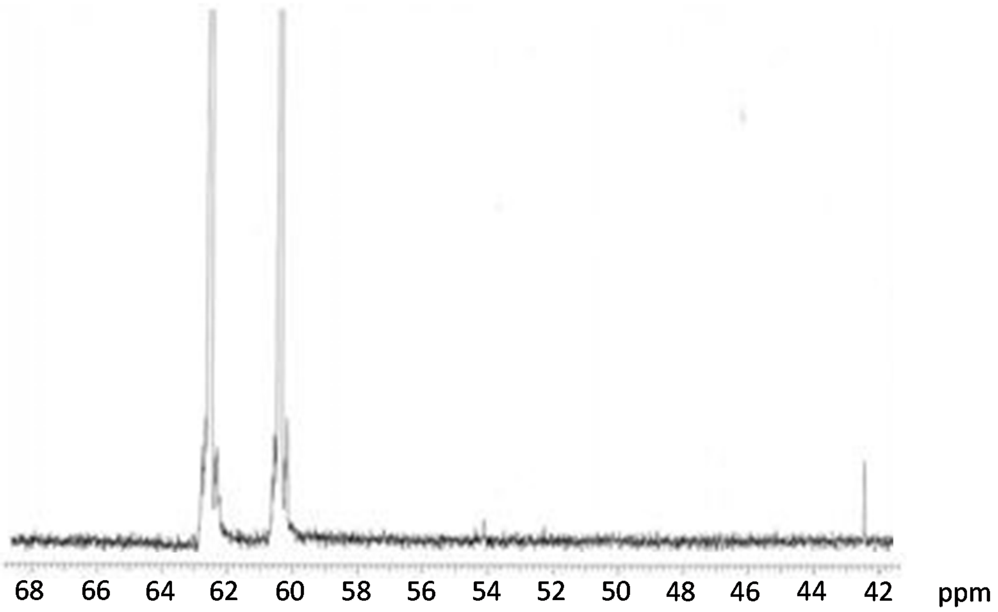


Figure 4.23 ^{31}P NMR spectra of the reaction mixture after 30 minutes of reaction at 100ºC.

Analyzing the ^{31}P NMR spectra obtained of the reaction mixture, the formation of a new phosphor compound is clearly evident. This new compound is the reaction intermediate where the catalyst is involved in its structure. When the reaction mixture is heated at 100ºC, the isocyanate conversion to carbodiimide is started, and in a first mechanism step, a reaction intermediate is formed, which is identified at 42.3 ppm by using ^{31}P NMR technique.

The identified reaction intermediate has the structure RP=NR', being R the CAT 1 structure and R' the DIPI structure. Similar products with this P=N bond has similar ^{31}P NMR, like cianamidotrimethyl phosphorane which has a phosphor signal at 36 ppm [17]. In this study, the signal appears at higher ppm due to the different substituents presents.

This is the first time that the reaction intermediate for this kind of reaction is identified by using NMR technique.

Furthermore, after 30 minutes of reaction both catalytic isomers are also identified. Both isomers (I and II) of CAT 1 appear at 62.87 and 60.53 ppm respectively. These values are slightly lower than the obtained in the previously study (see Figure 4.20) due to the use of DIPI as solvent.

In order to study if the catalyst is recovered at the end of the mechanism, another ^{31}P NMR spectrum was performed after 8 hours of reaction. Figure 4.24 shows the spectra at the beginning of the reaction (a), after 30 minutes of reaction (b) and after 8 hours of reaction (c).

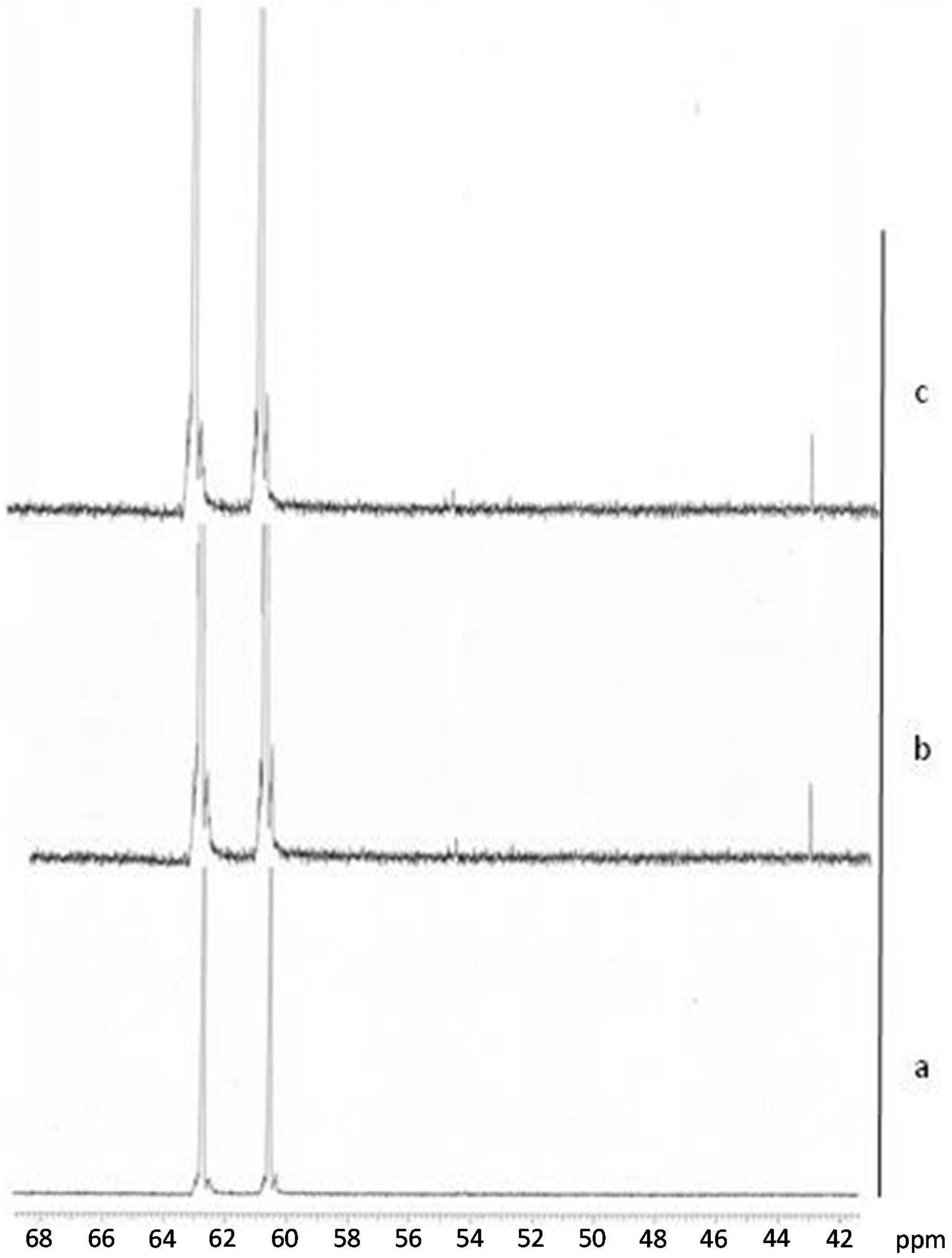


Figure 4.24 ^{31}P NMR spectra of the initial reaction mixture (a), after 30 minutes of reaction (b) and after 8 hours of reaction (c) at 100ºC.

The results demonstrate the postulated mechanism where the catalyst interacts with the isocyanate group to form an intermediate and carbon dioxide; finally, the catalyst can be recovered to restart again the reaction.

4.3 REFERENCES

1. Ulrich, H., *Chemistry and technology of carbodiimides*. 2008: John Wiley & Sons.

2. Ulrich, H., *Chemistry and technology of isocyanates*. 1996: Wiley.

3. Campbell, T.W., Monagle, J.J., and Foldi, V.S., *Carbodiimides. I. Conversion of isocyanates to carbodiimides with phospholine oxide catalyst.* Journal of the American Chemical Society, 1962. 84(19): p. 3673-3677.

4. AKTIENGESELLSHAFT, B., *Carbodiimidas y procedimiento para su producción*. 2004.

5. McCormack, W.B., *3-methyl-1-phenylphospholene oxide.* Organic Synthesis, 1973. 5: p. 787.

6. Corbridge, D.E., *Phosphorus: chemistry, biochemistry and technology*. 2013: CRC press.

7. Ulrich, H., Tucker, B., and Sayigh, A.A., *PN heterocycles. Synthesis and use in the catalytic conversion of isocyanates into carbodiimides.* The Journal of Organic Chemistry, 1967. 32(5): p. 1360-1362.

8. Laufer, W. and Eckert, A., *Method for stabilizing polymers containing ester groups*. 2013, Google Patents.

9. Stock, L.M., *The origin of the inductive effect.* J. Chem. Educ, 1972. 49(6): p. 400.

10. Monagle, J.J., *Carbodiimides. III. Conversion of isocyanates to carbodiimides. Catalyst studies.* The Journal of Organic Chemistry, 1962. 27(11): p. 3851-3855.

11. Pretsch, E., *Determinación estructural de compuestos orgánicos*. 2002: Elsevier España.

12. SciFinder, www.scifinder.cas.org.

13. Lyman, D.J. and Sadri, N., *Polycarbodiimides and their derivatives.* Macromolecular Chemistry and Physics, 1963. 67(1): p. 1-9.

14. Kilgore, U.J., et al., *Aryl Isocyanate, Carbodiimide, and Isocyanide Prepared from Carbon Dioxide. A Metathetical Group-Transfer Tale Involving a Titanium−Imide Zwitterion.* Inorganic chemistry, 2006. 45(2): p. 487-489.

15. Pakulski, Z., et al., *The classical Kagan's amides are still practical NMR chiral shift reagents: determination of enantiomeric purity of P-chirogenic phospholene oxides.* Tetrahedron: Asymmetry, 2003. 14(11): p. 1459-1462.

16. Quin, L.D., et al., *Synthesis of phosphinamides in the 5, 6-oxaphosphabicyclo [2.2. 2] octene series as possible precursors of metaphosphoramidates.* The Journal of Organic Chemistry, 1986. 51(17): p. 3341-3347.

17.Ruppert, I. and Appel, R., *Ein neues Verfahren zur Darstellung von N-Cyaniminophosphoranen.* European Journal of Inorganic Chemistry, 1978. 111(2): p. 751-758.

Chapter 5

Synthesis, sample characterization and catalyst isomerization

5. SYNTHESIS, SAMPLE CHARACTERIZATION AND CATALYST ISOMERIZATION

One of the main objective of this doctoral thesis is the preparation of carbodiimide oligomers to be used as polymer stabilizers. For this reason, once the reaction conditions to carry out the conversion of isocyanates to carbodiimides has been optimized, is necessary to optimize the carbodiimide synthesis process in order to obtain a better result which can also affects to the final application results.

Synthesis process optimization is understood as the study of the catalyst dose, nitrogen flow, vacuum application and additive addition necessary to obtain a correct product to be used with a correct application result.

The most important variable to be studied, is the catalyst dose. The amount of catalyst used, as happens in most of the polymerization reactions [1] affects to the length of the polymer or oligomer formed. The length or molecular weight of the synthetized polymer or oligomer also affects to the final application performance. In some tanning applications is needed a low molecular weight to assist the penetration to the pelt [2], while in other applications like water treatment, a molecular weight polymer as bigger as possible is required to improve the performance [3]. For this reason is necessary to study and to know what kind of synthesis process conditions allow to get different product characteristics. This knowledge is important to optimize each product for each application.

The rest of the mentioned variables are less important, but are also necessary to be known; because affects to the reaction time and/or the final product appearance.

The nitrogen flow applied to the reaction system is necessary to avoid the entrance of air and moisture which can react with the isocyanate functional groups [4], and to remove from the system the carbon dioxide generated. The nitrogen flow has to be enough to maintain an inert system and to remove constantly the CO_2 formed. This variable affects to the reaction time and in the final product appearance because if CO_2 is not removed, the reaction equilibrium is slightly displaced to reagents [5] and the kinetic slows down, and if air and moisture enter in the reaction system, different reactions can be occurred like urea formation or oxidizing reactions that can affects to the final yield and the product color [6].

Initially, the color of the product is not the most important factor, however, for commercial purposes, appearance is always a valuable characteristic. Moreover, the side reactions that can affects to the product appearance, also affects to the yield and consequently to its final activity.

The necessity of applying vacuum to the reaction system is supported by two reasons. The first one is to remove the CO_2 formed during the reaction process by applying vacuum periodically. The second reason is to remove from the system the un-reacted monomer and the catalyst. This step has been done once the polymer or oligomer has already synthesized and the reaction has been finished. It is important to obtain a product as least toxic as possible and to improve the final product activity because un-reacted monomer can reduce the carbodiimide group content.

The product appearance improvement is a secondary variable, but it is important for commercial purposes. In order to improve this variable exists additives that acts as an anti-oxidizing agents which allows to obtain clearly products through the free radical stabilization which can interact with our reaction system [7].

Regarding to one of the main objectives of the present doctoral thesis which is the synthesis of products to be used as polymer stabilizing agents, TMXDI, due to its high steric hindrance which finally provides an extra stability, will be used as precursor monomer for this purpose [8]. The use of a diisocyanate monomer is also required due to its final isocyanate functionality which make it able to be functionalized. By using monoisocyanate monomers the synthesis is concerned in get the carbodiimide dimer, no functionality or molecular weight modulation can be carried out.

Following the conclusions extracted from the reaction conditions optimization study, CAT 1 has been used as catalyst to prepare the samples, at 180ºC in order to get the conversion of TMXDI to its corresponding carbodiimide oligomer.

5.1 SYNTHESIS PROCESS OPTIMIZATION

To optimize the synthesis process to obtain carbodiimide oligomers as commented above, different samples has been prepared modifying different process steps, additive addition and catalyst dose.

As for other studies done, the synthesis of the carbodiimide oligomers is finished once the isocyanate content is close to 5%. This 5% of isocyanate content means that the reaction can continue, but this reactivity is left for further functionalization. TMXDI monomer has an isocyanate content of 34.4%. Reacting it until 5% means 85% conversion. An increase of this conversion ratio reduces the oligomer functionality capacity.

5 samples has been initially prepared to optimize the synthesis process, maintaining the catalyst dose constant. The catalyst dose used has been optimized and corresponds to 0.15% by weight regarding to the isocyanate monomer weight used. For all samples preparations 500g of TMXDI monomer has been used. Maintaining invariable the catalyst dose and the monomer amount, the observed differences between each sample prepared like reaction time and final product appearance will be caused for the rest of variables studied.

The final appearance of the products obtained are measured by using the Gardner color scale. This standard method is used for transparent liquids, but in order to get an idea of the color sample improvement, this useful method has been used.

Different trials has been done to adequate the vacuum step necessity, the nitrogen flow used and the BHT additive addition in order to study the differences between each sample prepared which enable to optimize the synthesis process. Table 5.1 shows the different samples prepared.

Table 5.1 R1 – R5 samples prepared to synthesis process optimization.

Sample	% CAT 1	N_2 (l/min)	BHT	Final NCO (%)	Vacuum step
R1	0.15	0	No	5.2	each 2.5 h
R2	0.15	0.5 - 1	Yes	4.9	each 2.5 h
R3	0.15	0.5 - 1	No	5.1	Final
R4	0.15	0.5 - 1	Yes	5.2	final
R5	0.15	2.5 - 3	Yes	5.0	final

BHT is added as 0.02% by weight regarding to the monomer weight, and vacuum is applied for 5 minutes each 2.5 hours of reaction, and 30 minutes if it is applied at the end of the reaction.

The reaction times obtained to reach the desired isocyanate content and the final appearance of the product are detailed below in Table 5.2 comparing the samples prepared.

Table 5.2 R1 and R2 final sample values.

Sample	**Reaction time (h)**	**Final NCO (%)**	**Gardner color**
R1	23.0	5.2	18
R2	21.8	4.9	18

Observing the results from R1 and R2 samples, the nitrogen flow and the additive addition have been modified. The results obtained for each sample (Table 5.2) shows similar final NCO content (which indicates similar conversion ratio) by using similar reaction times.

In R1 sample, the nitrogen-sparging step needed to remove the CO_2 generated, has been substituted by the vacuum step every 2.5 hours of reaction. However, the reaction time needed for a similar conversion is slightly higher than for R2. This is due to the fact that nitrogen-sparging step can better remove the CO_2 that is forming during the reaction. However, there is not a strong difference when vacuum is applied every 2.5 hours with or without using the sparging nitrogen step.

Regarding to the final product color, if the nitrogen-sparging step is not performed, the final product shows dark color reaching an 18 value in the Gardner scale. This effect is attributed to the presence of oxygen that can induce some oxidizing side reactions which finally darks the product. These side reactions are also increased if vacuum is applied. R2 has been prepared by sparging nitrogen and by using the antioxidizing agent, however its final color is not better than for R1 sample due to the vacuum steps.

The results for R1 and R3 are compared in Table 5.3.

Table 5.3 R1 and R3 final sample values.

Sample	**Reaction time (h)**	**Final NCO (%)**	**Gardner color**
R1	23.0	5.2	18
R3	26.3	5.1	16

Comparing samples R1 and R3, where the only process difference is the vacuum step and the nitrogen sparging, two main differences can be observed.

The first one is the increasing reaction time to finally reach similar isocyanate content, being necessary more than 3 hours for R3 than for R1; and the second difference is the improved color appearance for R3, reducing it into two units of the Gardner scale value.

An explanation for both differences is the vacuum step. Applying vacuum at the end of the synthesis process, remove the un-reacted isocyanate monomer once the oligomer is formed. If vacuum is applied each 2.5 hours to remove CO_2 from the system, un-reacted monomer is also removed periodically. This reduction in the monomer amount allows the R1 system to reach similar conversion in less time. Moreover, applying vacuum at the end of the process improve the final color product due to the inert system is not interrupted during all the process. Once vacuum is applied the inert atmosphere present in the system is broken and side reactions are easily carried out.

Observing these three initial prepared samples, the nitrogen sparging and the vacuum step applied at the end of the process are required to improve the synthesis process.

In order to check the effect of the antioxidizing agent, R3 and R4 synthesis are compared in Table 5.4.

Table 5.4 R3 and R4 final sample values.

Sample	Reaction time (h)	Final NCO (%)	Gardner color
R3	26.3	5.1	16
R4	26.1	5.2	14-15

R4 has been prepared with the above process improvements commented, including the BHT addition. As is seen in Table 5.4, this additive addition has no effect in the reaction time, but has shown a final clear color. This situation demonstrate that the presence of side reactions have some effects about the color of the product, and that the addition of BHT can avoid it.

As observed in the different samples prepared, the nitrogen sparging during the synthesis process is a very important variable, both for remove CO_2 from the system and also to reduce side reactions. R5 was prepared by applying a higher nitrogen flow. Table 5.5 shows the results obtained for R4 and R5 samples.

Table 5.5 R4 and R5 final sample values.

Sample	Reaction time (h)	Final NCO (%)	Gardner color
R4	26.1	5.2	14-15
R5	26.5	5.0	14-15

Any improvement has been observed increasing the nitrogen flow to more than the double. The reaction time was the same than in R4, and also similar color products has been obtained. For this reason, the nitrogen flow used in R4 sample preparation (0.5 – 1 l/min) has been considered as adequate to carry out the isocyanate conversion to carbodiimide.

In order to check and analyse all the samples prepared, the CO_2 amount generated and the carbodiimide content has been analysed. CO_2 has been determined by measuring the reactor weight and the carbodiimide content by using both FTIR and titration method. Results obtained are expressed in weight percentage regarding to the total isocyanate monomer used in the CO_2 determination; and in weight percentage regarding to the final sample amount in the NCN determination. The results are detailed in Table 5.6.

Table 5.6 Amount of CO_2 generated and NCN content of samples R1 – R5.

Sample	% CO_2	% NCN FTIR	% NCN titration
R1	23.43	14.38	14.93
R2	24.21	14.12	15.02
R3	14.02	14.78	15.37
R4	13.81	14.84	15.54
R5	13.57	14.65	15.23

Knowing the conversion mechanism, one mole of carbon dioxide and one mole of carbodiimide are generated for each two reacted isocyanate moles. For the R1 to R5 samples preparations, 500g of TMXDI monomer has been used, which means the formation of 76.5g of CO_2 and 69.6g of NCN with 85% conversion. This values represents 15.3% of CO_2 regarding to the initial monomer amount, and 16.4% of carbodiimide regarding to the final sample amount. A more accurate calculation can be done once the molecular weight is known.

Comparing the different amounts of CO_2 generated, it can be observe that R1 and R2 show higher values than for the rest of samples. This is due to they has experimented an extra loss weight once the vacuum has been applied each 2.5 hours. During this vacuum step, un-reacted monomer was removed from the system, causing an increase in the reactor weight difference, which that cannot be expressed as CO_2 generated.

R3, R4 and R5 have generated similar CO_2 content that slightly differs from the theoretical value.

Regarding the NCN content obtained, all values are very similar being 15% the average value. Analysis by using FTIR calibration method always gives lower values than the titration method. This difference can be explained by a side reaction of the oxalic acid used in the titration method.

The NCN content obtained in R1 and R2 experiments are slightly lower to the other experiments because of the monomer loss during the vacuum step. However, less carbodiimide has been formed, achieving a more weight difference. However, the percentage obtained are not so far from the other ones.

As for the CO_2 values, the NCN contents are lower than the expected ones. Lower values can be caused due to side reactions occurred during the reaction synthesis.

These NCN content are very similar to the results obtained in previous studies (see Table 4.1) indicating that the process is reproducible.

Taking into consideration all the data obtained in the different tests, the optimized synthesis protocol can be considered as:

- Nitrogen is sparged during all the process at 0.5 – 1 l/min.
- BHT is used as an antioxidazing agent in a weight percentage of 0.02% regarding to the monomer.
- Vacuum is applied at the end of the reaction.

All these requirements, as well as a reaction temperature of 180ºC, are necessary to optimize the synthesis process to produce carbodiimide oligomers based on TMXDI isocyanate monomer, in 25-26 hours with a final color of 14-15 and using CAT 1 as catalyst.

5.2 MOLECULAR WEIGHT STUDY

Once the synthesis process to obtain carbodiimide oligomers starting form highly hindered diisocyanate monomers is optimized, is necessary to carry out a molecular weight study in order to create different processes depending on the required characteristics of the final product, depending on the final application.

It is well known that catalyst is one of the most important factor to modulate the molecular weight in monomer polymerizations. Furthermore, the catalyst dose used is also of great importance [9]. At higher catalyst dose, more monomers are initiated to start the polymerization reaction, causing shorter chains and a lower molecular weight. Contrary, decreasing the amount of catalyst less monomers are initiated, and the chains obtained are longer causing an increase in the polymer molecular weight.

Additionally to the formation of the desired molecular weight depending on the application suggested, is necessary to get an equilibrium between the final yield of the product, the reaction time needed to obtain it and the final cost of all the process.

For all this purposes, a molecular weight study has been carried out by preparing three different samples (R6, R7 and R8) by using three different amounts of catalyst. CAT 1 was used as catalyst and TMXDI as precursor isocyanate monomer.

Table 5.7 shows the final isocyanate content of the samples prepared and the different catalyst dose used. The reactions have been performing following the optimized synthesis process, which use a constant nitrogen flow of 0.5 – 1 l/min with 0.02% of BHT, and applying 30 minutes of vacuum at the end of the reaction and a final conversion of 85%.

Table 5.7 R6 – R8 samples prepared for molecular weight study.

Sample	**% CAT 1**	**Reaction time (h)**	**Final NCO (%)**	**Gardner color**
R6	0.15	26.4	4.8	14-15
R7	0.30	22.6	5.1	14-15
R8	0.40	21.5	5.0	14-15

The catalyst dose for the expermiments R6, R7 and R8 have been 0.15%, 0.3% and 0.4%, respectively. The reaction was stopped once 5% of isocyanate content was reached.

Table 5.7 shows that an increase in the catalyst dose produces a decrease in the reaction time. Similar color for the samples have also been observed (between 14-15 in the Gardner color scale). In order to know the molecular weight, the samples have been characterized by using MALDI TOF mass spectrometry technique [10]. The obtained spectra for R6, R7 and R8 samples are shown in Figure 5.1.

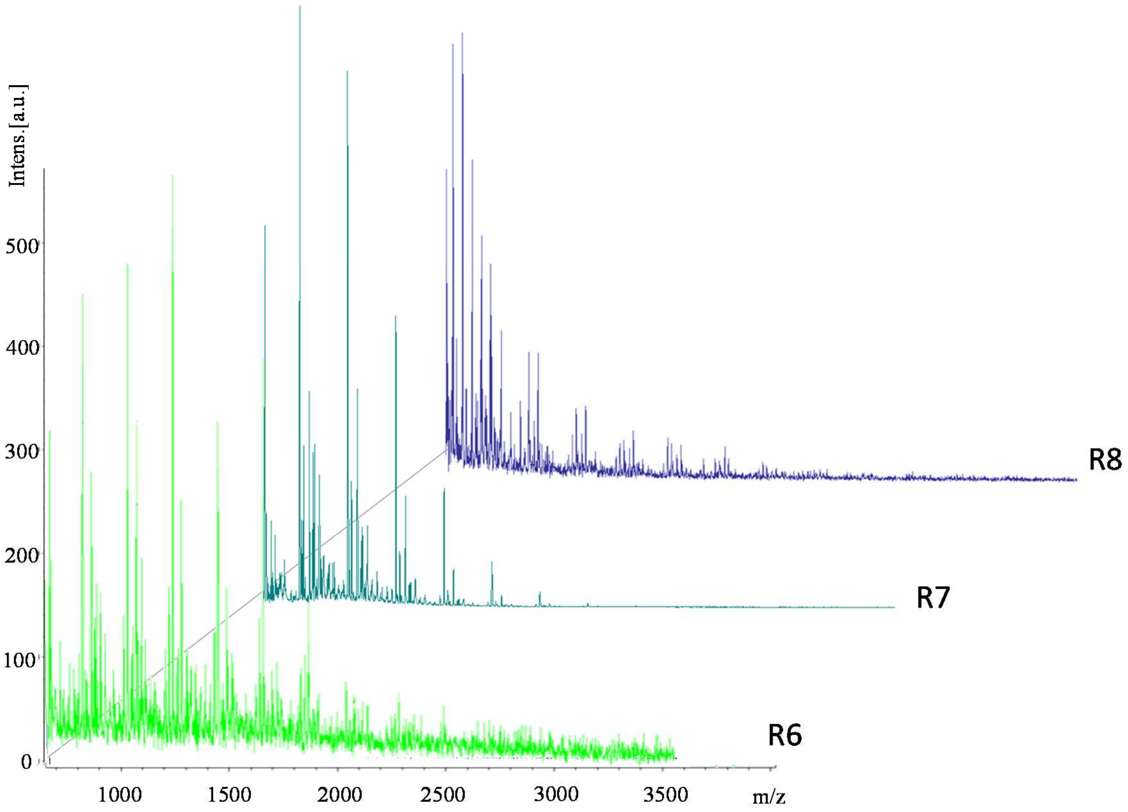


Figure 5.1 MALDI TOF mass spectra of samples R6, R7 and R8.

Observing the MALDI TOF mass spectra performed, a Gaussian distribution is clearly identified in each spectrum. This distribution is caused for the different molecular weight oligomers chains formed in the polymerization reaction. In all polymerization reactions exists a molecular weight distribution where different length chains are formed [9]. Each oligomer formed is ionized and depending its concentration in the final sample, different intensities are registered.

The maximum of the Gaussian distribution indicates, approximately, the molecular weight average of the oligomer synthetized. It is observed that once more catalyst is used to prepare the sample, the Gaussian distribution is displaced to lower molecular weight masses.

Using MALDI TOF mass spectrometry technique is possible to know the ratio between the oligomers with different number of monomer units present in the studied sample. In order to know this ratio and the final molecular weight average is necessary to identify the corresponding oligomer chain peaks in each spectra and relate its intensities.

In Table 5.8 are detailed the exact masses [11] calculated for each linear oligomer chain with 3 to 10 monomeric units presents. Furthermore, Table 5.8 also shows the different linear oligomer chains ionized masses with one sodium atom because this technique ionize the sample to be able to transport it until the detector. For this reason is usual to find the ionized masses in the spectrums. In this case, due to the use of NaTFA as dopant, the ionized masses contains the sodium atom.

Table 5.8 Linear oligomer masses and sodium ionized of carbodiimide oligomers based on TMXDI.

Monomer units	Linear masses (Da)	Ionized linear masses +Na (Da)
3	244.306	267.296
4	444.602	467.592
5	644.899	667.888
6	845.195	868.185
7	1045.492	1068.481
8	1245.788	1268.778
9	1446.084	1469.074
10	1646.381	1669.370

In order to study the molecular weight of the different samples, the different ionized masses of the linear oligomers have been identified in each sample spectrum. Figure 5.2, Figure 5.3 and Figure 5.4 show the MALDI TOF mass spectra with the linear masses identified with the “L” symbol of each oligomer depending on the number of monomer units expressed with the “number” symbol. For example L4 indicates that the linear oligomer contains four monomer units.

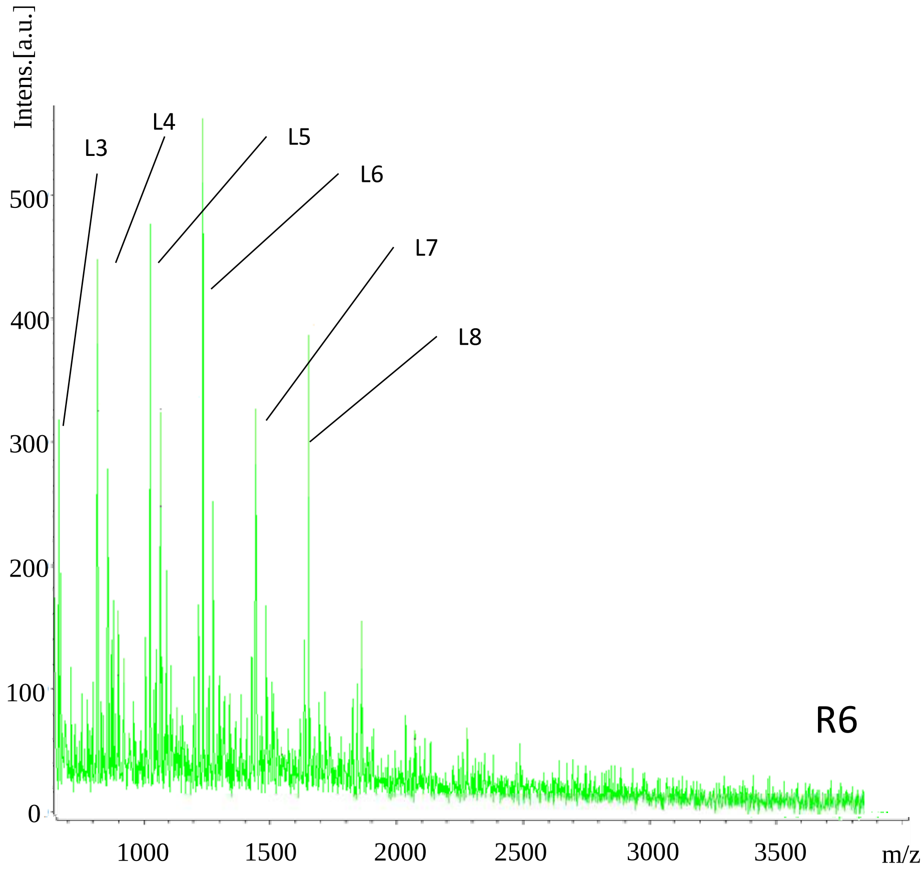


Figure 5.2 MALDI TOF mass spectrum of sample R6 with the ionized linear oligomer masses identified.

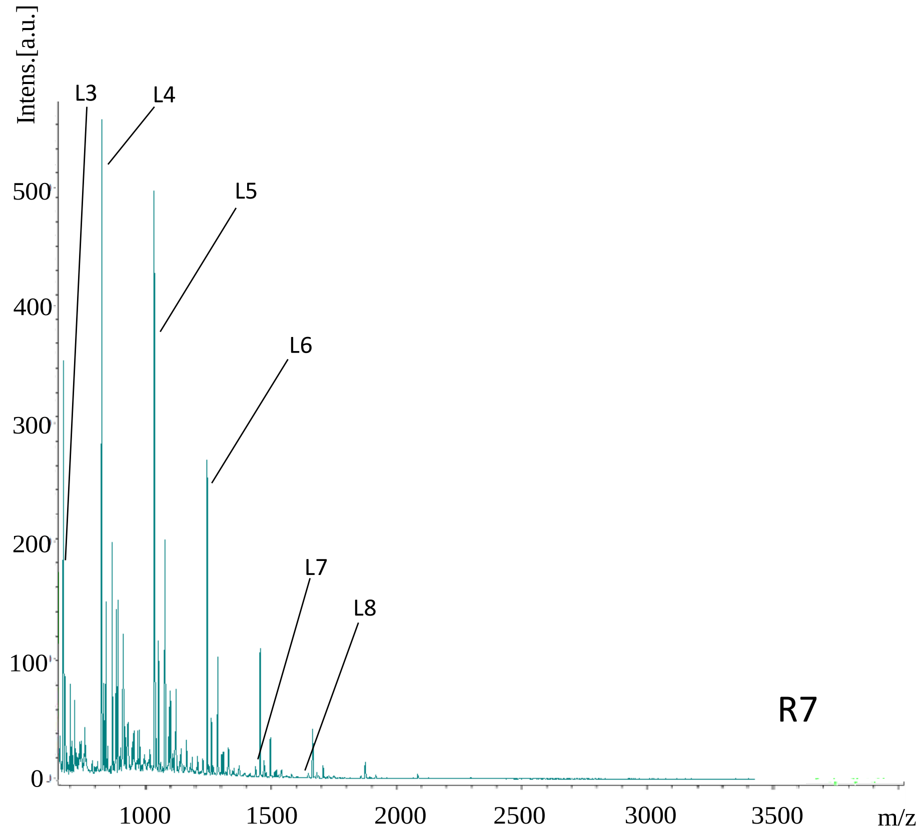


Figure 5.3 MALDI TOF mass spectrum of sample R7 with the ionized linear oligomer masses identified.

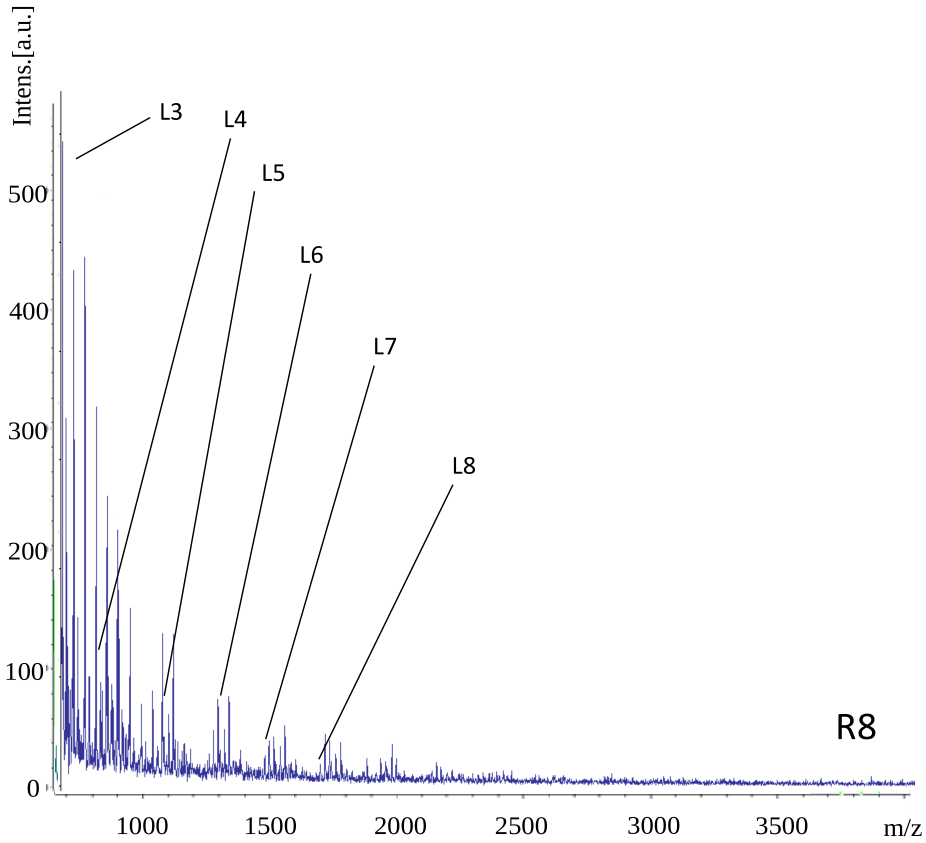


Figure 5.4 MALDI TOF mass spectrum of sample R8 with the ionized linear oligomer masses identified.

In each peak group, which corresponds to each oligomer present in the sample can be identified the sodium ionized linear oligomer mass. There is a difference in the mass value of around 200 mass units between all of them, which correspond to a TMXDI monomer unit (molecular weight 244 Da) that has lost a carbon dioxide molecule (molecular weight 44 Da) confirming the correct identification [12]. Comparing each peak intensity is possible to relate all the oligomers identified in order to calculate the experimental molecular weight average for each sample. In Table 5.9 are detailed all the identified masses, its peak intensities, its ratio and the calculated experimental molecular weight.

Table 5.9 Sodium Ionized masses and its ratio of linear oligomer carbodiimides based on TMXDI.

SAMPLE R6				
Peak	**Identified mass (Da)**	**Intensity**	**Ratio (%)**	**Molecular Weight (Da)**
L3	667.524	315	13.02	1146.645
L4	868.095	417	17.23	
L5	1068.289	463	19.13	
L6	1268.364	545	22.52	
L7	1469.403	310	12.81	
L8	1669.458	370	15.29	
SAMPLE R7				
Peak	**Identified mass (Da)**	**Intensity**	**Ratio (%)**	**Molecular Weight (Da)**
L3	668.239	180	11.50	979.587
L4	869.142	560	35.78	
L5	1068.769	490	31.31	
L6	1269.028	280	17.89	
L7	1468.175	40	2.56	
L8	1669.567	15	0.96	
SAMPLE R8				
Peak	**Identified mass (Da)**	**Intensity**	**Ratio (%)**	**Molecular Weight (Da)**
L3	668.253	595	55.35	849.192
L4	867.849	185	17.21	
L5	1068.675	110	10.23	
L6	1269.187	90	8.37	
L7	1468.952	50	4.65	
L8	1669.731	45	4.19	

Analyzing the results for each sample, it can be observe that the identified masses found in the MALDI TOF mass spectra are very similar to the theoretical masses shown in Table 5.8. It means that both the sample preparation for the analysis and the mass assignation has been done correctly. This correct identification allows to get also correct values of all the oligomers formed for each sample.

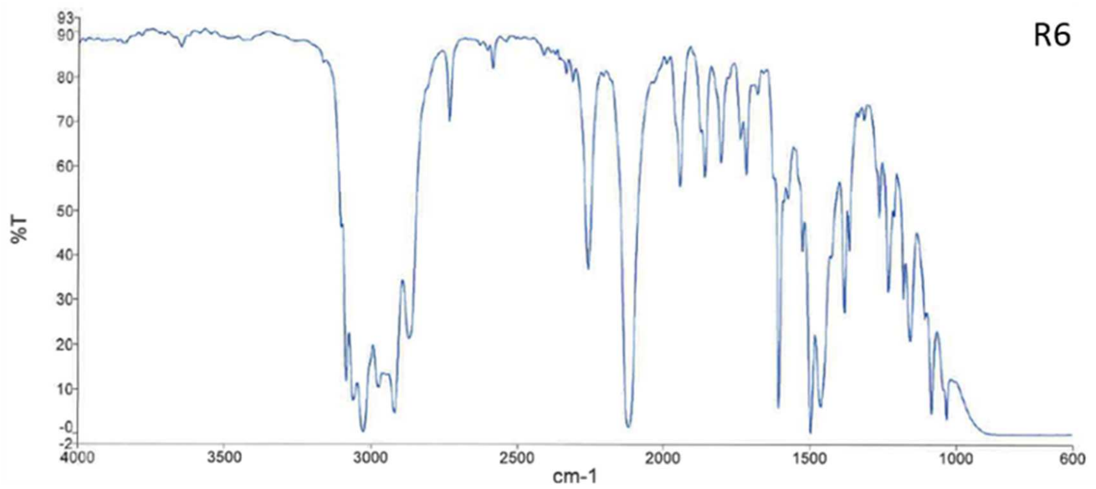
For sample R6 the most intense peak is the corresponding to the oligomer with 6 monomer units (L6 peak); for samples R7 and R8 the most intense peak found are the corresponding to the oligomers which contains 4 and 3 monomer units respectively (L4 and L3, respectively).

From these results, it can be conclude that an increase of the amount of catalyst used produces a decrease in the average molecular weight of the polymers. In Table 5.10 are summarized the molecular weight average for each sample prepared. The molecular weight average has been calculated by rating the peak intensities of the linear oligomers found in the MALDI TOF mass spectra. In Table 5.9 and Figure 5.2, Figure 5.3 and Figure 5.4 only has been identified oligomers with 8 monomer units as maximum. By using the synthesis conditions optimized, no higher oligomers have been formed.

Table 5.10 Molecular weight average for samples R6, R7 and R8

SAMPLE	% CAT 1	Molecular weight Average (Da)
R6	0.15	1146.645
R7	0.30	979.587
R8	0.40	849.192

As in other studies performed, the FTIR spectra of R6, R7 and R8 sample has also been registered (see Figure 5.5). Its analysis helps to confirm that the conversion has been carried out as expected.



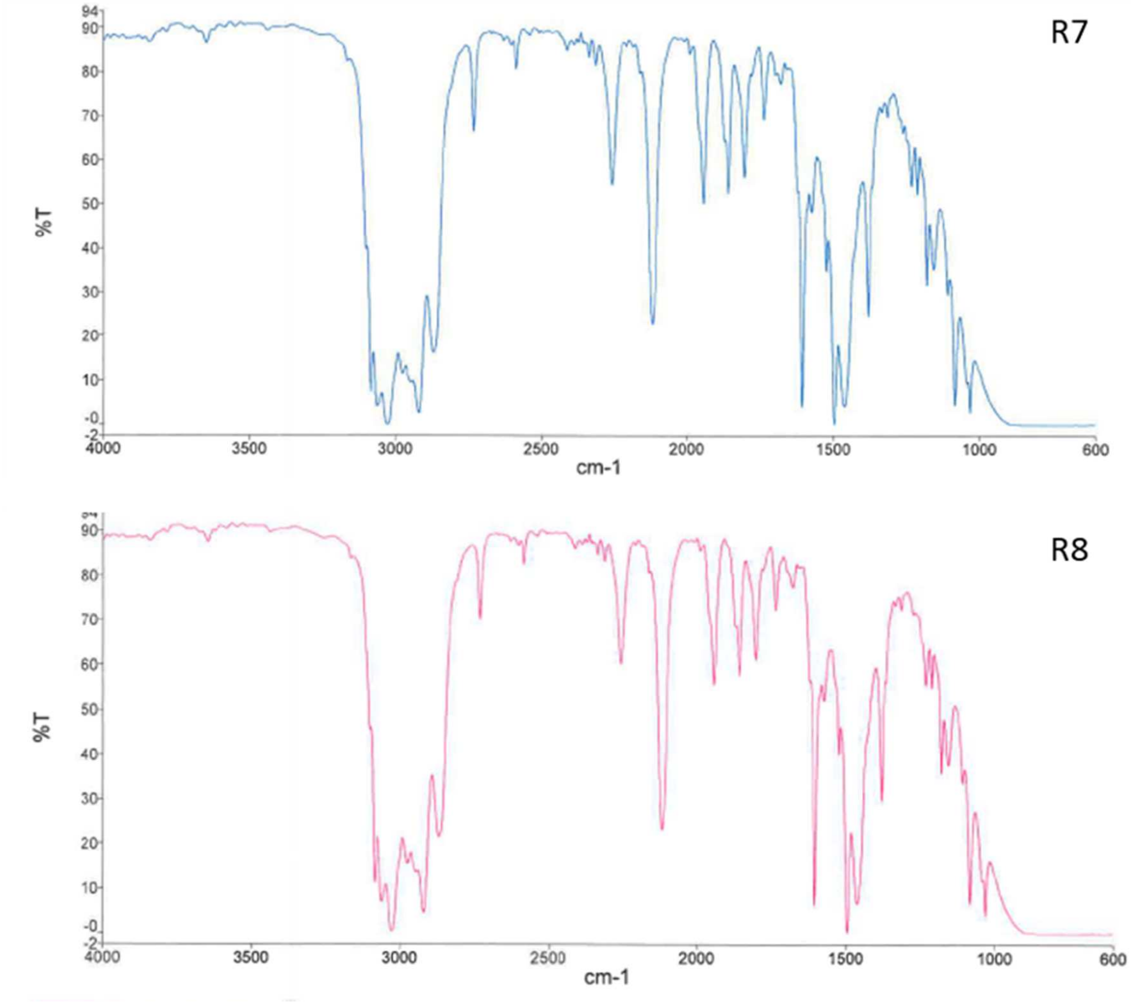


Figure 5.5 FTIR spectra of samples R6, R7 and R8.

In FTIR spectra is clearly observed at 2130 cm^{-1} the absorption band corresponding to the carbodiimide functional group, which demonstrate that the synthesis has been performed as expected. Moreover, due to the use of a diisocyanate monomer, there are still presence of isocyanate group, which is identified at 2240 cm^{-1} and corresponds to a content close to 5%.

In the spectra, can also be identified, as usual, the aromatic C-H stretching bands at 2800-3000 cm^{-1} and the toluene characteristic bands at 1700-2000 cm^{-1}.

The molecular weight differences also means different carbodiimide content. A higher molecular weight oligomer would contain more monomer units reacted, which also means a higher carbodiimide content and higher amounts of CO_2 generated during the synthesis.

Regarding to section 4.1.3 the CO_2 and NCN theoretical content were determined as if only one linear chain was formed. Once the molecular weight is determined, a more accurate calculation can be done by calculating the CO_2 and the NCN content generated for each oligomer chain present in the sample. In Table 5.11 are detailed the percentages for each oligomer chain. The CO_2 amount is expressed as weight percentage regarding to the initial monomer charge, and the NCN content is expressed as weight percentage of the final sample obtained.

Table 5.11 CO_2 and NCN content calculated for each oligomer chain identified in samples R6, R7 and R8.

SAMPLE R6					
Peak	**Ratio (%)**	**% CO_2**	**% NCN**	**% CO_2 average**	**% NCN average**
L3	13.02	12.02	12.42	14.43	15.35
L4	17.23	13.52	14.22		
L5	19.13	14.43	15.33		
L6	22.52	15.03	16.08		
L7	12.81	15.46	16.62		
L8	15.29	15.78	17.03		
SAMPLE R7					
Peak	**Ratio (%)**	**% CO_2**	**% NCN**	**% CO_2 average**	**% NCN average**
L3	11.50	12.02	12.42	13.97	14.78
L4	35.78	13.52	14.22		
L5	31.31	14.43	15.33		
L6	17.89	15.03	16.08		
L7	2.56	15.46	16.62		
L8	0.96	15.78	17.03		
SAMPLE R8					
Peak	**Ratio (%)**	**% CO_2**	**% NCN**	**% CO_2 average**	**% NCN average**
L3	55.35	12.02	12.42	13.10	13.72
L4	17.21	13.52	14.22		
L5	10.23	14.43	15.33		
L6	8.37	15.03	16.08		
L7	4.65	15.46	16.62		
L8	4.19	15.78	17.03		

The values detailed in Table 5.11 enable to calculate a more accurate theoretical amount for each variable, in order to compare it against the experimental values obtained.

In Table 5.12 are compared the theoretical values of NCN content versus the experimental ones determined by FTIR and titration methods for R6, R7 and R8 samples.

Table 5.12 Theoretical and experimental NCN content for R6, R7 and R8 samples.

SAMPLE	% CAT 1	MW (Da)	Theoretical NCN %	% NCN FTIR	% NCN titration
R6	0.15	1146.645	15.35	14.73	15.13
R7	0.30	979.587	14.78	13.87	14.43
R8	0.40	849.192	13.72	13.29	13.55

A good correlation is observed between the theoretical and the experimental results. An increase of the amount of catalyst also produces a decrease in the percentage of NCN in all cases. However, the experimental values are always slightly lower than the theoretical. This fact could means that other kind of structures are present in the sample [13] that can distort the theoretical values. The obtained theoretical values have been calculated as if only linear oligomers are formed. The presence of side reactions that can creates branched structures can also modify the CO_2 and NCN contents.

Both theoretical values and the analyzed ones, are more similar than the compared values in Table 4.1. A correct characterization needs to be performed in order to improve the analysis.

The NCN content analysis, also shows slightly higher results for the titration method analysis than for the obtained by FTIR. The differences between both results is lower once more amount of catalyst is used.

The amount of CO_2 generated is another important factor to analyze in order to know how the synthesis has been performed. Table 5.13 shows the experimental and theoretical amount of CO_2 produced during the reaction for R6, R7 and R8 samples. A relationship between the amount of CO_2, both theoretical and experimental (determined by reactor weight) and the amount of catalyst is observed. The CO_2 amount decrease when the amount of catalyst increases. This fact indicates that for the carbodiimide group, the CO_2 generation is directly related with the number of monomer units reacted [14].

Table 5.13 Theoretical and experimental CO_2 content for R6, R7 and R8 samples.

SAMPLE	% CAT 1	MW (Da)	Theoretical CO_2 %	% CO_2
R6	0.15	1146.645	14.43	13.86
R7	0.30	979.587	13.97	13.12
R8	0.40	849.192	13.10	12.64

Furthermore, the amount of CO_2 generated is also related with the conversion of NCN groups. The use of lower amount of catalyst produce higher amount of CO_2 that means that more isocyanate units has been converted to its corresponding carbodiimide, and for this reason, higher molecular weight is obtained.

The results also indicates that the CO_2 amount determination method by weight difference is an accurate process for this kind of determination. However, experimental values are, as the carbodiimide content, always lower than the theoretical ones. The little differences appreciated confirm that some side reaction during the process is produced, that needs to be studied.

The concordance between all the experimental results validates the optimization of the synthesis process.

All oligomeric carbodiimide samples has been prepared with 85% isocyanate conversion in order to maintain enough isocyanate functionality. An industrial scale process which needs more than 20-22 hours is considered of low productivity, even using small reactors. For this reason, the idea to prepare an increased molecular weight sample by using less amount of catalyst is discarded because more than 30-35 hours of production process can be expected to reach similar conversion ratios.

Another possible option to increase the oligomer molecular weight is to enlarge the isocyanate conversion until higher ratios than the 85% used. This idea requires to stop the reaction once the isocyanate content was close to 2% for example. This way is also unviable due to the long time required. Once less amount of isocyanate are present in the reaction system, the reaction rate decreases, increasing exponentially the reaction time. This situation can be observed in the figures of the isocyanate content evolution during the reaction (see Figure 4.3) where the reaction rate decreases at higher conversion.

All this options causes a notable increase in the reaction time over the 30 hours and the second option would cause a significant functionality reduction of the oligomer that can also affects to its final polymer inclusion.

For these reasons no more samples for increasing the molecular weight has been prepared.

5.3 BRANCHED STRUCTURES STUDY

Regarding the differences obtained between both theoretical and experimental values for the CO_2 and NCN content; side reactions that produce branched structures could be the reason which explain it.

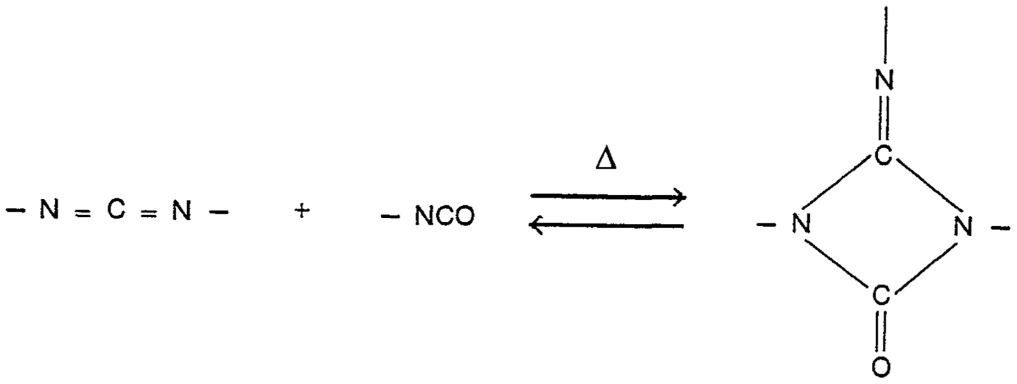
Until this section, all the studies and characterizations done has been focused in linear oligomers. Nevertheless, isocyanates can also dimerize or even trimerize producing branched structures.

There are a wide number of reactions where the isocyanate functional group can participate due to its high reactivity with many different functional groups [4, 15]. However, knowing that our reaction system is inertized, formed basically by the isocyanate monomer and the phospholene oxide catalyst and the carbon dioxide generated, the possible reactions present are limited to these three:

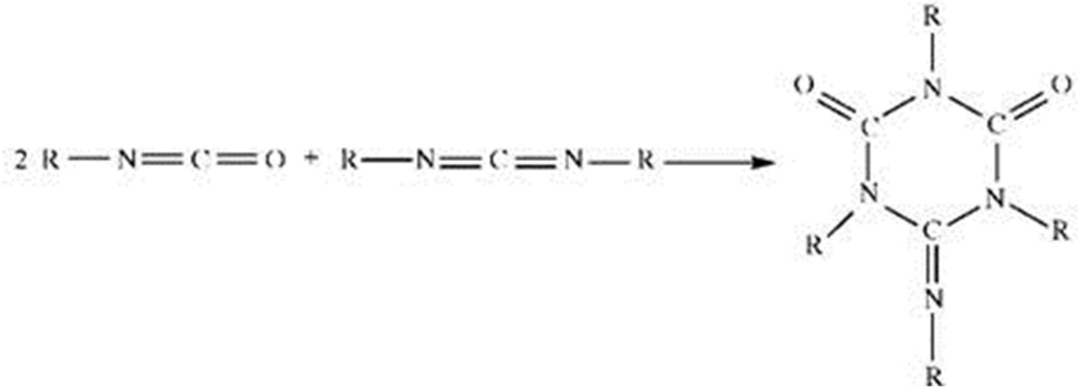
- Carbodiimide synthesis.
- Uretonimine synthesis.
- Carbodiiimide dimerization.

The carbodiimide structure synthesis, as has been checked in previously studies, is formed by the reaction of two isocyanate groups with its corresponding CO_2 generation.

Uretonimine structures are generated by the interaction of one isocyanate group and one carbodiimide group previously formed in the system; for this reason also CO_2 is generated during the carbodiimide group formation. This interaction forms a 4 ring cycloadduct, which can also react with more isocyanates or carbodiimide groups to finally form 6 membered cycloadducts rings which are more stables [16]. This kind of interaction is favored in high free isocyanate systems and for high temperatures. In Figure 5.6 are shown the reaction scheme of these structures formation [17].



Uretonimine trimer



Uretonimine tetramer

Figure 5.6 Reaction scheme of the uretonimine trimer and tetramer [17].

Carbodiimides can also dimerize in presence of some catalyst like tetrafluoroboric acid at room temperature, or even without catalyst by heating the system. This process is a thermal process and it is easy carried out once the carbodiimide is less hindered. This reaction requires the carbodiimide synthesis previously to afford this dimerization or trimerization adducts formation [16]. Carbon dioxide is also formed. In Figure 5.7 is shown the reaction scheme for this kind of structures.

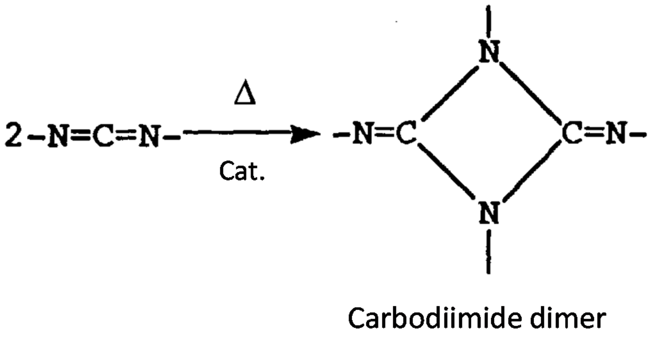


Figure 5.7 Reaction scheme of carbodiimide dimer [16].

In addition to these, there are other structures that can be formed through the reaction of isocyanates, like the Uretdione and isocyanurate synthesis.

Uretdione is the dimer structure formed by two isocyanate group interaction. This interaction is produced at mild temperatures without any catalyst. No CO_2 is generated. The interaction is reversible and can recover the initial isocyanate structure by heating [15, 16, 18]. Figure 5.8 shows the reaction scheme of this kind of structures.

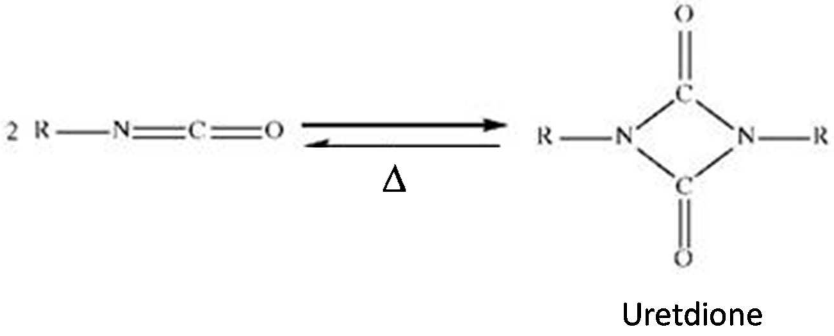


Figure 5.8 Reaction scheme of the uretdione formation [15].

Isocyanurate structure (Figure 5.9) is formed by three isocyanate groups. This restructuration, as for uretdione synthesis, do not generates CO_2, and contrary to the uretdione structure, this trimer structure is stable [19]. Its formation is catalyzed by tertiary amines and temperature [20].

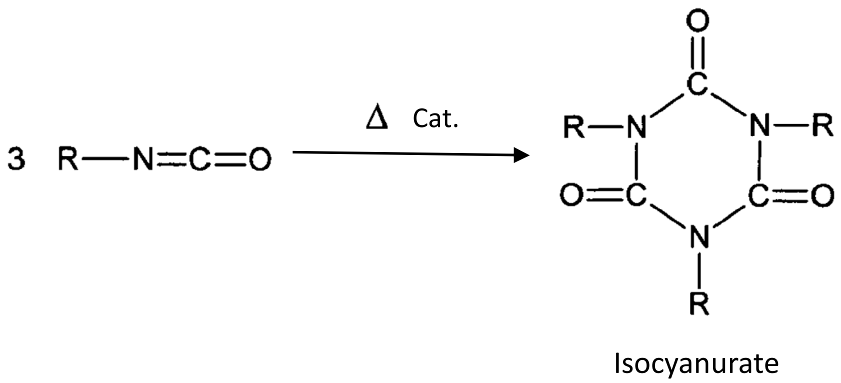


Figure 5.9 Reaction scheme of the isocyanurate formation [20].

Taking into account that isocyanurates and uretdiones structures are formed in other reaction conditions and by using different catalysts, only the formation of uretonimines and carbodiimide dimers are noted as possible side reactions during the synthesis of carbodiimide oligomer by using the optimized synthesis process. The high steric hindrance present in the carbodiimides formed by using TMXDI, the carbodiimide dimerization is a very unusual structure. For this reason the most possible substructure formation is the uretonimine. In Figure 5.10 is shown the uretonimine trimer structure based on TMXDI.

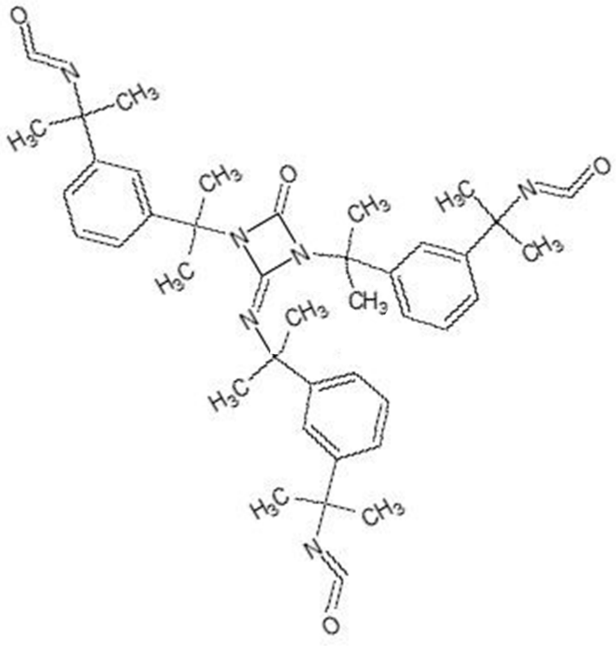


Figure 5.10 Uretonimine trimer structure based on TMXDI.

In order to understand the differences obtained in the CO_2 and NCN values, and to make a complete characterization of the samples prepared, an identification of this kind of structures has been carried out using the MALDI TOF mass spectrometry technique. Table 5.14 shows the theoretical masses for each oligomer chain with different number of monomer unit presents with one uretonimine group. The sodium ionized masses and the linear one are also detailed.

Table 5.14 Linear and uretonimine branched oligomer structure based on TMXDI masses.

Monomer units	**Linear structure**	**Uretonimine branched structure**	
	Mass (Da)	**Mass (Da)**	**Sodium Ionized mass (Da)**
3	244.306	688.909	711.898
4	444.602	889.205	912.195
5	644.899	1089.502	1112.492
6	845.195	1289.798	1312.788
7	1045.492	1490.094	1513.084
8	1245.788	1690.391	1713.381

Once the theoretical branched masses are known, and its possible presence is understood, the MALDI TOF mass spectra performed for R6, R7 and R8 are analyzed again in order to identify the presence of branched oligomers. In each sample has been identified the presence of this kind of product. In Figure 5.11, Figure 5.12 and Figure 5.13 are shown the MALDI TOF spectra with the linear “L” and the branched “B” peaks identified.

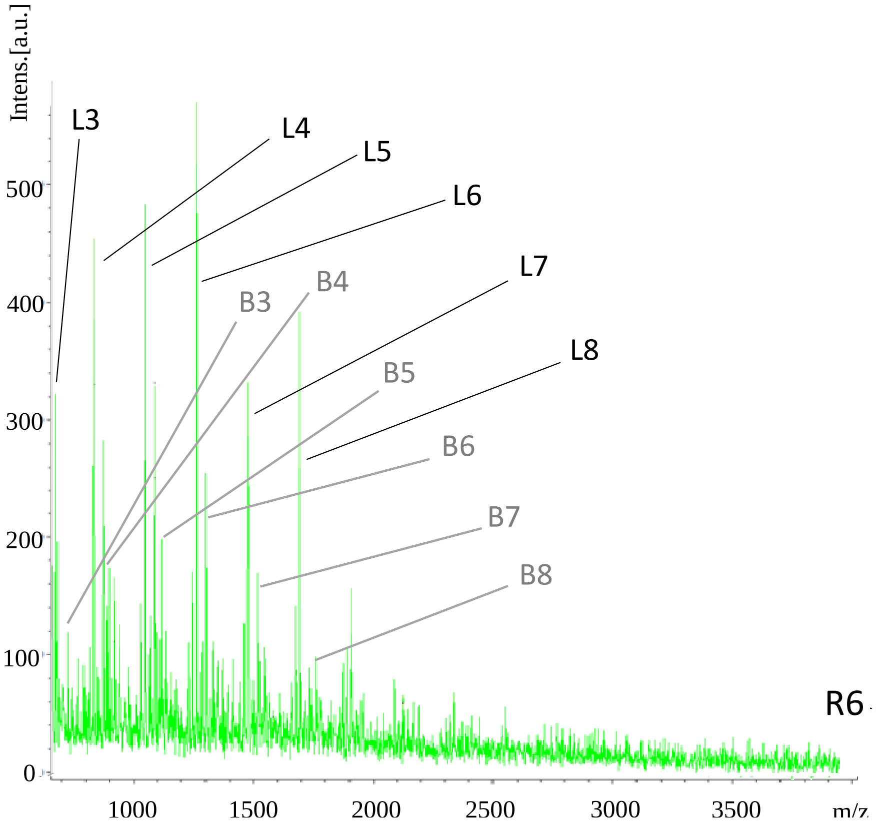


Figure 5.11 MALDI TOF mass spectrum of sample R6 with the ionized branched oligomer masses identified.

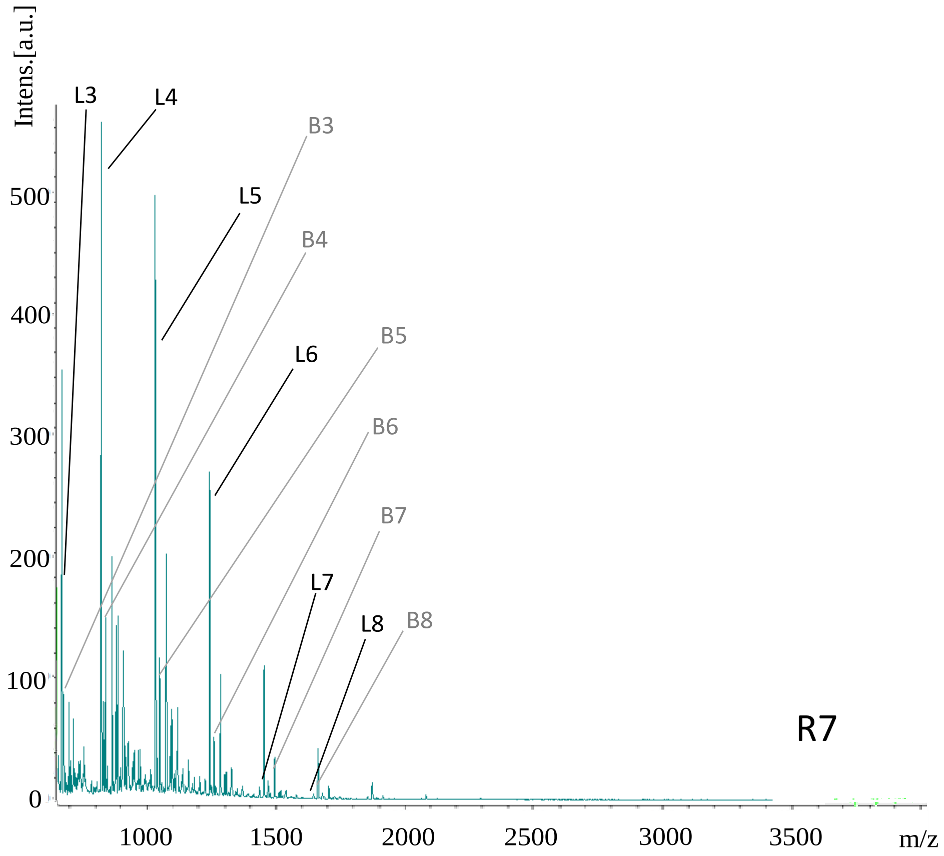


Figure 5.12 MALDI TOF mass spectrum of sample R7 with the ionized branched oligomer masses identified.

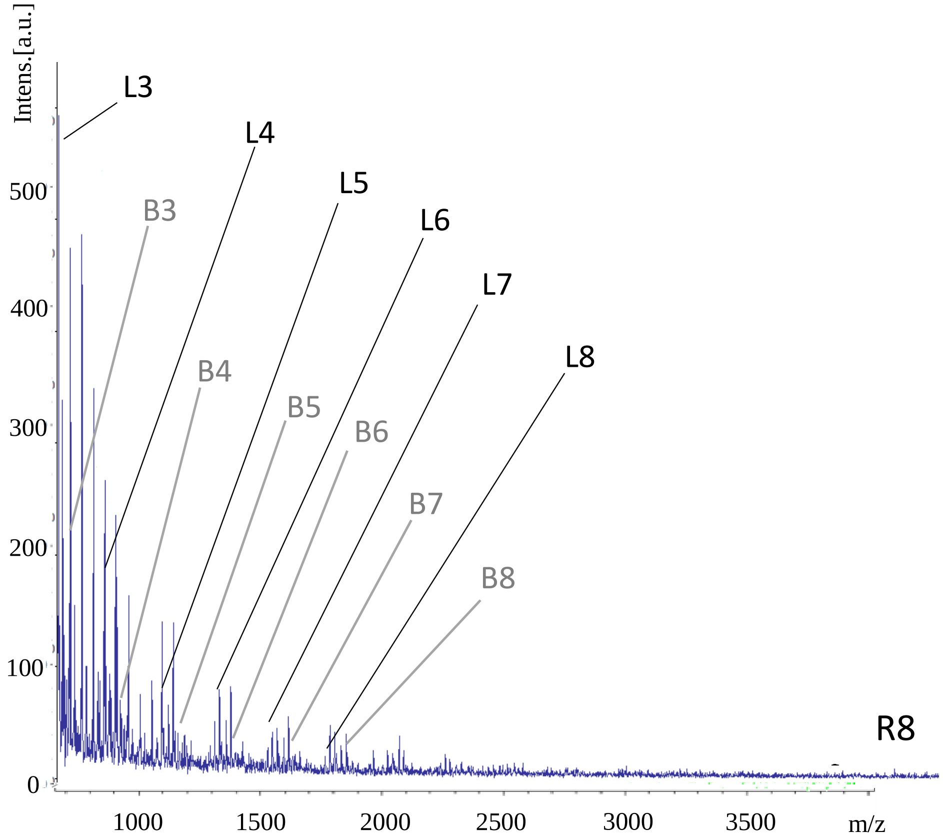


Figure 5.13 MALDI TOF mass spectrum of sample R8 with the ionized branched oligomer masses identified.

The spectra show, in addition to the linear masses commented, the identification of branched oligomer masses which corresponds to oligomers with the presence of one uretonimine group. The presence of uretonimine branched structures has been confirmed in all the prepared samples. In all cases branched structures has lower intensity than the linear ones which indicates that the rate for branched reaction is lower than the linear reaction

Exists the possibility of multibranched structures with the presence of more than one uretonimine. These masses has not been so clearly identified, for this reason we can conclude that if there is the presence of multibranched structures, they are present in a very low concentration which are negligible for this study. The carbodiimide dimer masses has also been checked and no identification was performed. This result confirms the low possibility of formation of this kind of highly hindered structures.

In order to study the ratio between linear and branched structures present in the prepared samples, the intensity ratio between the oligomer (linear and branched) which contains the same number of monomer units has been calculated for each sample. The values expressed as percentage are detailed in Table 5.15.

Table 5.15 Intensity ratios between linear and branched oligomers structures for samples R6, R7 and R8.

Monomer units	R6		R7		R8	
	% L	% B	% L	% B	% L	% B
3	9.46	3.45	9.18	4.08	44.91	9.06
4	12.52	4.50	28.57	7.65	13.96	5.28
5	13.90	5.41	25.00	5.36	8.30	1.51
6	16.37	7.21	14.29	2.04	6.79	0.75
7	9.31	4.35	2.04	0.77	3.77	1.51
8	11.11	2.40	0.77	0.26	3.40	0.75

The intensity percentages calculated between linear and branched oligomers, shows that by using the described synthesis process, branched structures are obtained independently of the catalyst amount used. However, analyzing the values, some differences has been observed between the prepared samples.

All samples prepared has higher amounts of linear oligomer than branched ones, around the 73% for R6, 78% for R7 and 81% for R8 are linear oligomers. The results also show that once more catalyst is used for sample preparation the branched structures concentration is reduced. The initiation step of the polymerization reaction is favored once more catalyst is added to the reaction system and the propagation reaction step is carried out faster, causing an increase in the linear structures concentrations and minimizing the side reactions occurred.

If a new theoretical calculation is performed for the CO_2 and NCN content, knowing the concentration of branched structures different values are obtained. In Table 5.16 and Table 5.17 are summarized the new theoretical values for each sample prepared, and the experimental values obtained.

Table 5.16 Theoretical NCN content calculated with branched structures and the experimental values obtained for samples R6, R7 and R8.

SAMPLE	% CAT 1	New Theoretical NCN %	% NCN FTIR	% NCN titration
R6	0.15	13.25	14.73	15.13
R7	0.30	12.89	13.87	14.43
R8	0.40	11.83	13.29	13.55

Table 5.17 Theoretical CO_2 content calculated with branched structures and the experimental values obtained for samples R6, R7 and R8.

SAMPLE	% CAT 1	New Theoretical CO_2 %	% CO_2
R6	0.15	13.44	14.73
R7	0.30	13.05	13.87
R8	0.40	12.20	13.29

Observing the new theoretical values calculated with the presence of branched uretonimines structures, both CO_2 and carbodiimide content values are lower than the experimental values obtained. This reduction content is due to the non CO_2 and carbodiimide contribution once uretonimine group is formed. The differences against the experimental values obtained show that less branched structures are present in the samples. The experimental values corresponds to an 82-85% of linear structures and only 15-18% of the branched uretonimine oligomers.

This difference can be explained by the difference in the ionization process during the MALDI TOF mass spectrometry analysis. Different structures, even branched can ionize different, by using the same sample preparation process. For this reason each sample needs to be previously optimized for its own analysis.

The side reactions are favored by an excess of isocyanate groups in the system and by high temperatures. Once the catalyst effect over this kind of processes has been studied a temperature study needs also to be done. To perform this study a new sample referenced as R9 has been prepared by using the same catalyst amount than for R6 preparation (0.15% of CAT 1) but increasing the reaction temperature from 180ºC to 220ºC.

In Figure 5.14 are represented the isocyanate evolution versus the reaction time during the preparation of R9 sample by using 0.15% of CAT 1 at 220ºC.

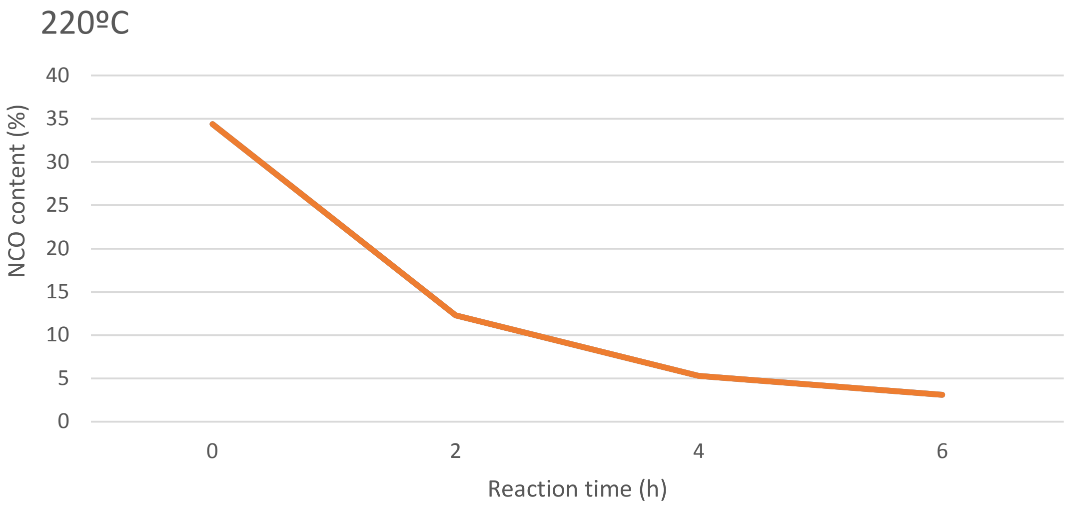
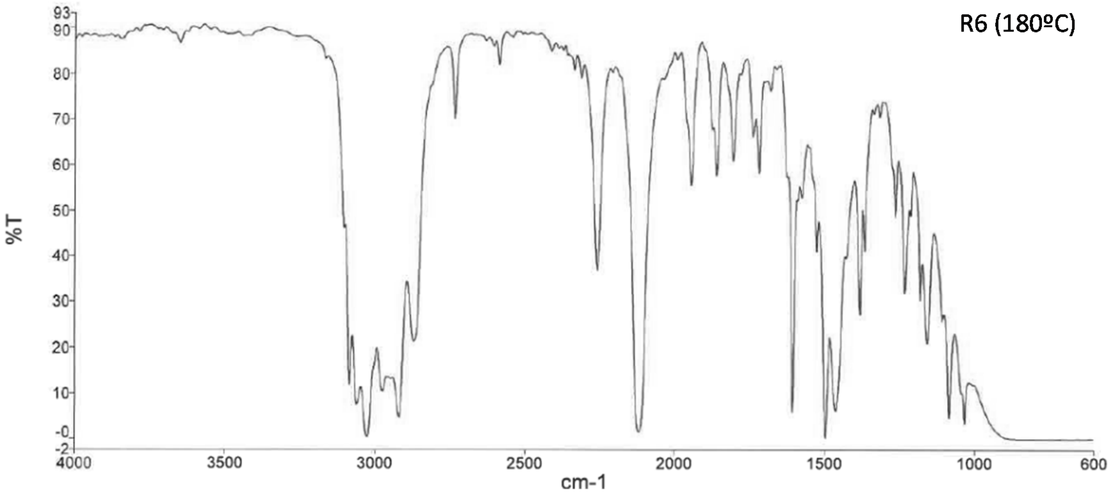


Figure 5.14 NCO content evolution versus reaction time for the TMXDI conversion at 220ºC by using 0.15% of CAT 1 as catalyst.

This Figure shows that the conversion of TMXDI to its carbodiimide oligomer at higher temperature, (220ºC) reaches a 0.5% of isocyanate content in only 6 hours, showing an important improvement with respect the reaction performed at 180ºC (more than 20 hours is needed at this temperature).

Consequently, an increase in the reaction temperature up to 220ºC can be beneficial due to the important reduction of the reaction time. However, the appearance of the obtained product is slightly darker due to the reaction conditions.

In order to complete this study and give an explanation to the reaction process, the samples have been analyzed by FTIR. Figure 5.15 shows the FTIR spectrum of samples R6 and R9 performed at 180ºC and 220ºC, respectively.



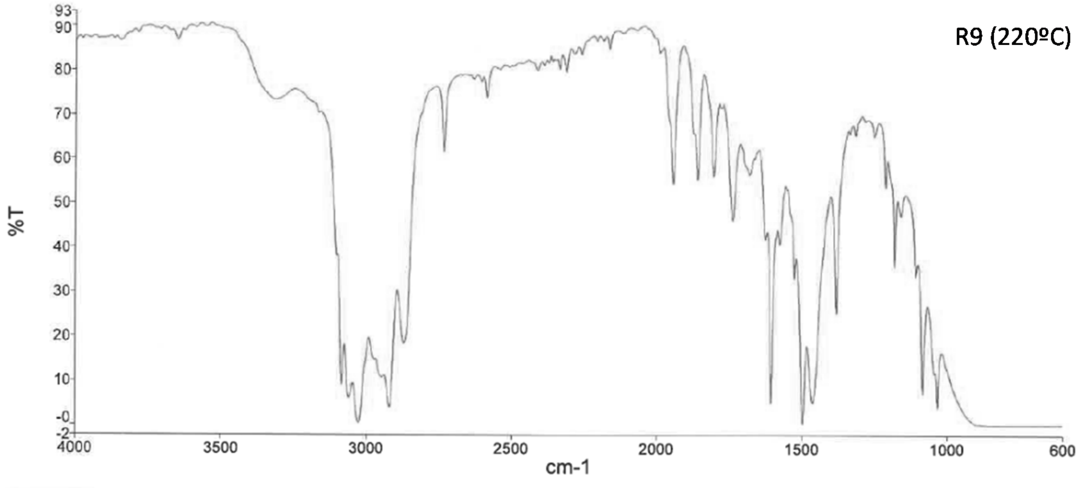


Figure 5.15 FTIR spectra of the samples R6 and R9.

For the sample obtained at higher temperatures (220ºC), the expected TMXDI carbodiimide absorption band which appears at 2140 cm^{-1} is not observed. R9 has achieved a final isocyanate content of 0.5% and for this reason, the absorption band of this functional group is not observed. The no presence of these functional groups indicates that tridimensional structures have been formed, generating a crosslinked TMXDI uretonimine product which can also explains de high reaction rate of the isocyanate and carbodiimide group. The most viscous appearance of the final product can also explains a crosslinking structure.

In the FTIR spectrum of the R9 sample are also observed the toluene characteristic absorption bands at 1700-2000 cm^{-1} and the intense absorption band at 1601 cm^{-1} corresponding to the C=N stretching. Another significant difference between samples carried out at 180ºC and at 220ºC, is the new absorption band at 3360 cm^{-1} which correspond to the stretching vibrations of the imino groups. These imino groups confirms the presence of the uretonimine structures [21]. This fact has been also observed for R6 sample. However, an increase in the reaction temperature produces an increase in the amount of these groups.

High temperatures and excess of isocyanate groups in the reaction favors the reaction conditions for uretonimine group generation. For the formation of the uretonimine it is necessary the previous formation of the carbodiimide with its corresponding release of CO_2. In Table 5.18 is shown de CO_2 amount generated (determinated by reactor weight) and the carbodiimide content (by FTIR calibration and by titration method) obtained for samples R6 and R9.

Table 5.18 CO_2 and carbodiimide content obtained for samples R6 and R9.

Sample	% CAT 1	Reaction temperature	% CO_2	% NCN FTIR	% NCN titration
R6	0.15	180ºC	13.86	14.73	15.13
R9	0.15	220ºC	11.74	0.01	19.40

From the results, we can observe that CO_2 is generated during the reaction synthesis of R9. It means that during the reaction, a carbodiimide intermediate group is formed, causing the CO_2 gas production. Once this carbodiimide intermediate has been formed, the high temperature applied in addition to the isocyanate group in excess finally induce the reaction between this carbodiimide intermediate and another isocyanate group, forming the uretonimine crosslinked structure.

Knowing that the final isocyanate content for R9 is close to 0%, the generation of 11.74% of CO_2 is a very similar value to the theoretical one calculated as if one mole of carbon dioxide is formed for each three isocyanate moles reacted. The theoretical value is 12.02% and it can be calculated by using the reaction scheme formation of uretonimine products (Figure 5.6). This similar value also verifies the formation of these kind of structures.

The formation of carbodiimide dimers is also discarded due to the low CO_2 amount generated. For the carbodiimide dimer formation, two groups of carbodiimide needs to be previously formed, with its corresponding CO_2 generation. This gas generation should be higher than the obtained, around 18% if carbodiimide dimer structures are formed. The CO_2 values obtained and the masses identification, indicates that uretonimine structures are produced by the side reaction in the isocyanate conversion to carbodiimide by using the optimized synthesis process [22]. Furthermore, the CO_2 formation also discards the commented side reaction of uretdione and isocyanurate formation.

Another important difference observed from the values obtained for sample R9 is the carbodiimide content. No carbodiimide group has been identified by FTIR. However, by analyzing this functional group by using the titration method, higher values are obtained reaching a value of 19.40%. This value shows that uretonimine group can also reacts with carboxylic groups. This kind of structures are reversible to the carbodiimide form once are heated, and it could be also explained by this carboxylic reaction. The carbodiimide content values determined by using this titration method, has higher values than from FTIR. The difference between the titration results and the FTIR ones are the branched structures present in the sample. It corroborates that there is the presence of uretonimine in all samples but in a lower concentration that the obtained by MALDI TOFF mass spectra analysis.

This structure study carried out corroborates the necessity to make a previously reaction condition study before start with the final samples preparations. Depending on the isocyanate selected and its characteristics, different reaction condition will be necessary to reach the desired carbodiimide. In this study more than 200ºC are required to prepare uretonimine, however, by using un-hindered aryl-isocyanates like MDI, only 105ºC is required [23].

5.4 CATALYST ISOMERIZATION

Is well known that cyclic phospholene oxides are the most used catalyst for the conversion of isocyanates to carbodiimides [24]. As has been commented in previous sections, the most active catalyst to carry out the conversion of TMXDI to its corresponding carbodiimide oligomer is CAT 1 (1-methyl-1-oxo phospholene oxide).

One of the objectives of the present doctoral thesis was to find new catalysts to carry out the isocyanate conversion to carbodiimide. It is an important industrial necessity due to the high cost of the most conventional used catalysts. High cost is caused due to the raw materials involved in their synthesis and for the few number of suppliers for this exclusive products.

In previous section (see chapter 4), different catalysts have been tested and we have observed that the most active to carry out the isocyanate conversion to carbodiimide is CAT 1. No catalytic activity was observed by using other products. Observing this result, with no catalyst change possibility, a study to optimize CAT 1 activity was performed. Due to the difficulty to find molecules capable to catalyze this kind of reaction, a study of the optimization of the catalytic activity of CAT 1 has been performed.

1-methyl-1-oxo phospholene oxide catalyst, named CAT 1 in this Doctoral Thesis, has shown the best conversion activity of isocyanates to carbodiimides by using

TMXDI as diisocyanate starting monomer. CAT 1 is purchased from Clariant with the CAS number 31563-86-7. This CAS number corresponds to an isomer mixture between 1-methyl-1-oxo-2-phospholene oxide and 1-methyl-1-oxo-3-phospholene oxide which also have de CAS numbers 872-45-7 and 930-38-1 respectively. Both isomers structure are shown in Figure 5.16, and has also been identified by using ^{1}H, ^{13}C and ^{31}P NMR technique (see section 4.2.1.2).

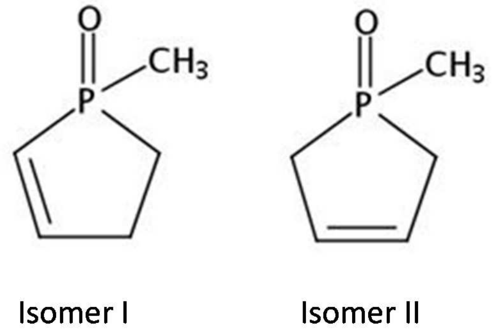


Figure 5.16 Isomers present in the commercial mixture of CAT 1.

A study was carried out to find which isomer is the most active to carry out the reaction.

To carry out this test, due to the difficulties found to obtain the pure isomers separately caused for the mixture of both 2 and 3-phopspholene oxides achieved during the cyclic phospholene oxides synthesis [25], an isomerization reaction has been carried out in order to modify the isomer concentration in the commercial CAT 1 mixture and check what changes are observed dring the reaction.

It is well known that the addition of alkali catalyzes this isomerization reaction [26, 27]. Consequently, an alkali addition to the catalyst has been performed in order to modify the isomer concentration.

Initially Sodium and potassium methylate has been used. However, these alkalis are provided as 32% methanolic solution. This methanol present in the solution reacts with the isocyanate group present from the monomer forming urethane groups. This functional group formation produces a carbodiimide yield decrease. In order to avoid this urethane formation, a more pure alkali is required. For this reason potassium tert-butoxide 98% has been used to carry out this study. Moreover, this product is even more alkali than the methylates commented and can carry out better the isomerization process.

The amount of alkali used is the half part in moles regarding to the catalyst moles used. Once Potassium tert-butoxide is added to the catalyst, the color solution changes suddenly from light yellow to orange, which indicates some interaction between the catalyst and the alkali. Figure 5.17 shows this color change observed at room temperature.

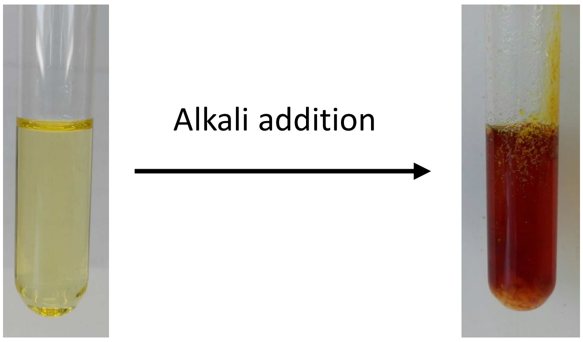


Figure 5.17 Catalyst color change once alkali is added at room temperature.

Before use the isomerized catalyst is necessary to know how this alkali addition has modified the initial CAT 1 mixture. ^{31}P NMR has been performed before and after the alkali addition in order to check the isomer concentrations. As in the previously catalyst study carried out, $CDCl_3$ is used as solvent and a H_3PO_4 capillary has been used to reference the obtained signals.

In this study is necessary to quantify the amounts of isomer I and isomer II present in the samples; for this reason the ^{31}P NMR has been performed by using a single scan. By using a single scan quantification, the integration of each signal is independent of the different nucleus relaxing times. Once the pulse is applied all nucleus are on its initial state; if more pulses were applied a signal intensity decrease will be produced in nucleus with slow relaxing time (magnetization not in equilibrium) causing wrong integration results [28, 29]. For low concentration samples multiple scans are required to accumulate signals. In this case a quantification is possible by using single scan technique.

In Figure 5.18 are shown the ^{31}P NMR spectra of CAT 1, before and after the alkali addition (spectrum a and b, respectively).

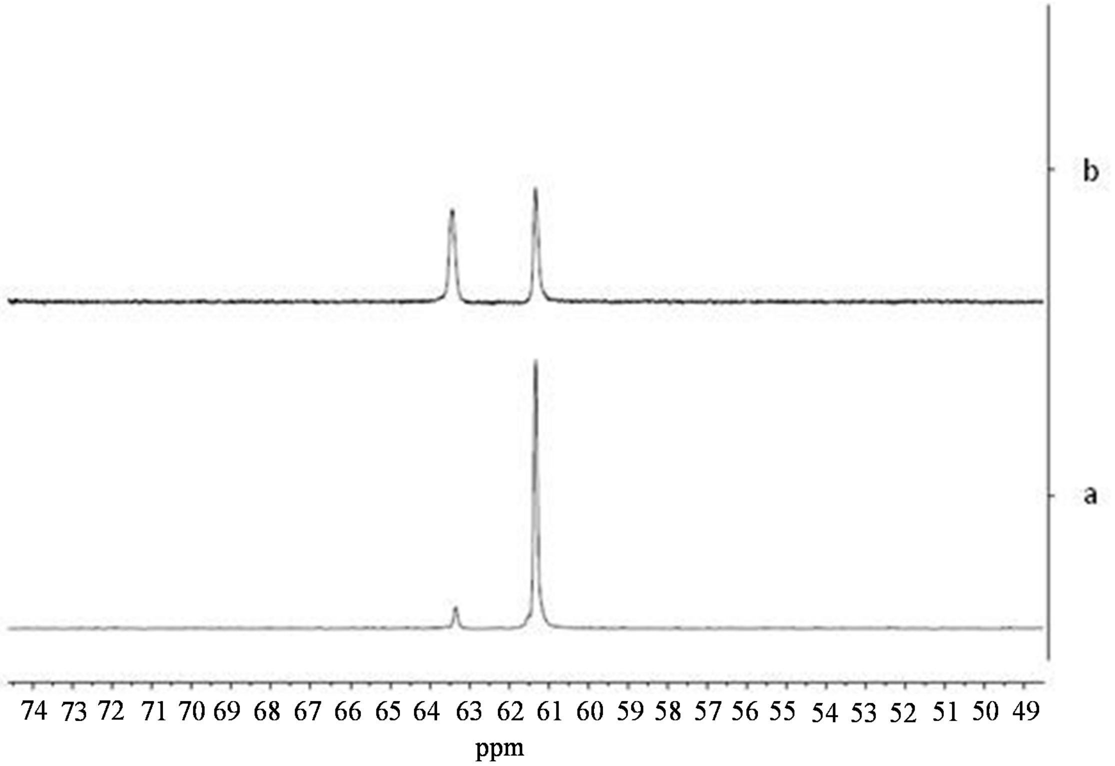


Figure 5.18 ^{31}P NMR spectra of CAT 1 before (a) and after (b) potassium tert-butoxide addition.

In ^{31}P NMR a and b spectra two phosphor species has been identified at 63.42 and 61.37 ppm which corresponds to isomer I and isomer II respectively. Same displacements were observed during the initial CAT 1 characterization in Figure 4.20 by using the same solvent. This facts means that no more different species has been formed during the alkali addition.

The NMR study has been performed by using only one scan and it allows to quantify the ratios between both species, being in spectrum a, a ratio of 8.5:91.5 for isomer I and isomer II respectively. This results shows that CAT 1 is an isomer mixture formed by higher amounts of isomer II.

Regarding to the ^{31}P NMR spectrum b, the alkali addition at room temperature has produced an isomerization of the isomer II to isomer I, modifying the concentration ratio of isomer I and isomer II until 52.7:48.3 respectively. Once alkali is added both isomer species did not modify its ^{31}P NMR displacements.

The addition of the 50% by moles of alkali, regarding to the catalyst moles, has been increased the isomer I concentration from 8.5 until 52.7% in the isomer mixture. If more alkali is added to the catalyst, until the same molar dose, the ratio between both isomers did not increase. For this reason the initial 50% by moles amounts is achieved as the optimum alkali amount required to isomerize CAT 1.

In order to justify the isomerization produced, the ^{1}H and the ^{13}C NMR has been also performed before and after the alkali addition.

In Figure 5.19 is shown the ^{1}H NMR before (spectrum a) and after (spectrum b) alkali addition.

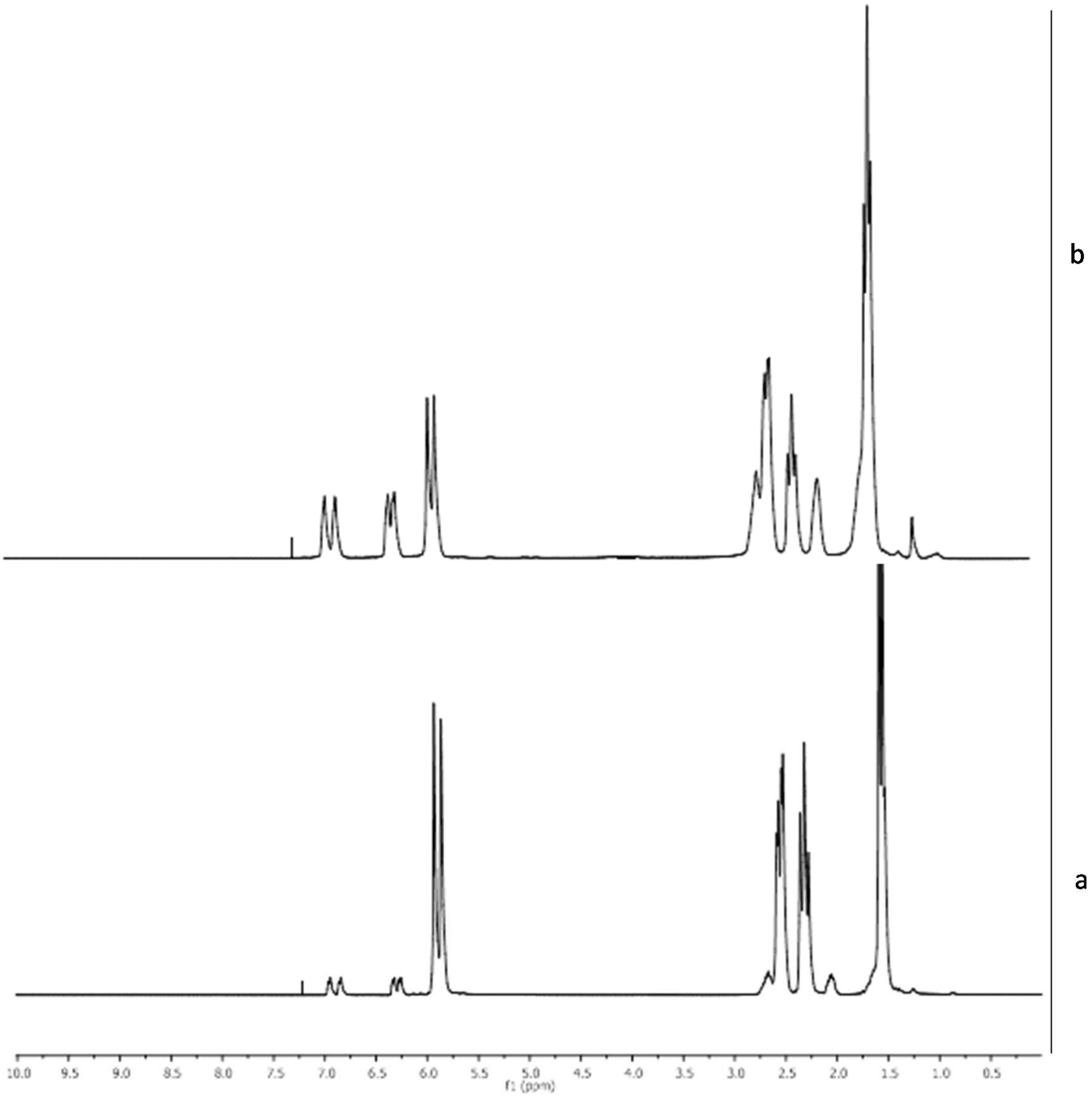


Figure 5.19 ^{1}H NMR spectra before (a) and after (b) alkali addition.

In the ^{1}H NMR spectra recorded, can also be identified the signals corresponding to the isomer I and isomer II with the same displacements observed in studies done before.

Comparing both a and b spectra there are some peaks that have increased its intensities once alkali was added.

In spectrum b, recorded after alkali addition, a new signal at 1.2 ppm appears which corresponds to the potassium tert-butoxide added, more concretely to the methyl groups.

The 1.5 signal, which is assigned to the methyls *1* and *1'* (following the nomenclature used in figure 4.17) of CAT 1 has increased. In this signals there are two very close signals, which the one on the left seems to have increased. This left signal corresponds to the methyl *1* because the closer presence of the unsaturation produces a slightly displacement.

The signal observed at 2 ppm has also increased once alkali is added and is identified as the protons *4*. Protons named *5* appear at 2.6 ppm, and is another signal that has achieved an increase.

Another signals that has experienced an increase after alkali addition are the doublet of doublets which appear at 6.2 and 6.8 ppm and are assigned to the protons *3* and *2* respectively.

The rest of peaks are assigned to the isomer II in the same manner than is detailed in section 4.2.1.2 where the doublet of doublets present at 2.4 – 2.6 ppm corresponds to protons *2'* and the 5.8 ppm doublet is assigned to protons *3*'. Signal at 7.2 ppm corresponds to the $CDCl_3$ solvent [30].

All this results show that the signals that have been increase its intensities corresponds to the isomer I protons. It confirms the results obtained in the ^{31}P NMR spectra where an increment of the isomer I concentration has been achieved after alkali addition.

In order to give more information about the catalyst isomerization reaction, ^{13}C NMR has been performed. In Figure 5.20 are shown the ^{13}C NMR before (spectrum a) and after (spectrum b) alkali addition.

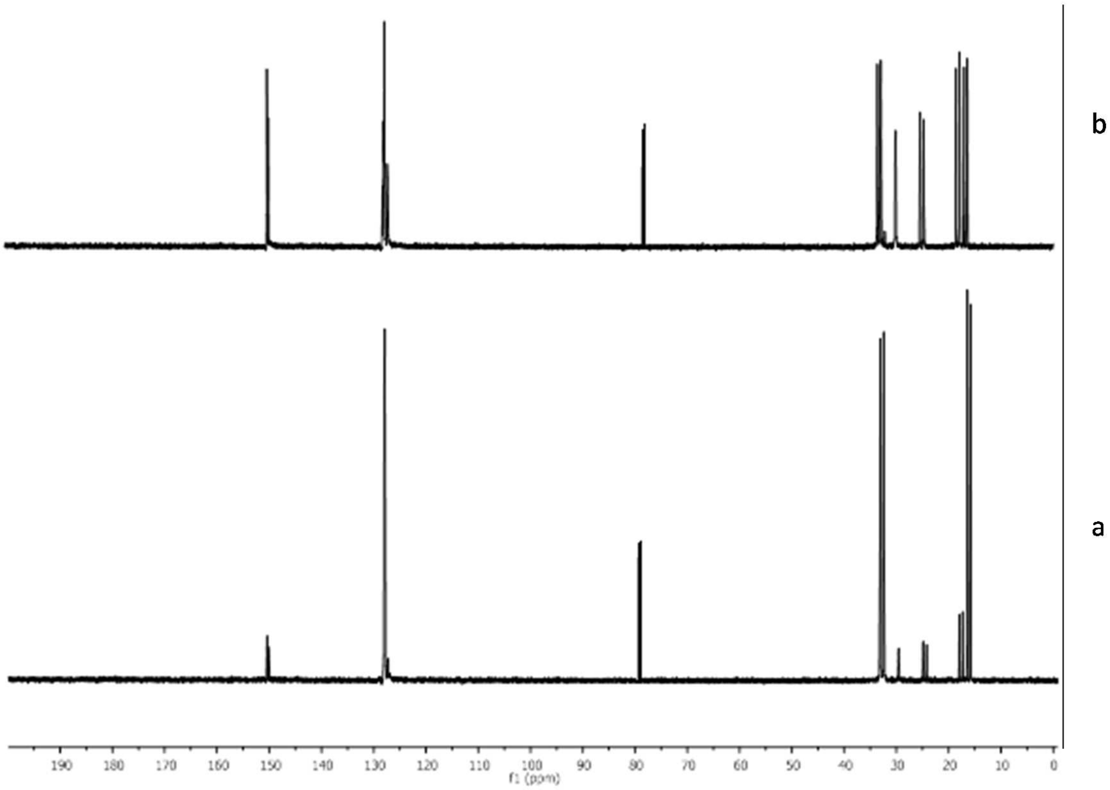


Figure 5.20 ^{13}C NMR spectra before (a) and after (b) alkali addition.

As in the ^{1}H NMR spectra, some signals have increased its intensities in the ^{13}C NMR spectra after the alkali addition (b). However, all signals appears at the same ppm than the CAT 1 study done before.

At 15 – 17 ppm are observed a group of signals assigned to the methyls named *1* and *1'*. Nevertheless in the spectrum b performed after alkali addition, the 17 ppm signal experience an intensity increasing until the same level than the 15 ppm signal. These signal are doublets due to the carbon coupling with the phosphor nucleus. The most displaced one corresponds to methyl *1* (isomer I) which is the signal that have increased its intensity.

In this first group of signals, the methyls signals corresponding to the tert-butoxide alkali is also observed in spectrum b at 15 ppm very close to the other ones.

Signals at 24 and 29 ppm corresponds to the carbons *5* and *4* respectively and in spectrum b have also achieved an increase in its intensity. Carbon *5* signal (24 ppm) is a doublet due to its coupling with the phosphor nucleus.

Carbon *3* of the isomer I is assigned to the 127 ppm signal, and is another signal that increases its intensity once alkali is added compared against the 128 ppm signal which corresponds to the carbon *3'* of the isomer II.

Signal at 150 ppm which are assigned to carbon *2* has also increased its intensity.

The signal appeared at 79 ppm is the characteristic peak of the solvent used [30].

Analyzing the ^{13}C NMR spectra, also is observed that all the peaks which have increased its intensity corresponds to the isomer I signals, demonstrating that the addition of potassium tert-butoxide, produces an isomerization reaction converting the isomer II into isomer I. Similar isomerization processes has been observed by using potassium tert-butoxide as alkali reagent, obtaining similar results in 2-methylpentene-1 [31].

Both for ^{1}H and for ^{13}C NMR, the signals corresponding to the isomer II, contrary to the isomer I ones, modify its intensities to finally reach similar ratios.

Once the CAT 1 is modified and its isomer ratio checked, the new isomerized catalyst is used as another catalyst to prepare a new sample. In order to study the differences between using high isomer I concentrated catalyst and high isomer II concentrated catalyst, R10 has been prepared by using the same synthesis process than for R6 preparation but using isomerized CAT 1 as catalyst.

In Table 5.19 are detailed the final reaction values obtained during the sample R10 preparation compared to R6 values.

Table 5.19 Final reaction values obtained for samples R6 and R10.

Sample	% CAT 1	CAT type	Reaction time (h)	Final NCO (%)	Gardner color
R6	0.15	Commercial	26.4	4.8	14-15
R10	0.15	Isomerized	20.2	4.9	16

The reaction times obtained for each sample to reach similar conversion yields (4.8 and 4.9% isocyanate content), shows a faster kinetics once the catalyst is isomerized and the isomer I concentration in the commercial mixture is increased. By using the same amount of CAT 1, a reduction of the reaction time in 5 hours is observed, indicating that isomer I is the most active isomer to catalyze the conversion of isocyanates to carbodiimides.

Analyzing the final color product obtained, slightly darker product is obtained once CAT 1 is isomerized by alkali. This color change starts once the catalyst is isomerized (see Figure 5.17) and also affects to the final reaction mixture.

FTIR spectrum has been also registered (Figure 5.21) in order to quantify the carbodiimide content.

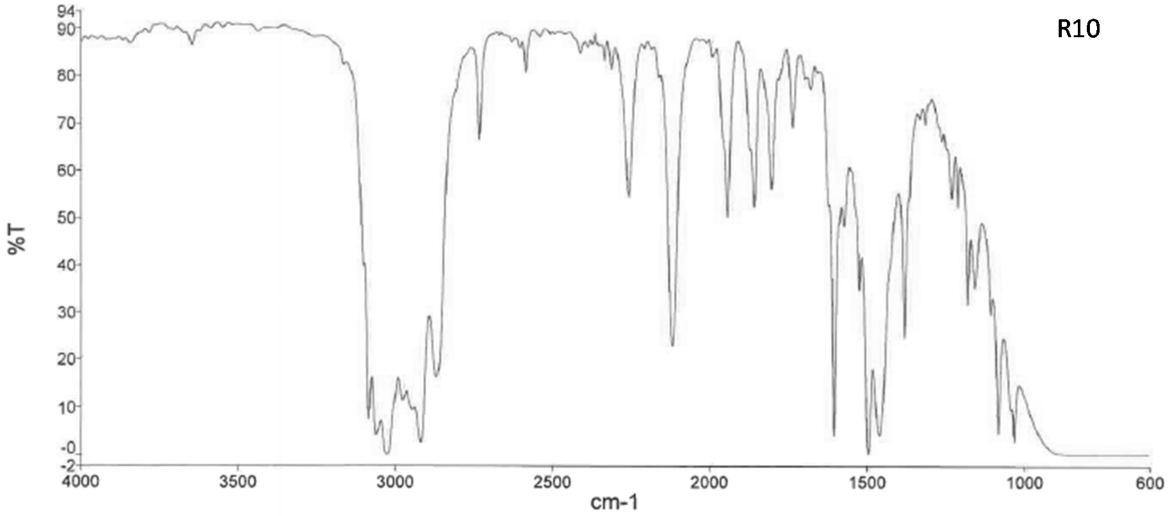


Figure 5.21 FTIR spectrum of sample R10.

Observing the FTIR spectrum the most important and characteristic bands are also recorded, as for the other samples prepared by using the same synthesis process with the commercial CAT 1. At 2120 cm^{-1} the NCN band which has a carbodiimide content of 12.97%, and at 2240 cm^{-1} the NCO band are identified. The correct band assignation indicates a correct conversion by using the isomerized catalyst.

As for the other samples, both CO_2 and carbodiimide content has been determined in order to compare the isomerization effect against other samples prepared by using the commercial isomer mixture of CAT 1. In Table 5.20 are shown the results obtained for samples R6 and R10.

Table 5.20 CO_2 and carbodiimide content for samples R6 and R10.

SAMPLE	% CO_2	% NCN FTIR	% NCN titration
R6	13.86	14.73	15.13
R10	12.48	12.97	13.08

Observing the amount of CO_2 formed, a lower content is shown which is also corroborated by the lower carbodiimide content obtained by both FTIR and titration analysis. The carbodiimide content obtained by titration analysis is, as observed in previously studies, higher than the value obtained by using the FTIR calibration method. However, the differences between both methods are lower for sample R10. It can be produced by the lower presence of uretonimine structures compared to the R6 sample.

These lower values comparing both R6 and R10 samples are attributed to lower molecular weight. This fact is probed by performing the MALDI TOF mass spectrum study. In Figure 5.22 are compared the MALDI TOF mass spectra of sample R6 and R10.

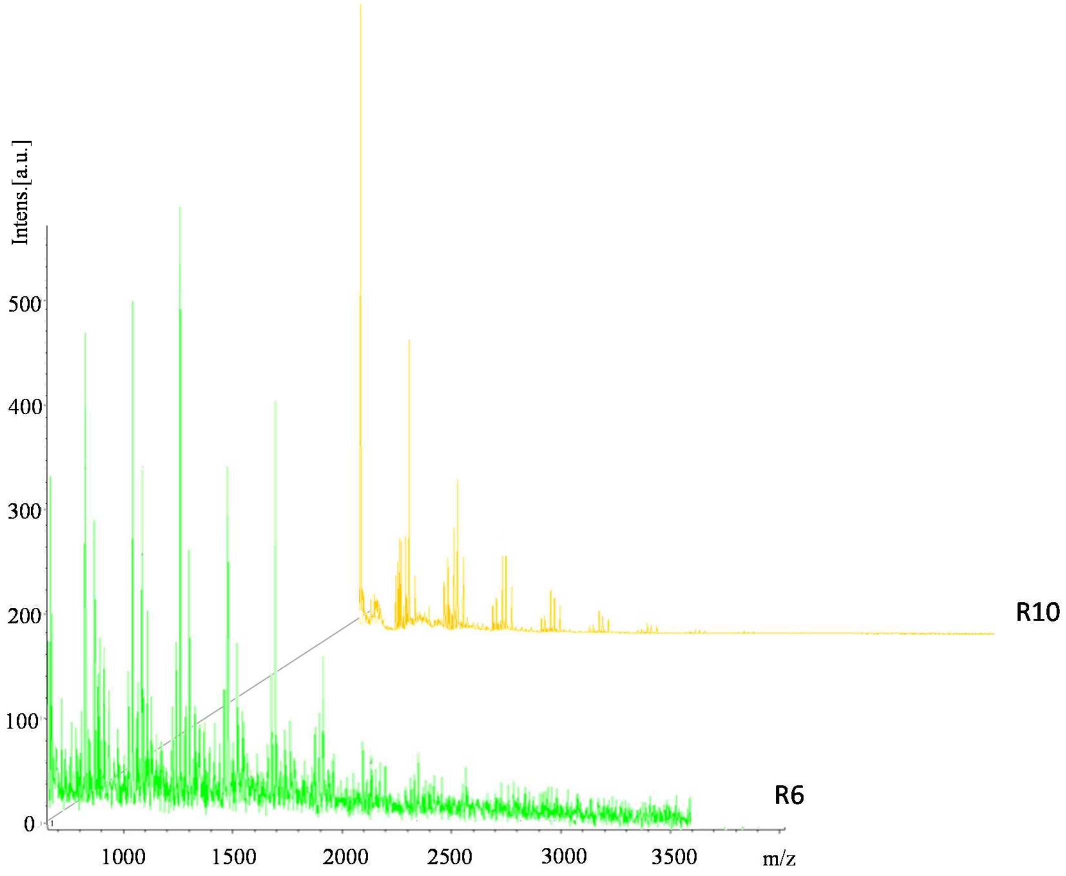


Figure 5.22 MALDI TOF mass spectra of samples R6 and R10.

Comparing both registered spectra, a Gauss distribution displacement to lower molecular weights is observed in sample R10. It means that the carbodiimide oligomer molecular weight obtained by using the same amount of CAT 1 isomerized is lower than using the commercial CAT 1 mixture.

This situation can be explained in the same way than for the use of different catalyst dose. It has been demonstrated that the potassium tert-butoxide addition to CAT 1 produces an isomerization of the isomer II to isomer I, increasing its concentration in the resulting CAT 1 isomer mixture. Once the isomer I concentration is increased, which has demonstrated to be the most active isomer to carry out the conversion of isocyanates to carbodiimides, the use of the new isomerized CAT 1 produces the same effect as if more catalyst was added to the reaction mixture, favoring the polymerization initiation step, reducing the reaction time, and decreasing the length of the oligomer chains causing a lower molecular weight.

All the registered data like CO_2 and carbodiimide content, reaction time required and MALDI TOF mass technique, confirms the higher catalyst activity of the isomer I against the isomer II to carry out the isocyanate to carbodiimide conversion.

The slightly differences between both carbodiimide content assays, indicates a very low presence of uretonimine structures. In order to study how the catalyst isomerization affects to the side reactions produced during the conversion reaction, in Figure 5.23 are identified both linear and branched structures masses present in sample R10.

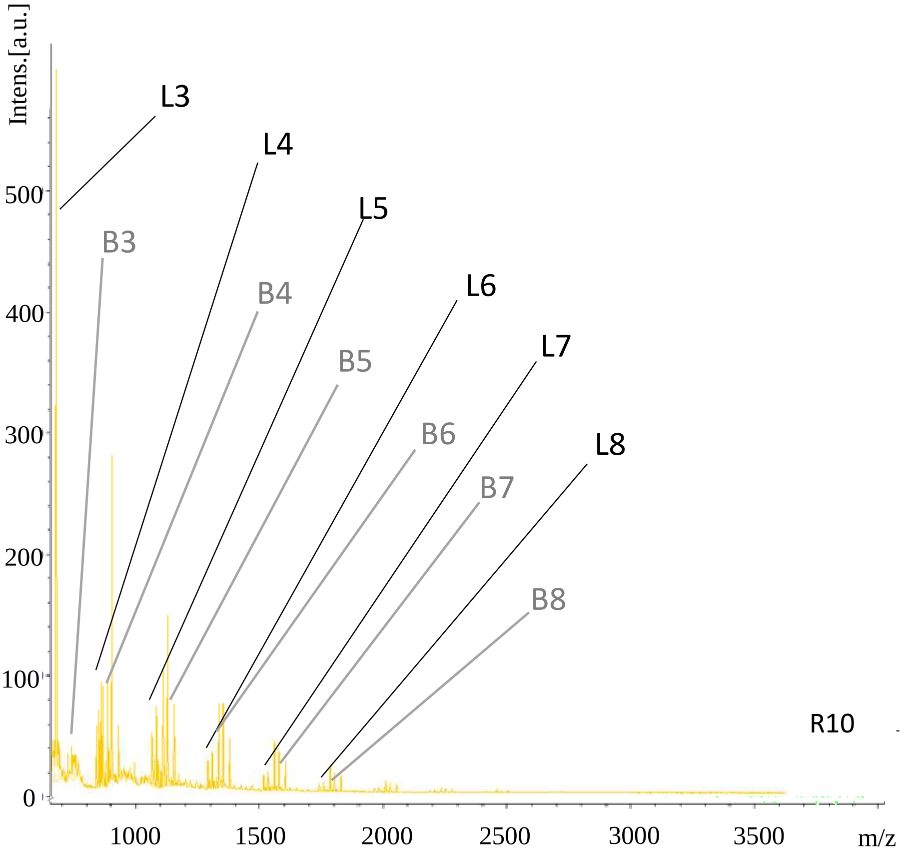


Figure 5.23 MALDI TOF mass spectrum of sample R10 with the linear and branched oligomer masses identified.

As in the other reported samples, it is possible to identify linear and branched structures with one uretonimine group present until 8 monomer units. No multibranched structures are identified.

Knowing the intensities of each peak, the same calculations than in section 5.2 by using the linear oligomers has been done in order to compare it against samples R6, R7 and R8 prepared by using CAT 1. In Table 5.21 are shown the linear oligomer contribution and the molecular weight for sample R10.

Table 5.21 R10 sodium ionized masses and its ratio of linear oligomer carbodiimide.

SAMPLE R10				
Peak	**Identified mass (Da)**	**Intensity**	**Ratio (%)**	**Molecular Weight (Da)**
L3	668.124	580	67.88	778.271
L4	867.643	100	12.12	
L5	1068.468	87	10.55	
L6	1267.685	45	5.45	
L7	1470.006	22	2.67	
L8	1667.995	11	1.33	

The molecular weight obtained for sample R10 is 778.271 Da which is lower than the molecular weight obtained for sample prepared by using the same amount of CAT 1 (R6) and even lower than the obtained for R8 which was prepared by using 0.4% of CAT 1. This facts confirms that isomer I is the most active isomer.

Once the chain distribution is known, CO_2 and carbodiimide content amounts contribution can be calculated for each oligomer chain. In Table 5.22 are shown the theoretical values expressed as weight percentage regarding to initial monomer amount for the CO_2 content, and regarding to the final sample amount for the carbodiimide content.

Table 5.22 CO_2 and carbodiimide theoretical content for sample R10.

SAMPLE R10					
Peak	**Ratio (%)**	**% CO_2**	**% NCN**	**% CO_2 average**	**% NCN average**
L3	67.88	12.02	12.42	12.76	13.32
L4	12.12	13.52	14.22		
L5	10.55	14.43	15.33		
L6	5.45	15.03	16.08		
L7	2.67	15.46	16.62		
L8	1.33	15.78	17.03		

Analyzing the theoretical values obtained in Table 5.22 against the experimental values shown in Table 5.20, lower values has also been obtained. The difference between both are caused for the presence of uretonimine structures which has been identified in the MALDI TOF mass spectrum.

However, comparing these values against the obtained for R6 sample, which was made by using the same amount of CAT 1, more similar values compared against the theoretical ones are obtained. This fact means that the side reactions which finally produces uretonimine structures are reduced by using the isomerized CAT 1 as catalyst.

Knowing the theoretical ratio between isomer I and isomer II in the commercial mixture CAT 1, and in the isomerized CAT 1 catalyst, it is possible to calculate the real percentage of isomer I used in each sample prepared. In Table 5.23 are summarized the isomer I dose used for the different samples prepared.

Table 5.23 Carbodiimide oligomer molecular weight obtained for samples R6, R7, R8 and R10.

SAMPLE	% CAT 1	CAT 1 Type	% Isomer I	Reaction time (h)	MW (Da)
R6	0.15	Commercial	0.013	26.4	1146.645
R7	0.3	Commercial	0.025	22.6	979.587
R8	0.4	Commercial	0.034	21.5	849.492
R10	0.15	Isomerized	0.079	20.2	778.271

The results indicate that when isomer I is present in the reaction mixture faster conversion is observed and lower molecular weight is obtained. An increasing in the kinetics and in the initiation polymerization step are obtained when the catalyst is more active.

Uretonimine structures has been identified in the MALDI TOF mas spectrum for R10 sample, and has been also noticed its presence due to the slightly differences presents between the linear theoretical values and the experimental obtained for CO_2 and carbodiimide content. In order to study how the catalyst isomerization affects to the side reactions, the ratio between linear and branched uretonimine structures has been calculated. In Table 5.24 are shown the intensities ratios for each R10 oligomer chain identified.

Table 5.24 Intensity ratios between linear and branched oligomers structures for R10 sample.

Monomer units	**R10**	
	L	**B**
3	55.93	3.86
4	9.64	3.86
5	13.50	2.41
6	4.34	1.93
7	2.12	0.96
8	1.06	0.39

Considering the percentages for both linear and branched uretonimine structures calculated for each oligomer chain identified, higher amounts of linear oligomers are found in R10. Once more catalyst is added or in the case of R10, more active isomer is added; the initiation polymerization step is favored and the side reactions are reduced. R10 has 86.6% content of linear oligomers, even higher that the value found for R8 which was prepared by using 0.4% of CAT 1. This situation also indicates that isomer I is the most active isomer present in the CAT 1 isomer mixture.

Finally, all data obtained shows the higher conversion activity of isomer I. Knowing the conversion mechanism, now confirmed by NMR technique where the catalyst interacts to form the reaction intermediate; is enable to think that the isomer which makes the phosphoryl bond more active due to its higher polarity, to start the nucleophilic attack to the isocyanate group is Isomer I. The resonance of the positive charge, increase the negative charge in the oxygen atom which also enhance the nucleophilic activity of the phosphoryl bond that increases the conversion activity of isocyanates to carbodiimides.

5.5 CATALYST ISOMERS CONTENT STUDY

Depending on the isomer ratio present in the catalyst different conversion activities are observed. Is important to know the isomer ratio present in the catalyst selected to be used in order to optimize the required amount to obtain the desired product characteristics.

Knowing the importance of the isomers content, a ^{31}P NMR study has been carried out in the catalysts used during the reaction condition and catalyst optimization section. 1-phenyl-3-methyl-1-oxo phospholene (CAT 2) and triphenylphosphine oxide (CAT 3) has been analyzed by ^{31}P NMR to quantify the isomer ratio present in the commercial sources.

Catalysts were analyzed before and after the potassium tert-butoxide addition in the same ratio than the optimized in section 5.4, 50% by moles regarding to the catalyst to check how the isomerization works in each catalyst. Triphenylphosphine oxide has only one isomer, but it was also tested in order to know if any change were observed.

^{31}P NMR spectra were performed by using $CDCl_3$ as solvent and a capillary of H_3PO_4 as reference material. Only one scan was performed to quantify the ratio between species.

In Figure 5.24 and Figure 5.25 are shown the ^{31}P NMR spectra registered for CAT 2 and CAT 3 respectively, were the spectrum a is before the alkali addition and spectrum b is after the potassium tert-butoxide addition.

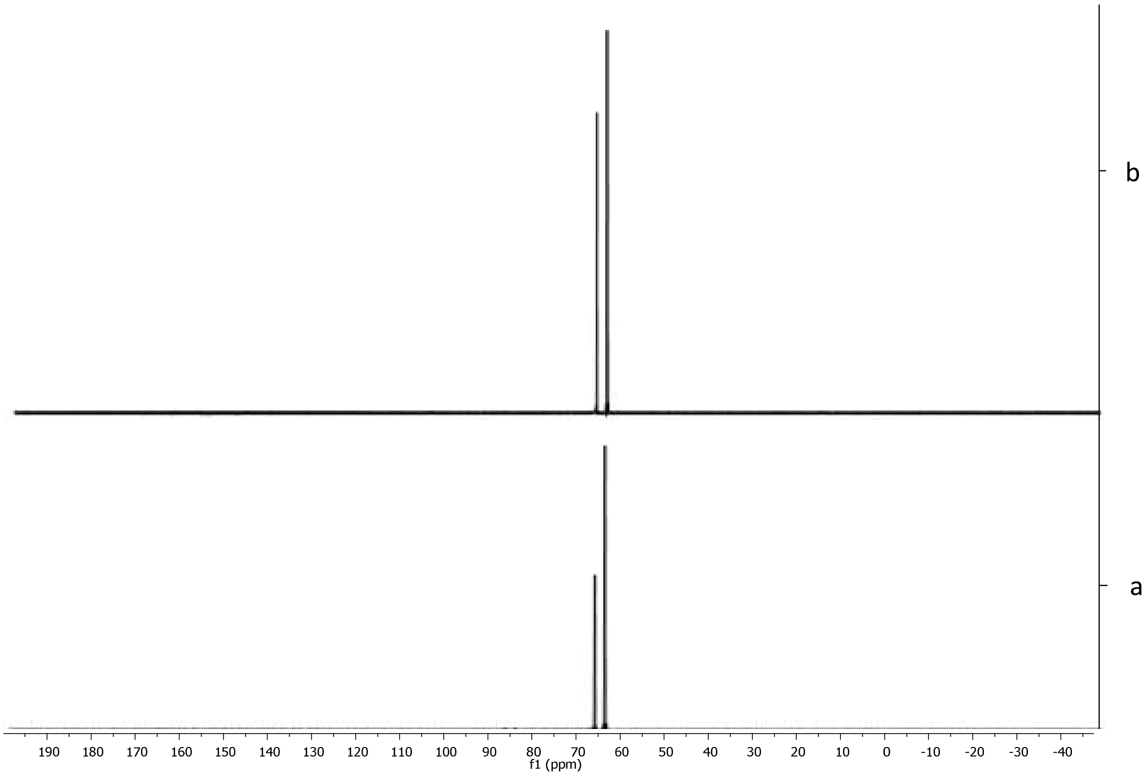


Figure 5.24 ^{31}P NMR spectra of CAT 2 before (a) and after (b) alkali addition.

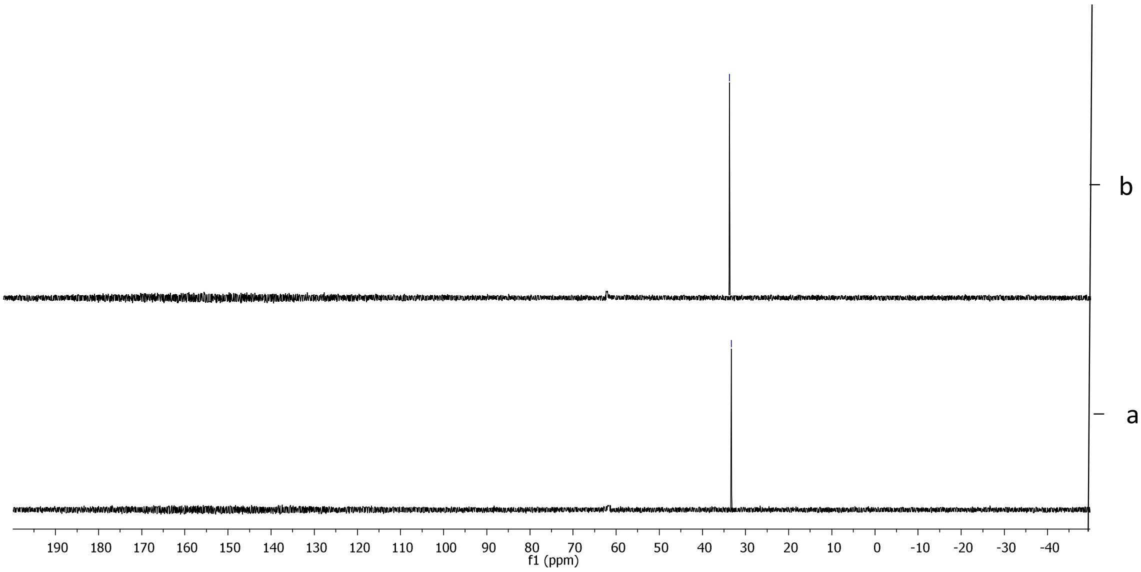


Figure 5.25 ^{31}P NMR spectra of CAT 3 before (a) and after (b) alkali addition.

In the ^{31}P NMR registered for CAT 2 two phosphor species are identified at 65.89 ppm and 63.56 ppm. Both peaks corresponds to the 1-phenyl-3-methyl-1-oxo-2-phospholene and 1-phenyl-3-methyl-1-oxo-3-phospholene, respectively. The most displaced peak corresponds to the isomer with the unsaturation closer to the phosphor nucleus. This species are slightly more displaced than the CAT 1 isomers due to the phenyl presence as substituent [32, 33].

As for CAT 1, the most active isomer expected is the isomer which has the unsaturation closer to the phosphor nucleus, like isomer I of CAT 1.

Initially, as can be seen in Figure 5.24 a, the isomer ratio was 37.01:62.99 respectively for isomer I and II of CAT 2. Once alkali is added to the catalyst, an isomerization is observed increasing the ratio to 46.83:53.17 respectively (see Figure 5.24 b). Potassium tert-butoxide produces an isomerization of the isomer II to isomer I also in CAT 2. However, in this case the isomerization is done in lower concentration.

Nevertheless, ^{31}P NMR spectra for CAT 3 (Figure 5.25), only shows one phosphor specie at 33.73 ppm which remains constant once alkali is added. No change in the phosphor specie has been observed by adding potassium tert-butoxide to triphenylphosphine oxide [34].

In Table 5.25 are summarized the ratios between isomer I and isomer II for each catalyst studied before and after the potassium tert-butoxide addition.

Table 5.25 Isomer I and II ratio present in commercial catalyst CAT 1, CAT 2 and CAT 3 before and after alkali addition.

Catalyst	Commercial ratio	Isomerized ratio
CAT 1	8.50 / 91.50	52.70 / 47.30
CAT 2	37.01 / 62.99	46.83 / 53.17
CAT 3	No isomers	No isomers

Observing the commercial isomer ratios the better conversion activity of CAT 1 against CAT 2 is confirmed even having a lower initial concentration of isomer I. CAT 2 even though having more isomer I concentration in the commercial mixture, is less active than CAT 1 to carry out the conversion of isocyanates to carbodiimides. This fact corroborate the depolarization of the phosphoryl bond and the steric hindrance produced by the phenyl substituent, which affects to the initiation step of the nucleophilic attack.

Considering the importance of the isomer I concentration in CAT 1, is important to analyze and quantify the isomer ratio of each catalyst batch used because little differences in the catalytic activity can cause big differences in the final product obtained by using exactly the same reaction conditions.

5.6 REFERENCES

1. Matyjaszewski, K., Cationic Polymerizations: Mechanisms, Synthesis & Applications. 1996: CRC Press.

2. Covington, A.D. and Covington, T., Tanning chemistry: the science of leather. 2009: Royal Society of Chemistry.

3. Song, Z., High molecular weight cationic polymers obtained by post-polymerization crosslinking reaction. 2007, Google Patents.

4. Ulrich, H., Chemistry and technology of isocyanates. 1996: Wiley.

5. Segarra Ortí, C., Rajadell Viciano, Fernando, Planelles Fuster, Josep, Equilibrio químico: El principio de Le Chatelier revisitado con ayuda de las nuevas tecnologías. Departamento de Química Física y Analítica. Escuela Superior de Tecnología y Ciencias Experimentales Universidad Jaume I de Castellón, 2008.

6. Mijangos, F., Varona, F., and Villota, N., Changes in solution color during phenol oxidation by Fenton reagent. Environmental science & technology, 2006. 40(17): p. 5538-5543.

7. Yehye, W.A., et al., Understanding the chemistry behind the antioxidant activities of butylated hydroxytoluene (BHT): A review. European journal of medicinal chemistry, 2015. 101: p. 295-312.

8. AKTIENGESELLSHAFT, B., Carbodiimidas y procedimiento para su producción. 2004.

9. Mark, H., Encyclopedia of Polymer Science and Technology, 12 Volume Set. 2005, John Wiley & Sons, Inc.

10. Gies, A.P., et al., MALDI–TOF/TOF CID Study of Polycarbodiimide Branching Reactions. Macromolecules, 2013. 46(19): p. 7616-7637.

11. Wieser, M.E. and Coplen, T.B., Atomic weights of the elements 2009 (IUPAC Technical Report). Pure and Applied Chemistry, 2010. 83(2): p. 359-396.

12. Okamoto, K., MALDI Mass Spectrometry of Synthetic Polymers. R&D Review of Toyota CRDL, 2006. 41(3): p. 29-34.

13. Narayan, T., Liquid carbodiimide-uretonimine modified polymethylene polyphenylene polyisocyanates and polyurethane foams made therefrom. 1988, Google Patents.

14. Appleman, J.O. and DeCarlo, V.J., Conversion of isocyanates into carbodiimides with isopropyl methylphosphonofluoridate as catalyst. Kinetic studies. The Journal of Organic Chemistry, 1967. 32(5): p. 1505-1507.

15. Rogers, M.E. and Long, T.E., Synthetic methods in step-growth polymers. 2003: John Wiley & Sons.

16. Ulrich, H., Chemistry and technology of carbodiimides. 2008: John Wiley & Sons.

17. Riegel, E.R., Kent and Riegel’s Handbook of Industrial Chemistry and Biotechnology, Vol. 1. 2007, New York: Springer.

18. Spyrou, E., Weiss, J., and Grenda, W., Polyurethane composition which contains an uretdione group. 2005, Google Patents.

19. Kordomenos, P., Kresta, J., and Frisch, K., Thermal stability of isocyanate-based polymers. 2. Kinetics of the thermal dissociation of model urethane, oxazolidone, and isocyanurate block copolymers. Macromolecules, 1987. 20(9): p. 2077-2083.

20. Kent, J.A., Riegel's handbook of industrial chemistry. 2012: Springer Science & Business Media.

21. Sawinski, P.K., et al., Single-crystal neutron diffraction study on guanidine, CN3H5. Crystal Growth & Design, 2013. 13(4): p. 1730-1735.

22. Ibbotson, A., Carbodiimides. 1977, Google Patents.

23. Savino, T. and Bananto, S., Uretonimine-modified isocyanate composition and method of forming the same. 2009, Google Patents.

24. Campbell, T.W., Monagle, J.J., and Foldi, V.S., Carbodiimides. I. Conversion of isocyanates to carbodiimides with phospholine oxide catalyst. Journal of the American Chemical Society, 1962. 84(19): p. 3673-3677.

25. Yamada, M., et al., Preparation and characterization of novel 4-bromo-3, 4-dimethyl-1-phenyl-2-phospholene 1-oxide and the analogous phosphorus heterocycles or phospha sugars. Bioorganic & medicinal chemistry letters, 2010. 20(19): p. 5943-5946.

26. Arbuzov, B., et al., Isomerization of 1-oxo-1-chlorophospholenes in the presence of phosphorus trichloride. Chemistry of Heterocyclic Compounds, 1971. 7(12): p. 1502-1505.

27. Hoechst, A., Verfahren zur isomerisierung von 1-alkyl-1-oxo-phospholenen. 1986.

28. Gorenstein, D.G., Phosphorous-31 NMR: Principles and applications. 2012: Academic Press.

29. Shrot, Y. and Frydman, L., Single-scan NMR spectroscopy at arbitrary dimensions. Journal of the American Chemical Society, 2003. 125(37): p. 11385-11396.

30. Pretsch, E., Determinación estructural de compuestos orgánicos. 2002: Elsevier España.

31. Alan, S. and Rowe, J.C.A., Monoolefin isomerization process. 1965, Google Patents.

32. Reddy, V.K., et al., Synthesis and characterization of the novel l-(substituted phenoxy/phenyl)-2-phospholene and phospholane 1-oxide derivatives. Journal of heterocyclic chemistry, 2002. 39(1): p. 69-75.

33. Moedritzer, K. and Miller, R.E., Improved Syntheses and Characterization of the Isomers of 3-Methyl-1-Phenylphospholene 1-Oxide. Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 1978. 8(2): p. 167-184.

34. SciFinder, www.scifinder.cas.org.

Chapter 6

Carbodiimide oligomer functionalization and application

6. CARBODIIMIDE OLIGOMER FUNCTIONALIZATION AND APPLICATION

The main objective of the present doctoral thesis is the incorporation of the carbodiimide prepared samples in different polymers to improve its degradation resistance against hydrolysis and ageing [1, 2]. Carbodiimides can be used in different applications such as organic synthesis and biological applications, but the most important industrial use is as polymer stabilizers [3].

Depending on the final application field, the carbodiimide oligomers have been used with different functionalization and solvents, in order to guarantee the compatibility against the doped polymer and to optimize its stabilizing application.

The carbodiimide incorporation over other products or polymers can be done as an additive, just mixing, or incorporate the additive to the polymer chain as if other raw material was employed. The oligomer carbodiimide function in the final application are similar independently of the application way and field where were used. The main function of carbodiimide group is to react with the carboxylic groups present in the media. However, the difference between applications is the carboxyl groups precedence with which carbodiimide should react [4]. The scavenging of carboxyl groups generated during the degradation processes with carbodiimide, prevents its degradation caused by the catalytic effect produced by these generated carboxyl groups [3, 5].

The carboxylic groups susceptible to react with the carbodiimide functional group can be presents in the system or can be generated in-situ by indirect actions over the final product tested. In the first case, the carbodiimide acts as a crosslinker reacting the carboxyl groups and creating a tridimensional structure. In the second case carbodiimide is added to react when it will be necessary. This situation is necessary in the case of polyesters, polycarbonates or polyurethanes, which are degraded for external agents (light, humidity, temperature and aggressive chemical conditions) which causes a properties loss. Once the product starts to degrade carbodiimide reacts with the generated carboxyl groups during the degradation, rebuilding again the polymer chain and recovering part of the lost properties. For crosslinking application highly hindered carbodiimides are less efficient. Nevertheless, these kind of carbodiimide, like the carbodiimides oligomers based on TMXDI, are the most stable; for this reason are the most employed in polymer stabilizing applications [6].

Knowing the required functions of the carbodiimide products in different applications, different samples have been prepared to be incorporated to the polymer chain. If the carbodiimide is included in the main chain, the regenerating action could be optimized [7].

To incorporate the prepared carbodiimide oligomers based on TMXDI to different polymer matrix, is necessary to functionalize it because not all system requires isocyanate functionality. Once the oligomer is prepared double terminal isocyanate groups are present in the structure. If another functional group is required to optimize the final application, a functionalization of the final oligomer needs to be performed.

To carry out the desired functionalization is necessary to use compounds with double functionality. One related to the desired final functionality and another one with a high isocyanate reactivity. This kind of compounds show a fast isocyanate reaction leaving unreacted the desired final functionality. Alcohols and amines are common used as a high reactive groups against isocyanates.

The functionalization reaction consist in react all the isocyanate groups present in the initial carbodiimide oligomer with the desired functionalizing compound in each case. The required amount of functionalizing agent is calculated as a molar ratio of 1:1 by analyzing the final isocyanate content of the prepared carbodiimide oligomer which usually is around 5%. The reaction is carried out at different temperatures depending on the compound used. The correct functionalization can be checked by analyzing the final isocyanate content once the reaction is finished. The result should be close to 0%.

In addition, to dote the oligomer with the desired functionality, is necessary to know that this kind of oligomers have a very high viscosity, even before being functionalized. This viscosity is higher in products with higher content of uretonimine structures, and higher molecular weight. For the major part of applications the product has to be workable, for this reason is necessary to dilute the final functionalized oligomer in the most appropriate solvent to improve the working conditions.

The solvent selection must be done knowing that the solvent should be inert and compatible with the final polymer or product application. Depending on the final application required, some solvents will be not able to use due to its physico-chemical characteristics or its toxicity; for this reason is important to know the final application.

After the different optimization studies done in sections before; different functionalized samples have been prepared depending the polymer to be doped in order to study the final carbodiimide application. The carbodiimide oligomers prepared to be functionalized have been synthetized following the optimized process used for the sample R6 and R10 preparation, which consist in use 0.15%ww of CAT 1 regarding to the TMXDI monomer amount used, and adding or not the alkali to isomerize it.

In the chemical industry exists a wide variety of different fields, which are dedicated to different products and applications. This doctoral thesis is focused in polyurethanes and vinyl chemical fields to test and evaluate the final carbodiimide oligomers application. In addition, different kind of functionalization are described, such as to obtain water soluble polycarbodiimides.

6.1 POLIURETHANE SYSTEM APPLICATION

The polyurethane industry is the field of the chemical industry which uses isocyanates as main raw material to react it with alcohols. From the isocyanate and alcohol reaction, a urethane group is formed. In Figure 6.1 is shown the general reaction scheme of urethanes synthesis. If diisocyanates and diols are used as starting raw materials, polyurethanes will be obtained. Tertiary amines, tin catalysts or UV rays are commonly used to catalyze this synthesis [8, 9]

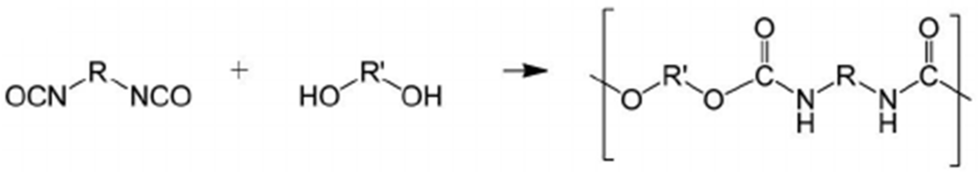


Figure 6.1 Reaction scheme of urethane synthesis [9].

The benefits of the prepared polyurethane depends on the isocyanate and diol selected as precursors monomers. Long chain diols produce a softer and elastic polyurethane. If a rigid polyurethane is required a little amount of polyol should be used in order to obtain certain amount of crosslinked units. The diols precedence are varied, being polyester diols and polyether diols the most used. Also exists special diols like polycarbonate diols or polycaprolactone diols which are used for high resistance applications [10, 11].

To modify the polyurethane properties, different diisocyanate monomers mixture can also be used. As commented sections before, there are a wide variety of this raw material that can be classified depending its aromaticity or its steric hindrance. Depending on the desired polyurethane properties different combination of all this raw materials commented can be used to optimize the formulation.

If a diisocyanate molar excess is used in the formulation, an isocyanate functionalized polyurethane is obtained. Contrary, if a diol molar excess is used, a diol functionalized polyurethane is obtained. Each polymer obtained is called A part and B part respectively; where the mixture of both parts produces a curing reaction which is the base of the adhesives industry.

Polyurethanes can be used in a wide variety of applications such as construction, furniture, packaging, adhesives, coating, leather, footwear and textile [12].

6.1.1 Non functionalized carbodiimide oligomers for polyurethane applications.

Carbodiimide synthesis uses isocyanates as a main raw material, producing oligomers with double terminal isocyanate groups. This initial isocyanate functionality facilitates its incorporation to polyurethane polymers because it can be used as another diisocyanate monomer during the polymer preparation.

The carbodiimide oligomers base prepared are practically solids at room temperature. This elevated viscosity makes the product unworkable at room temperature, for this reason is necessary to dilute it until viscosities lower than 6000 cps, in order to facilitate its manipulation.

The dilution of this un-functionalized carbodiimide oligomers must be done by using inert solvents to isocyanate reaction and to the rest of raw materials involved in the polyurethane synthesis. The most used solvents in polyurethane industry are toluene and N-Ethyl-2-pirrolidone (NEP), but also exists other solvents able to be used like ethyl acetate or Lauryl Benzoate. All this solvents will be removed from the system in the final curing step.

To reduce the oligomer viscosity below 6000 cps, is necessary to dilute it at 70% of solid content approximately, by using the solvent mentioned above. This concentration oligomer in NEP solvent allows to reach 5300 cps at 25ºC. The dilution should be done once the reaction is finished and maintaining the temperature about 70ºC. This temperature allows to keep the product agitated and to add the solvent without evaporation risk, because the boiling temperatures are 111, 81, 77 and 250ºC respectively for each solvent described [13]. Once the dilution has been done, the final product can be used as another diisocyanate monomer in the polyurethane reaction system.

Two samples have been prepared to be used in a polyurethane system as a diisocyanate monomer. Both samples R11 and R12, have ben synthetized by following the optimized method for sample R6 and R10 respectively.

In Table 6.1 are shown the final characteristics obtained for both samples.

Table 6.1 Final values obtained for samples R11 and R12.

Sample	Final NCO (%)	Solid content (%)	Solvent	Final NCN (%)
R11	5.2	70.2	NEP	15.21
R12	5.0	70.4	NEP	13.32

Samples R11 and R12 have achieved similar final values than the samples prepared before by using the same processes R6 and R10. For this reason a molecular weight average of 1150 Da is estimated for sample R11 and 750 Da for sample R12 which has been prepared by using the isomerized CAT 1 as catalyst to reduce the reaction time.

6.1.1.1 Accelerated ageing study in polyurethane films

Once samples R11 and R12 are prepared, were incorporated in a standard polyurethane formulation based in polyester diol and Isophorone diisocyanate (IPDI) as precursor monomers, which is named PU.

This test objective is to improve the stability and the resistance to external agents of this standard polyurethane based in polyester. In order to study the improvement degree, a polyurethane dispersion is prepared without the carbodiimide incorporation to be used as a blank or reference sample. In addition to this reference sample, four polyurethane doped with carbodiimide samples were also prepared modifying the carbodiimide amount and the carbodiimide sample used.

For the stability and resistance study the following listed samples were prepared by following the polyurethane dispersion synthesis process described in section 3.2.2.1.

- PU (Reference sample)
- PU + 2% CARBODIIMIDE R11
- PU + 5% CARBODIIMIDE R11
- PU + 2% CARBODIIMIDE R12
- PU + 5% CARBODIIMIDE R12

After the polyurethane dispersions preparations, all samples are tested against the UV radiation and to temperature and humidity variations by using a Xenotest equipment which reproduces rapidly the effects of external agents over the sample. To carry out the test is necessary to prepare the film test specimens by following the process detailed in section 3.2.2.1.

Once the test specimens are prepared for each sample, the external agents ageing test is carried out by following the procedure described in section 3.4.2.2.

In order to evaluate the improvement degree, an appearance assessment and a FTIR study has been carried out before and after the test. Below are shown the pictures of the different polyurethane films tested before and after being subjected to 200 hours of exposure.

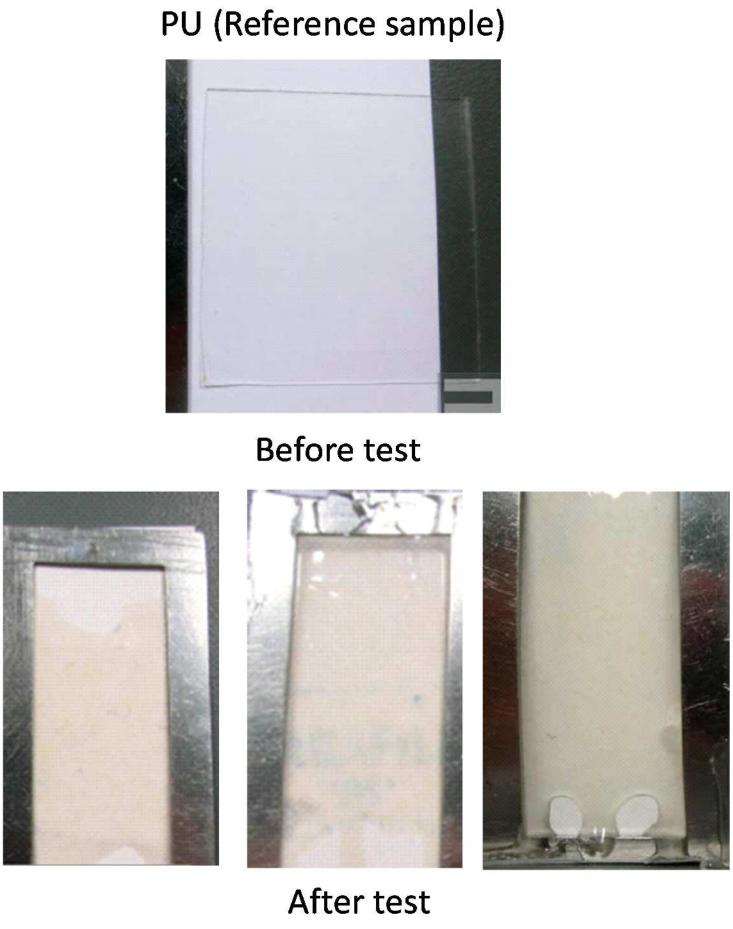
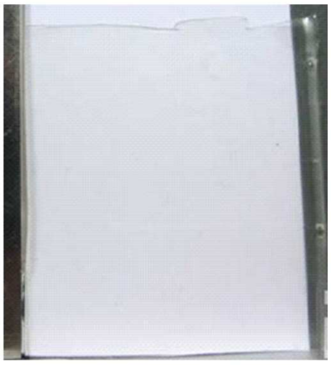
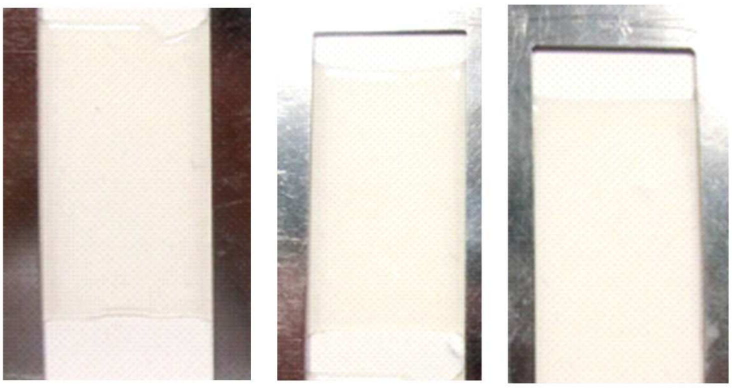


Figure 6.2 PU reference sample before and after 200 h subjected to external ageing test.

PU + 2% CDI R11



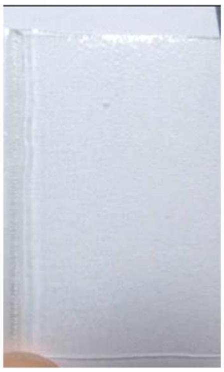
Before test



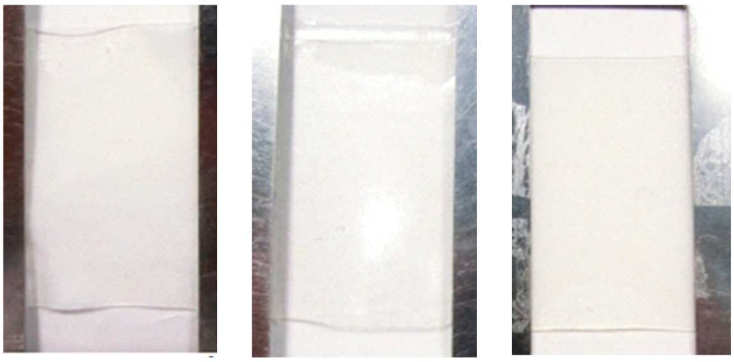
After test

Figure 6.3 PU with 2% of CDI R11, before and after 200 h subjected to external ageing test.

PU + 5% CDI R11



Before test



After test

Figure 6.4 PU with 5% of CDI R11, before and after 200 h subjected to external ageing test.

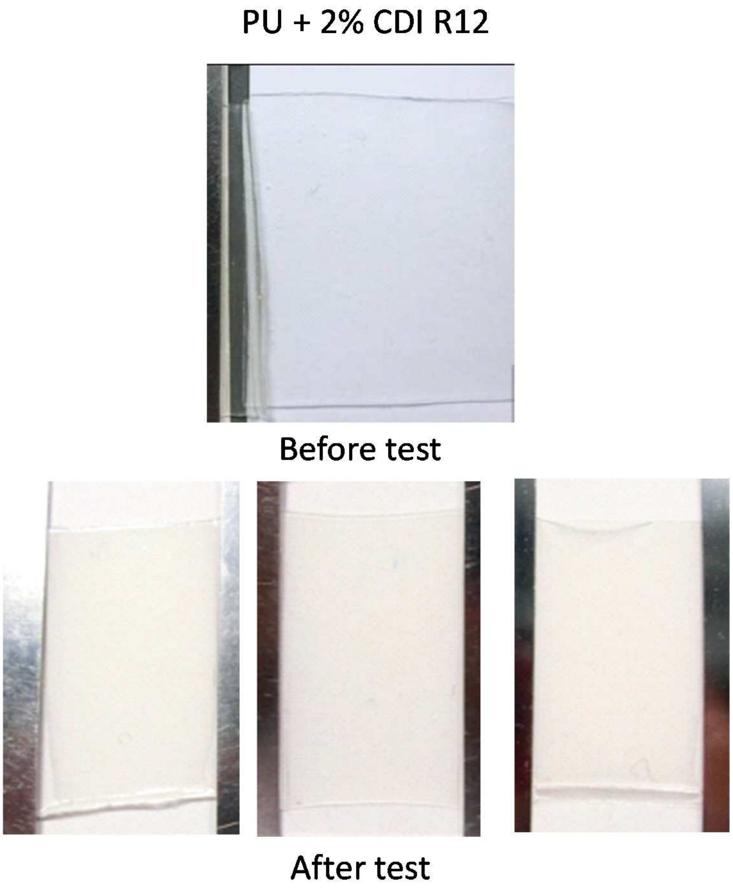


Figure 6.5 PU with 2% of CDI R12, before and after 200 h subjected to external ageing test.

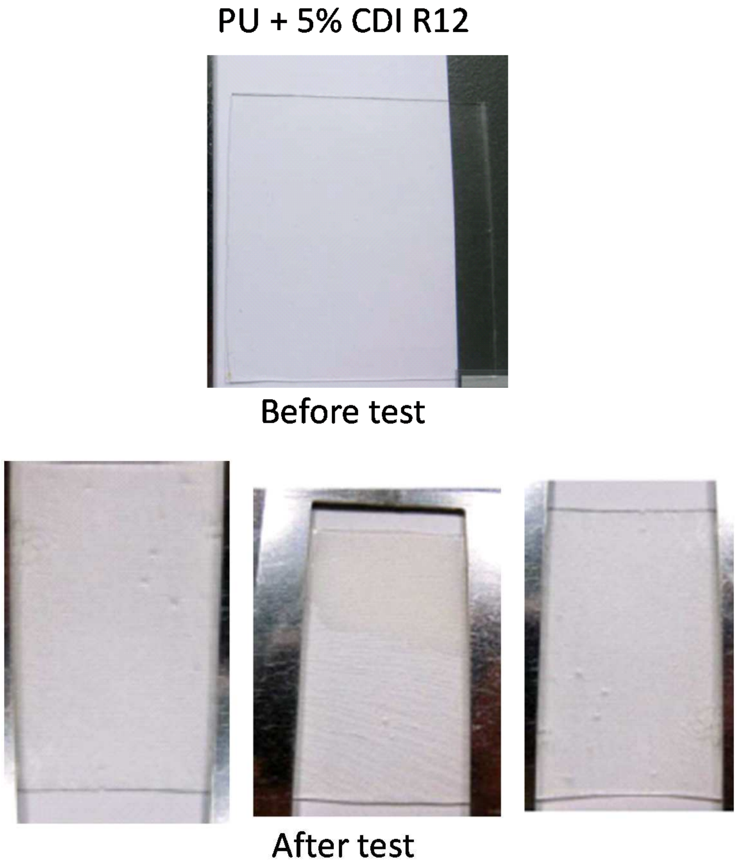


Figure 6.6 PU with 5% of CDI R12, before and after 200 h subjected to external ageing test.

Observing the pictures and after submitting the specimen test to 200 hours under accelerated external agents, some appearance differences can be noted.

The most clear difference is the totally degradation of the reference sample (see Figure 6.2) which was prepared without carbodiimide addition. The rest of the samples with different quantities of carbodiimide added remains stable. The reference specimen test has been completely melted and has acquired an intense yellow color.

Analyzing the rest of samples tested, all samples with carbodiimide included maintains its structure and appearance. This difference against the reference material is caused by the carbodiimide action. The polyester and polyurethane structure present in the doped samples are also degraded like in the reference material, but once new groups are generated, carbodiimide is able to react it decreasing the chain scission and its consequent degradation, maintaining the properties and the initial appearance [3, 14].

Comparing the carbodiimide doped test specimens, slightly differences can also be observed. In Table 6.2 are shown the characteristics of the doped PU samples.

Table 6.2 Carbodiimide doped polyurethanes characteristics.

Sample	Final NCN (%)	Final NCN PU (%)	Appearance	Structure
R11	15.21	2	Slightly yellow	Ok
R11	15.21	5	No change	Ok
R12	13.32	2	Slightly yellow	Ok
R12	13.32	5	No change	Ok

From the pictures and the results analysis is shown that independently of the tested sample (R11 or R12) once more carbodiimide groups are present in the specimen test, better performance and resistance to external agents degradation is obtained. Specimen tests can be classified in two classes, the polyurethanes doped with 2 or with 5% of carbodiimide content. The first group maintains the structure after 200 hours of exposure but a slightly color change is observed, having a little bit more yellow color. On the other hand, the second group maintains the structure and even the color of the final polyurethane film tested.

The appearance and the physical changes observed in the reference sample confirms the high degradability of the polyester based polyurethane which is degraded under the assays conditions, generating carboxyl and hydroxyl groups from the polyester degradation and hydroxyl and amine groups from the polyurethane hydrolysis (see Figure 6.7). High humidity, temperature and irradiance time are key factors in the polyester based polyurethane degradation, generating less compact and stables structures which produces the deterioration of the final sample [15].

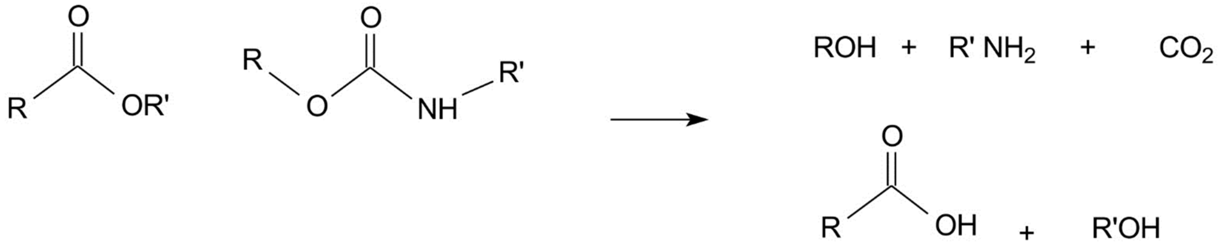
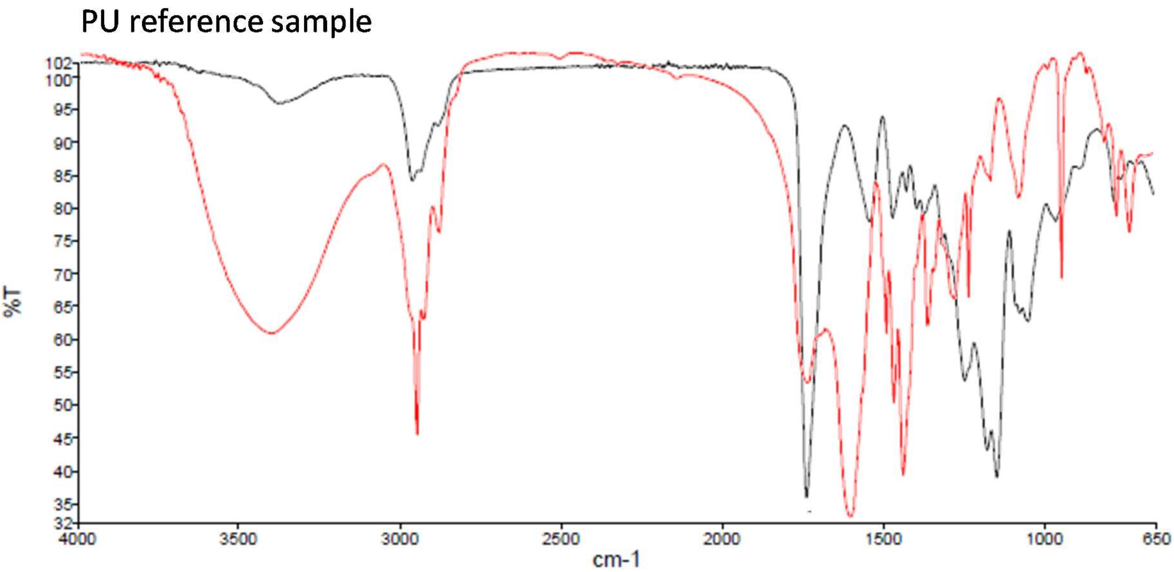
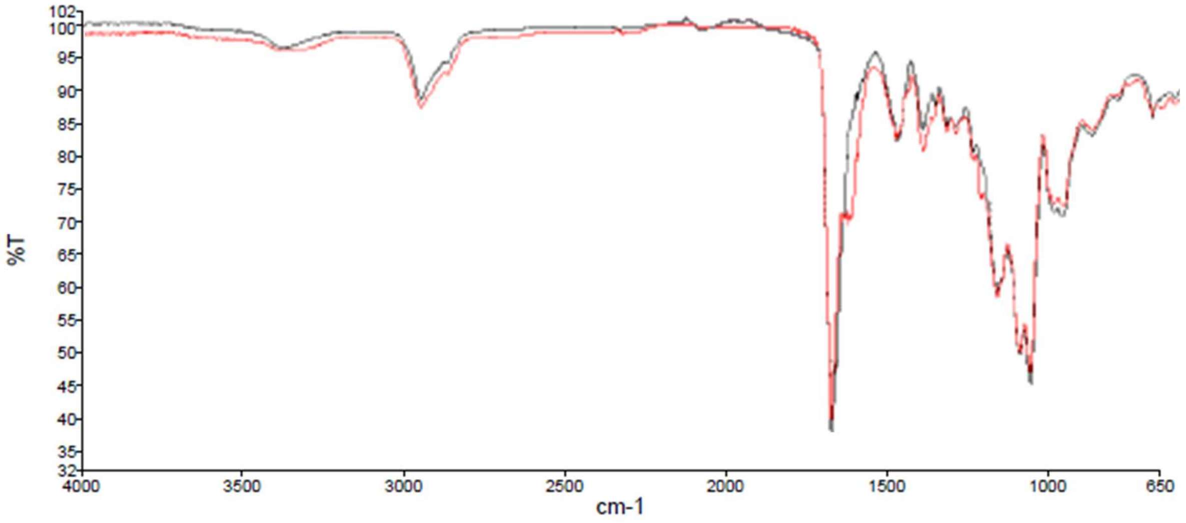


Figure 6.7 Polyester based polyurethane possible degradation compounds [16].

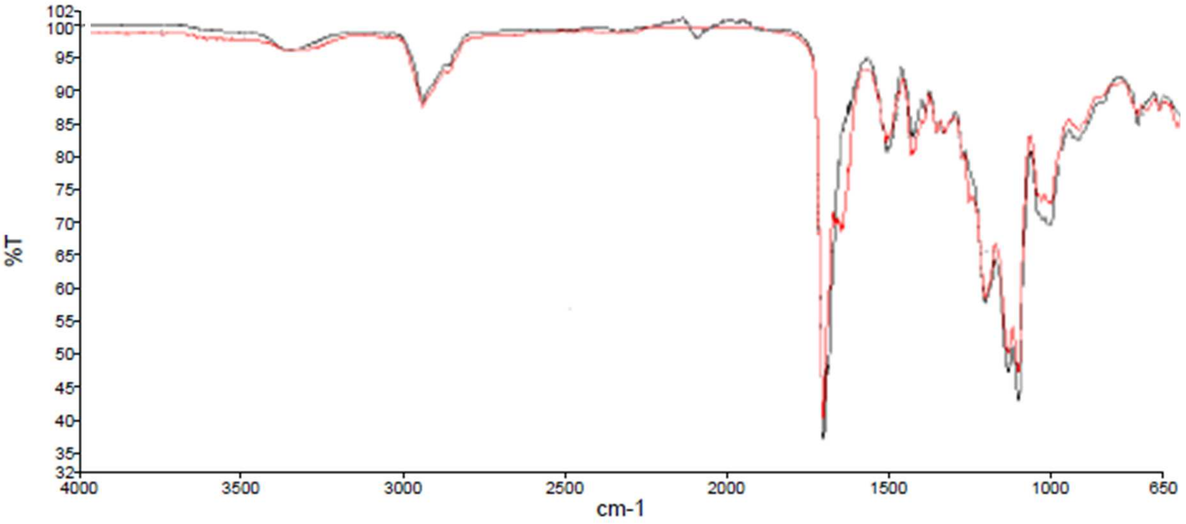
A FTIR study has been also carried out to identify the different new functional groups generated during the polyester based polyurethane ageing degradation, and to confirm the differences observed in the specimen test appearance. In Figure 6.8 are shown the FTIR spectra recorded of the polyester based polyurethanes specimen test before and after being exposed to the accelerated ageing study in black and red respectively.



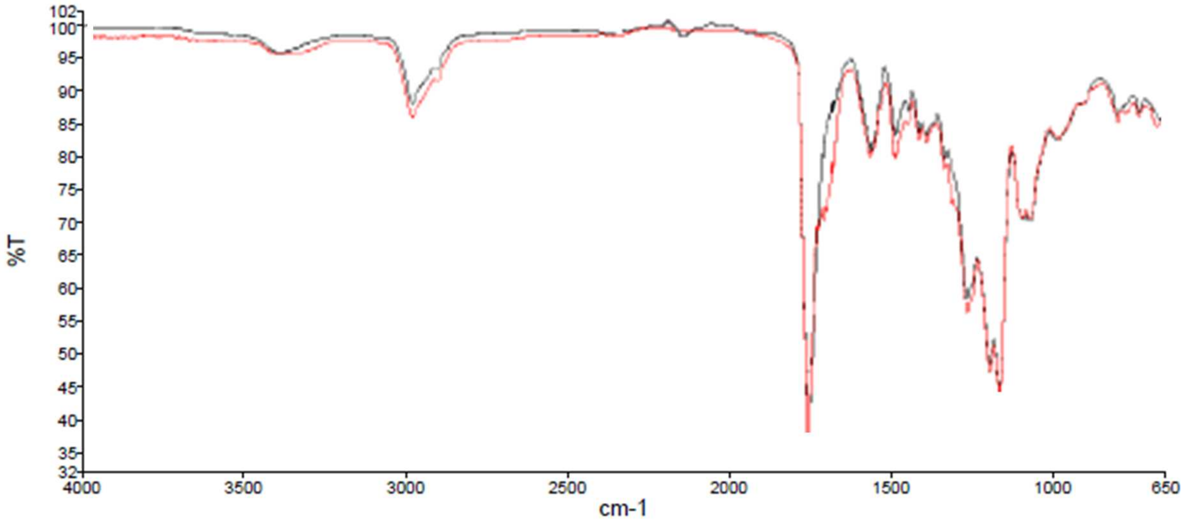
PU + 2% CDI R11



PU + 5% CDI R11



PU + 2% CDI R12



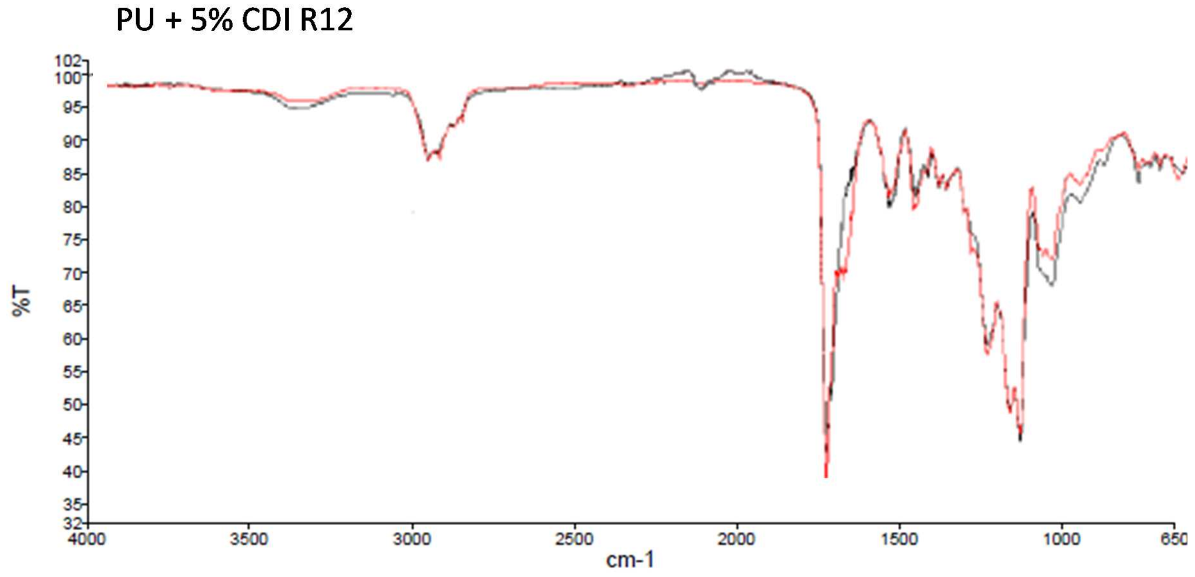


Figure 6.8 FTIR spectra recorded of the polyester based polyurethanes specimen tests before (black) and after (red) being exposed to the accelerated ageing test.

In the initial FTIRs registered before exposition of the specimen test, are clearly identified in all the samples the carbonyl absorption band at 1720 cm^{-1} and the N-H absorption band at 3360 cm^{-1}. These two signals are the polyurethane basic signals corresponding to its principal functional group, the urethane. In addition, signals at 2950 cm^{-1} and 1300-1200 cm^{-1} are assigned to the C-H stretching band and to the ester group corresponding to the alkyl chain of the polyester diol used. Polyester also contributes to the carbonyl signal.

The main differences observed are caused by the addition of the carbodiimide oligomer. Carbodiimide group (-N=C=N-) is identified at 2120 cm^{-1}. The intensity of this absorption band is higher in the specimen test with 5% of carbodiimide addition.

After 200 hours of ageing test exposition, the reference sample with no carbodiimide added, shows the bigger differences. An increase in the absorption band at 3360 cm^{-1} is shown, which correspond with the hydroxyl and carboxyl new groups generated during the degradation of the polyester based polyurethane non doped sample. Moreover, the absorption bands at 1300-1200 cm^{-1} have been decreased. It could be explained by the polyester chain degradation, which have been transformed into carboxyl and hydroxyl groups. The signal present at 1590 cm-1 which is assigned to the N-H bending signal has been also increased due to the polyurethane degradation.

Contrary, the samples with carbodiimide added, shows a slightly increase in the absorption band present at 1670 cm^{-1} which is assigned to the C=N absorption band of the O-Acylisourea. This compound is formed by the reaction between carbodiimide and carboxyl group. The transformation of the carboxyl groups formed decrease the degradation kinetics. In addition, the absorption band initially present at 2120 cm^{-1} which is assigned to the carbodiimide group, disappears after the test exposition and indicates its transformation. The new band appeared corresponding to C=N signal, the disappearing of the N=C=N signal, and the non-increasing absorption band at 3360 cm^{-1} (which corresponds to the amine and carboxyl absorption band), demonstrate that carbodiimides act as a polymer stabilizer transforming the degradation byproducts formed. The result is a stable product which maintains its structure [17, 18] .

No differences are appreciated between the different carbodiimide doped samples in the FTIR study. All FTIR spectra registered are similar and shows the same effects of the carbodiimide over the carboxyl group.

In addition to the appearance and the FTIR study, the traction mechanical properties study has been also carried out in the specimen test prepared before and after being exposed to the accelerating ageing test. In Table 6.3 are shown the obtained results.

Table 6.3 Traction test results of each polyurethane specimen test before and after being exposed to accelerating ageing test.

Sample	**Traction strength (MPa)**		**Traction elongation (%)**	
	Before	**After**	**Before**	**After**
PU Reference material	30.2	*	750.2	*
PU + 2% R11	38.6	29.3	710.0	708.5
PU + 5% R11	40.5	35.2	706.7	710.2
PU + 2% R12	37.4	33.1	715.7	716.4
PU + 5% R12	41.8	35.9	698.8	704.5

*specimen test completely degraded.

Comparing the values obtained before being exposed, it can conclude that the carbodiimide oligomer addition produces an increase in the maximum of the traction strength and a slightly decrease in the elongation percentage values which means that a more rigid product has been obtained once carbodiimide has been added to the polyurethane system. This mechanical properties changes are caused by the difference in the volume present between polymer chains once carbodiimide is added.

As is seen in Figure 6.2, the totally degradation of the reference specimen test makes impossible to make the traction test after the exposition. Contrary, specimen tests with carbodiimide sample added, maintains the mechanical properties after 200 hours of exposition independently of the carbodiimide amount used.

All the results shown, manifests that working with carbodiimide oligomers between 1200 and 700 Da, its distribution in the polyurethane chain do not affects to the final application. The only variable that affects to the final stability result is the amount of carbodiimide groups present in the tested system which are able to react and to stop the hydrolytic degradation. This variable only affects to the color appearance of the specimen, because the mechanical properties remains constant by using both 2 and 5% of carbodiimide sample.

The prepared carbodiimide oligomer by following the optimized synthesis process are able to be used as polyester based polyurethanes stabilizing agents. In addition, the use of TMXDI as a precursor monomer allows to obtain stable water dispersion carbodiimide doped polyurethanes.

6.1.1.2 Final polyurethane leather application

Cromogenia Units has its most important business in the products for leather treatment. The standard polyester based polyurethane doped with carbodiimide which has demonstrated good stability properties in section 6.1.1.1, has also been tested in a final leather application as a coating.

In order to know how the molecular weight of the carbodiimide oligomer samples used affects to this final leather application, the PU reference sample, the PU + 2% CDI R12 and PU +5% CDI R11 has been tested.

The leather samples prepared were exposed to the fastness test which is detailed in section 3.4.2.5. The results obtained are shown in Figure 6.9.

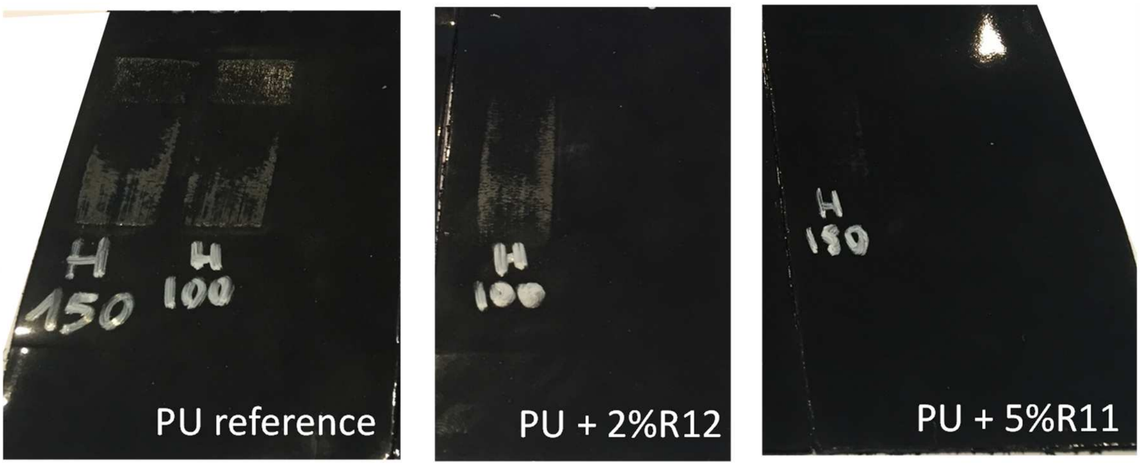


Figure 6.9 Leather samples after fastness test.

Observing the final leather results, it can conclude that the incorporation of carbodiimides increases the mechanical resistance to fastness. The reference sample is degraded after 100 cycles and even more after 150 cycles. The addition of 2% of R12 to the initial polyurethane, slightly increase the resistance after 100 cycles obtaining a less degraded leather. Once more amount of carbodiimide groups are added to the sample, the mechanical resistance is highly increased obtaining a non-degraded leather sample after 150 passes. The properties improvement can be explained for the more rigid polyurethane sample obtained once carbodiimide oligomer are added to the matrix (see Table 6.3).

Fastness test do not produces chemical degradation to the leather sample to force carbodiimide to react, however, the mechanical properties changes produced by its addition and the extra stability shown against yellowing and chemical degradation, makes this developed carbodiimide oligomers very suitable to be applied in final leather applications.

Moreover, as seen in section 6.1.1.1, the molecular weight of the oligomer do not affects to the leather application. The most important factor is the amount of carbodiimide oligomer added to the final sample.

6.1.2 Functionalized carbodiimide oligomers for polyurethane applications.

During this doctoral thesis development, has been appeared the necessity to reproduce some products present in the market, which have the polyurethane chemical field as its final industry application. The mentioned product is used in the solid polyurethane industry to produce thermoplastic pieces destined to be exposed outdoor.

Knowing the initial product specifications, a new functionalization of the carbodiimide oligomer has been designed in order to increase the final standard product activity. The initial product specifications are as follows:

- Isocyanate content: <0.1%
- Viscosity at 25ºC: 1000 – 6000 cPs
- Solid content: 45 -50%
- Carbodiimide content: 6%

The functionalizing compound used to increase the final product activity was named "CDI MODIFIER COMPOUND" and Cromogenia Units wants to maintain it under industrial secret. This product allows Cromogenia Units to enter in this exclusive market. For this reason is wanted to preserve the chemistry of this compound used.

CDI MODIFIER COMPOUND is used once the carbodiimide oligomer synthesis is finished and its isocyanate and carbodiimide activity are checked. The main function of this compound is to react the isocyanate content present in the sample to maintain the initial product specifications.

Sample R13 was prepared by using the optimized synthesis process used for R6 preparation in order to maximize the molecular weight obtained and to increase as maximum as possible the carbodiimide content. After the CDI MODIFIER COMPOUND functionalization, the FTIR spectrum was performed (Figure 6.10) in order to check the final isocyanate content.

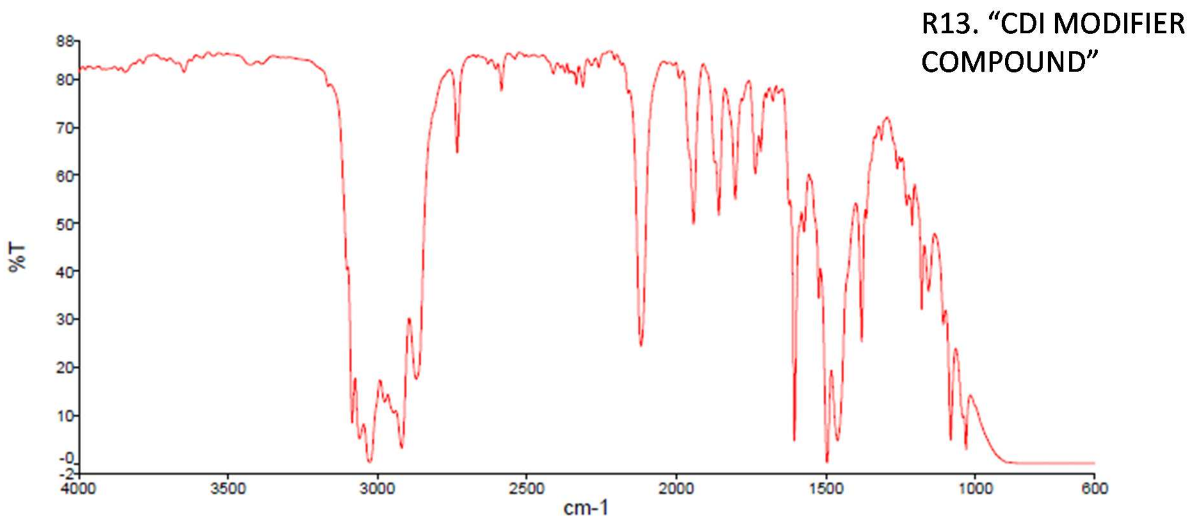


Figure 6.10 FTIR spectra of sample R13 after functionalization.

The FTIR spectrum shows as usual, the toluene and the C-H stretching bands, and the carbodiimide characteristic absorption band at 2120 cm^{-1}. The functionalization reaction has been carried out correctly because no isocyanate band has been identified.

The use of this modifying compound is required to increase the activity. In Table 6.4 are shown the results of the sample R13.

Table 6.4 Isocyanate and carbodiimide content of R13 functionalized sample.

Sample	Final NCO (%)	Final NCN (%)
R13	0.02	19.16

The final carbodiimide content value obtained, is very similar to the value obtained for sample R9 by preparing the carbodiimide oligomer applying high temperatures. However, in the R9 sample, no carbodiimide signal has been identified in the final FTIR spectrum due to the presence of uretonimine multibranched structures. In the R13 sample, carbodiimide absorption bands are observed.

Once the oligomer is well functionalized, the dilution step is started. As for samples R11 and R12; R13 also requires the use of solvent to obtain a workable product at room temperature. In this case, the final application needs the use of a non-toxic solvent with a high boiling point for this reason lauryl benzoate is used. By using this solvent the carbodiimide oligomer R13 is diluted until 45% of solids content. In Table 6.5 are shown the results obtained compared with the reference product.

Table 6.5 Final properties of sample R13 compared against the reference product.

Properties	R13	Reference product
Appearance	Light orange	Light orange
Isocyanate content (%)	0.02	<0.1
Viscosity 25ºC (cps)	670	1000-5000
Solid content (%)	45.1	45 - 50
Carbodiimide content (%)	8.63	6

Observing the final results obtained for sample R13 a similar product with a slightly higher activity has been performed. In order to check the final application of the product, the obtained carbodiimide oligomer was tested by a final customer by using it in a polyurethane formulation and compared with a reference product. A hydrolysis test has been carried out during 3 weeks, at 70ºC and 95% of relative humidity and traction tests were performed each week. In Figure 6.11 are detailed the obtained results.

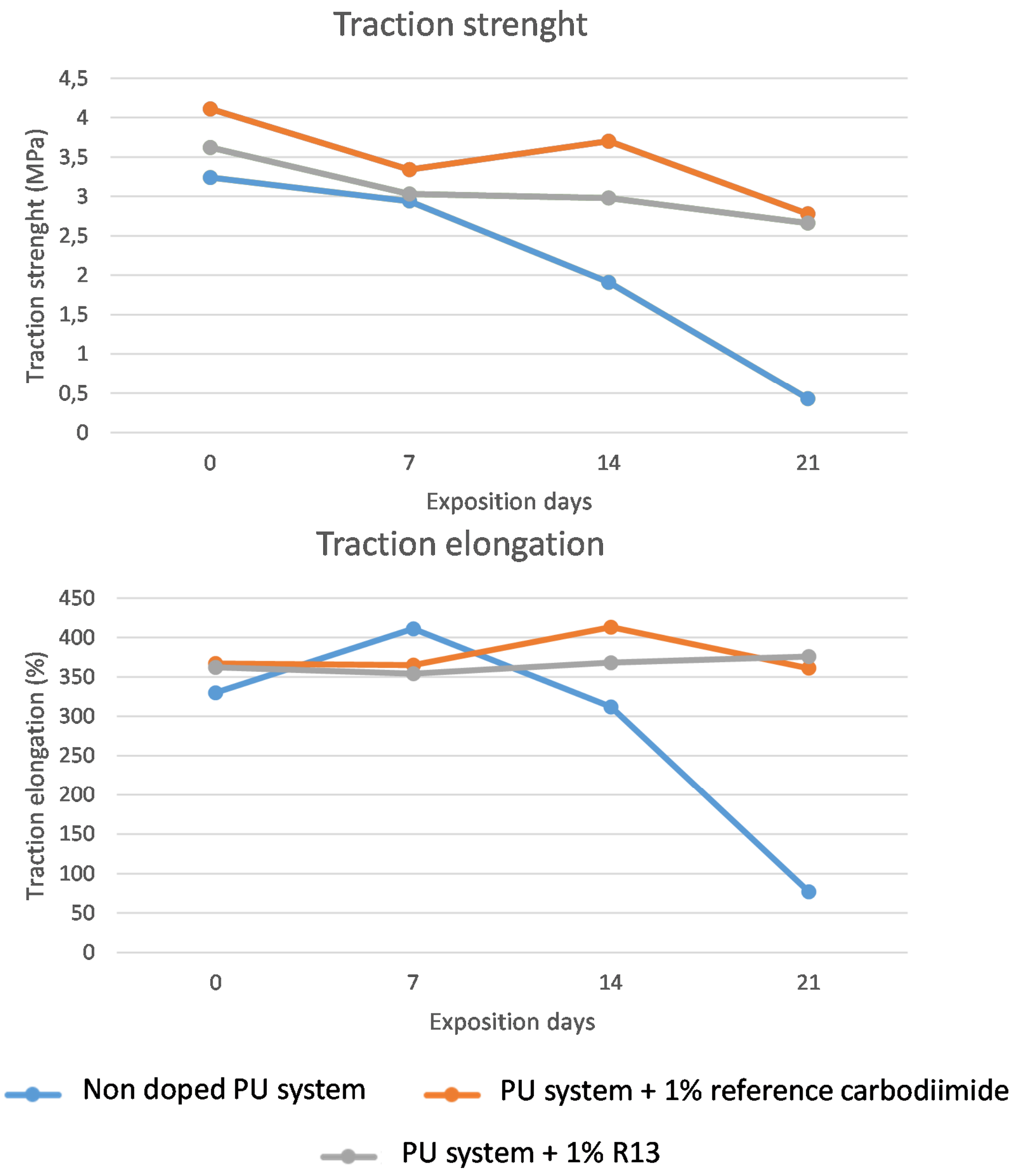


Figure 6.11 Traction test results performed on PU formulation by using R13 and a carbodiimide reference product.

In the same way than for the polyester based polyurethane tested, the addition of carbodiimide to this new polyurethane system also increases the traction strength, making the specimen test less rigid, as was seen in the first polyurethane test. However, in this new polyurethane system, the carbodiimide addition seems to act as a plasticizer due to the slightly higher initial elongation values.

The different values obtained in the traction test are caused by the different polyurethane system used and the different specimen test prepared by the costumer.

Results shows similar performances of R13 compared to the reference carbodiimide used by the costumer. The un-doped polyurethane specimen test shows a high decrease of the mechanical properties after 2-3 weeks of exposition. Nevertheless, the addition of carbodiimide to the polyurethane system, as seen in the first test, improves the hydrolysis resistance maintaining the mechanical properties. It also can be explained by the reaction activity of the carbodiimide groups against the degradation groups generated.

Even having more carbodiimide content, similar results have been obtained in the test conditions. Probably if the conditions tests are stronger, higher difference will be achieved between the carbodiimide samples.

Comparing both products tested, R13 can be used as a substitute of the reference carbodiimide sample, with a more potential stability activity due to its higher carbodiimide content.

6.2 VINYLIC SYSTEM APPLICATION

Vinylic systems are a wide field which englobe all the polymers prepared by using monomers containing one or more than one terminal double carbon-carbon bond. The most used vinylic monomers are acrylic and methacrylic acid and acrylamide [19].

This kind of polymers are synthetized by a free-radical polymerization process where the polymer is formed by the successive addition of free-radical building blocks. Initiation is the first step of polymerization process. In this case, an active center is created from which the polymer chain is generated. Initiation has two differentiate steps; in the first one, one or two radicals are created from the initiating molecules, and in the second step these radicals are transferred from the initiation molecules to the monomer units present [20].

These free radicals can be formed by different types of initiators, and the most important are thermal decomposition, photolysis, persulfates, redox system and radiation [21].

Once the monomers are initiated, the propagation step starts until a non-radical monomer is added. In Figure 6.12 is shown the reaction synthesis scheme for this kind of polymers.

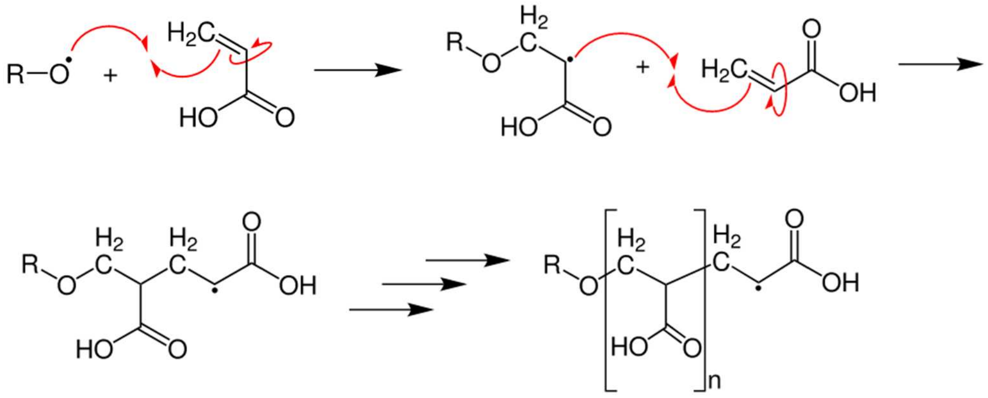


Figure 6.12 Free-radical polymerization scheme [19].

This kind of polymers are also used in a wide variety such as construction, water treatment, cosmetics, textile, coating, and others.

Knowing the polymerization mechanism in vinylic systems, is necessary to functionalize the carbodiimide oligomer prepared in order to include it in the vinyl polymer chain. The functionalization process is the same than the commented for polyurethane systems but using a different functionalizing compound to give the desired functionality to the oligomer.

To include carbodiimide oligomers in vinyl systems is required a bifunctional compound with vinyl functionality and another group with a very high isocyanate reactivity. The most suitable compound which has all the requirements is 2-hydoxyethyl methacrylate (HEMA). It has the vinyl function and the hydroxyl group which link the oligomer to the desired activity. Moreover HEMA is a common industrial product easy to obtain. In Figure 6.13 is shown the HEMA structure.

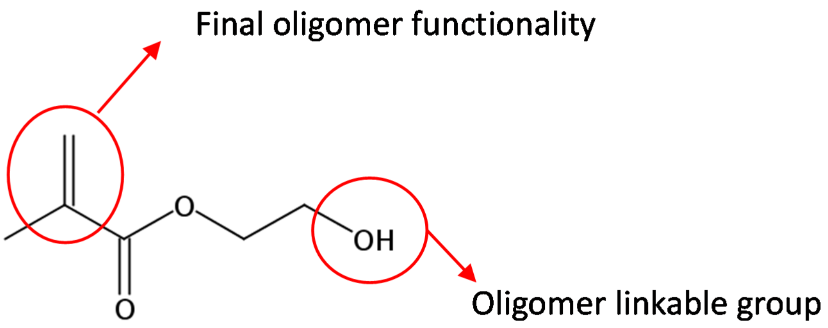


Figure 6.13 HEMA chemical structure.

HEMA has a boiling point of 189ºC [13], which permit its functionalization reaction against the isocyanate group at 80ºC with no product loss risk and maintaining the oligomer base liquid to improve the homogeneity of the reaction mixture. 80ºC is the optimum temperature to carry out the reaction between the isocyanate and the hydroxyl group to form the urethane group [9] which links the oligomer to the final desired functionality.

Once the product is functionalized, a dilution is again required to obtain a workable final product at room temperature. The solvent must be inert and must be as least toxic as possible. One of the most used applications of this kind of products is the extrusion pieces elaboration. Dipropylene glycol dimethyl ether is a very suitable solvent for this kind of applications.

A carbodiimide application study in vinylic systems has been carried out by studying the mechanical and surface properties of polypropylene (PP) extruded materials, with and without carbodiimide oligomers included in the final chemical structure before and after being exposed to different conditions.

To perform the study, new carbodiimide oligomer samples have been prepared by using the R6 optimized synthesis process. Finally the oligomer base obtained were 50% and 100% functionalized by using different amounts of HEMA, obtaining two final samples R14 and R15 respectively. Finally, both R14 and R15 sample were diluted until 40% solid content by using dipropylene glycol dimethyl ether. In Table 6.6 are detailed the final characteristics obtained for samples R14 and R15.

Table 6.6 Final characteristics obtained for R14 and R15 samples.

Properties	R14	R15
Appearance	Light yellow	Light yellow
Isocyanate content (%)	2.2	0.03
Viscosity 25ºC (cps)	560	785
Solid content (%)	40.03	39.78
Carbodiimide content (%)	6.52	6.16

R14 and R15 samples were prepared by using the same base oligomer. By using the R6 synthesis process, a molecular weight of 1150 Da is obtained. The difference observed in the carbodiimide content is caused for the different functionalization percentage. Viscosity also shows higher values once the oligomer is highly functionalized.

Once carbodiimide samples are prepared, the polypropylene (PP) test specimens are prepared by including 1% by weight of the carbodiimide samples R14 and R15. Procedure to prepare the specimen test is detailed in section 3.2.2.2.

The main objective of this test is to study the performance of the carbodiimide inclusion in a vinyl system. These systems, concretely thermoplastics, are very stables to degradation due to its carbon-carbon structure. For this reason, lower amounts of carbodiimide are used. In addition, the effect on the functionalization degree, which affects to the inclusion and the compatibility of the carbodiimide oligomer and the system has been also studied by using R14 and R15 samples.

The specimen test prepared to be exposed are as follows:

- PP (used as reference material).
- PP + 1% carbodiimide R14 (50% functionalization).
- PP + 1% carbodiimide R15 (100% functionalization).

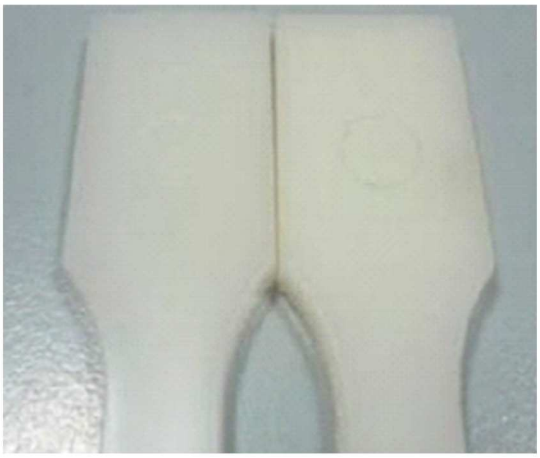
6.2.1 Accelerated climate cycles test.

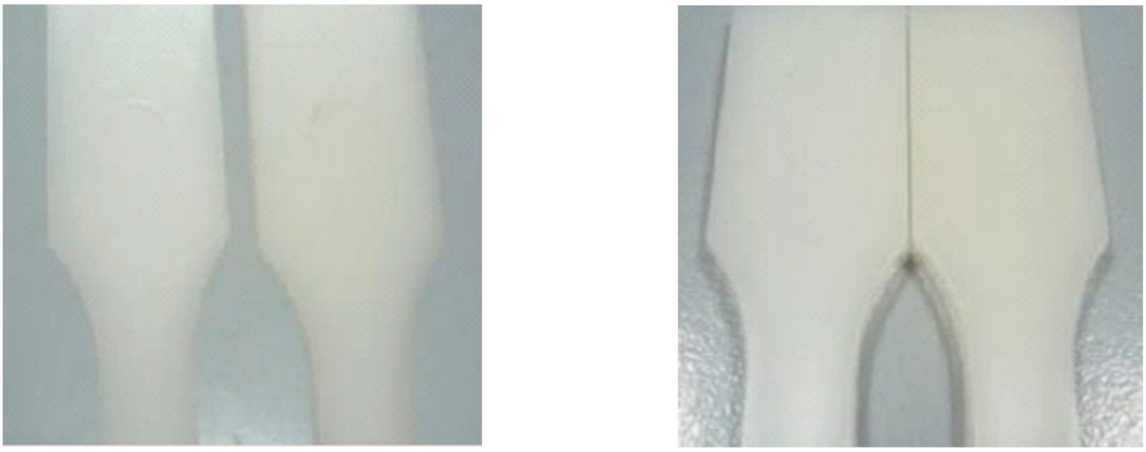
First of all, the specimen test prepared was exposed to a climate cycles accelerated test exposing the samples to different temperature and humidity cycles as is detailed in section 3.4.2.1. Knowing the high thermal stability of polypropylene, this soft test is initially carried out in order to check both if carbodiimide are compatible with the polypropylene matrix and if its addition produces any stability improvement. After the ageing test, specimen test exposed were characterized to evaluate its resistance. Appearance, FTIR analysis and mechanical properties studies were carried out to analyze the carbodiimide behavior in the polypropylene system.

6.2.1.1 Appearance evaluation

In Figure 6.14 are shown the specimen tests after 14 cycles of climate cycles exposure. Specimen tests on the left are the initial samples without being exposed, and the samples to the right are the samples after 14 climates cycles exposition.

PP reference material





PP + 1% R14

PP + 1% R15

Figure 6.14 Polypropylene specimen tests before (left) and after (right) being exposed to climate cycles test.

Observing the pictures obtained after the test, all samples maintains its structure. The reference specimen shows more yellow color after the test. This effect is slightly observed in the specimens with carbodiimide added. However, the 100%

functionalized sample (R15), shows lower yellowing effect. This fact indicates the importance to do a correct functionalization of the sample to improve the final application results. In addition, little cracks as degradation effects are observed in the reference material without carbodiimide addition caused for the degradative processes which weaken the sample (see Figure 6.15).

PP un-additived

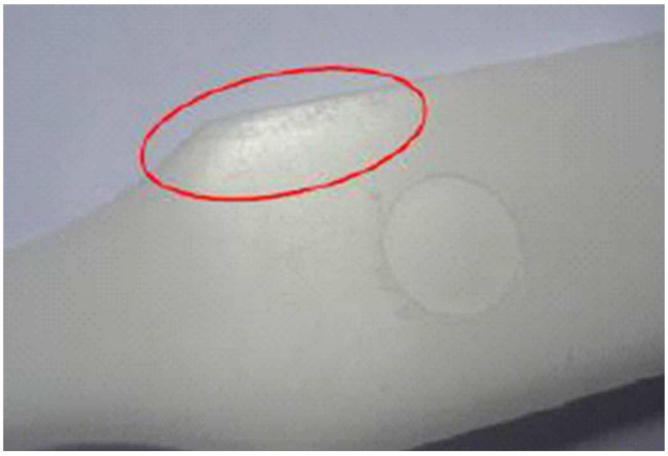


Figure 6.15 Amplified picture of the polypropylene reference specimen after the climate cycles test exposition.

The amplified picture shows the slight cracks appeared in the reference material. This surface degradation is not so high, but it do not appears once carbodiimide is applied.

The yellowing effect and the surface cracks are caused by the initial, soft and superficial degradation processes caused during the ageing test. These polypropylene degradation processes are caused by heat and moisture. Oxidation is the most common polypropylene degradation mechanism, and usually occurs at the tertiary carbon atom present in every repeat unit. A free radical is formed here, and then reacts further with oxygen, followed by chain scission to yield aldehydes and carboxylic acids (see Figure 6.16) [22, 23]. For this reason an easy manner to check if polypropylene has been degraded, is to follow the carbonyl signal [24]. Observing the specimen tests, a very slightly degradation has been produced by using the soft climate cycles test. Nevertheless, the carbodiimide addition has been improved the yellowing effect.

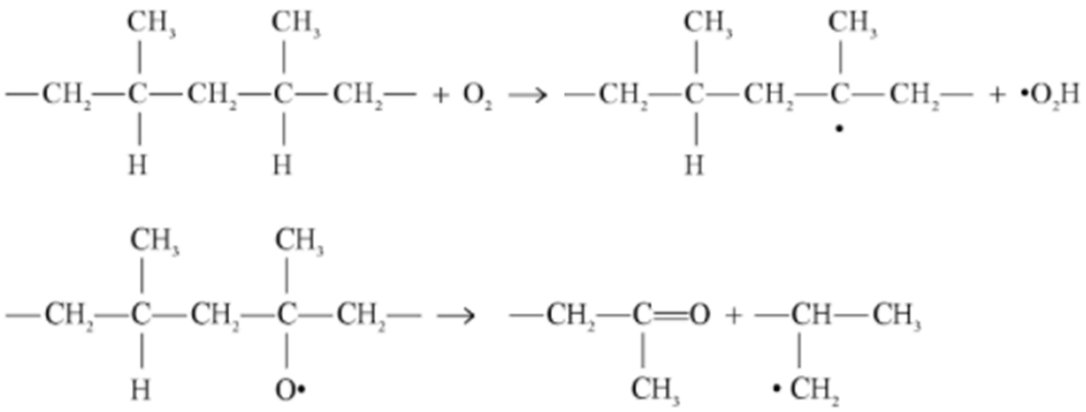
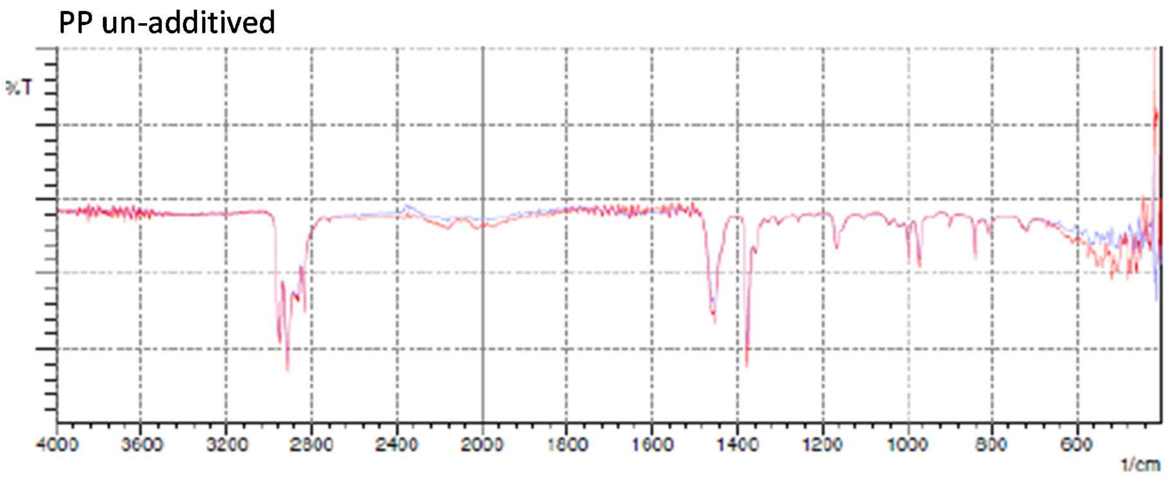
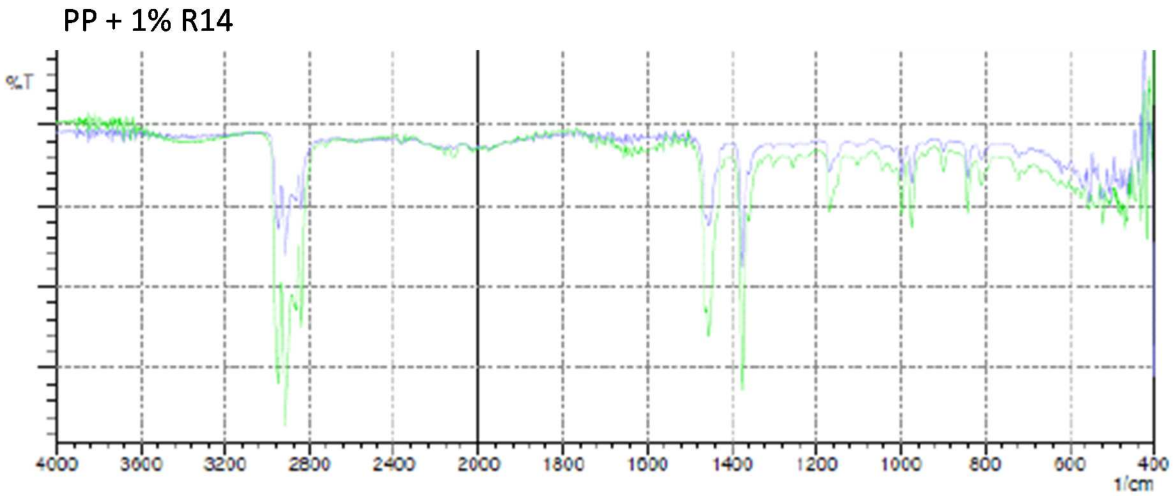


Figure 6.16 Polypropylene oxidation scheme [22].

6.2.1.2 FTIR study

FTIR spectra of the specimen tests were performed before and after being exposed to the climate cycles test in order to observe if any degradation evidence were detected. The FTIRs spectra registered are shown in Figure 6.17.


PP un-additived


PP + 1% R14

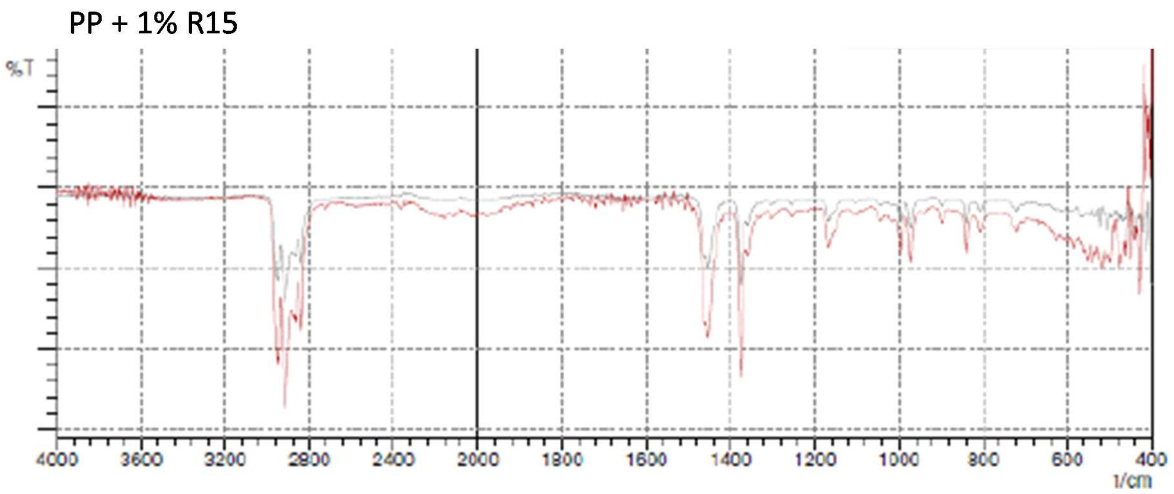


Figure 6.17 FTIR spectra of the polypropylene specimen tests before and after being exposed to climate cycles test.

The FTIR spectra recorded do not shows difference between the exposed and the un-exposed samples. All FTIR spectra are very similar, and it is possible to identify the C-H stretching and bending at 3000 cm^{-1} and 1400-1500 cm^{-1} respectively [18, 25]. The low amount of carbodiimide sample added in the doped samples makes difficult its FTIR identification.

Specimen tests after being exposed shows slightly appearance degradation effects, which cannot be detected by using FTIR technique. The humidity and temperature cycles applied during this ageing test, are not aggressive enough to show clear degradation evidences, which corroborates the high thermal stability of this kind of structures. In addition, the carbodiimide oligomer inclusion to the polypropylene matrix have been shown a slightly yellowing improvement which indicates that both compounds are compatible, even more once highly functionalized are the carbodiimide oligomer.

In order to study the carbodiimide addition effect is necessary to expose the specimen test to another more extremely ageing assay and to increase the exposure time. The structures with carbon-carbon bonds, like polypropylene, are very stable, for this reason more aggressive conditions assays are required to finally detect degradation side products.

6.2.2 UV light test resistance

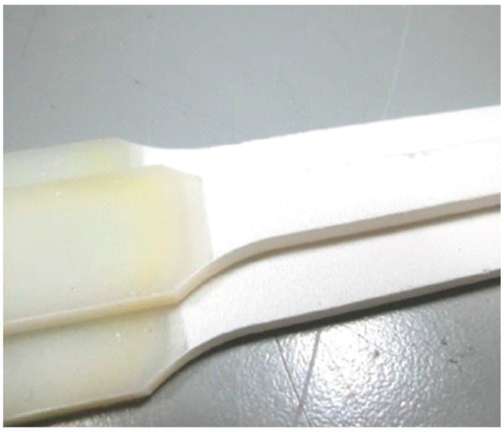
In order to force the degradative processes in the different polypropylene samples, new specimen tests were prepared to be exposed to an UV light test. This test include the UV samples radiation in addition to temperature exposition. UV light added to high temperature promotes easier the degradation processes in very stable products like polypropylene. Time exposure has been increased until 1000 hours. The test conditions are detailed in section 3.4.2.3.

Appearance, molecular structure analysis by FTIR, surface analysis by SEM and mechanical properties study were carried out before and after the UV ageing test exposure of the polypropylene specimen test. Results are shown in the following sections:

6.2.2.1 Appearance evaluation

Figure 6.18 shows the specimen tests appearance after 1000 hours exposed to the UV light test.

PP un-additived



PP + 1% R14

PP + 1% R15

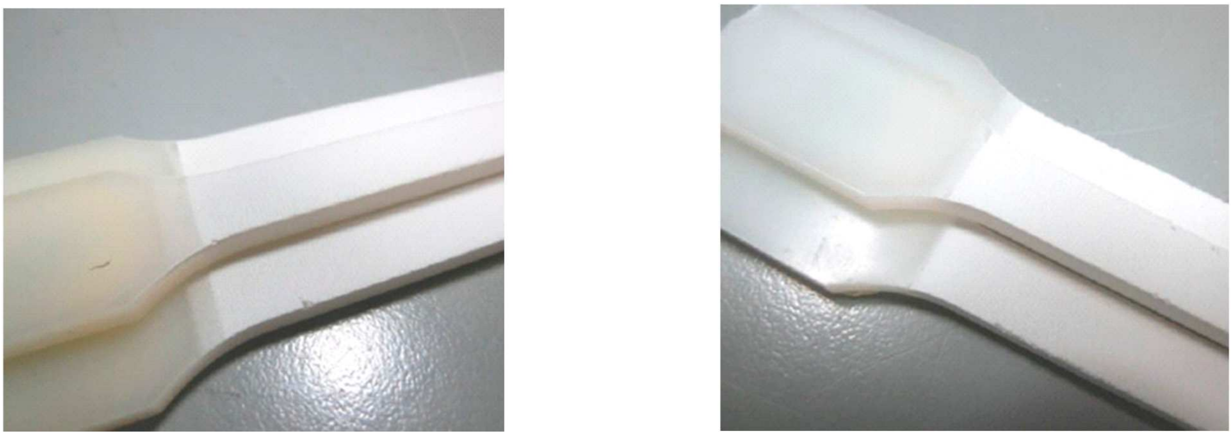


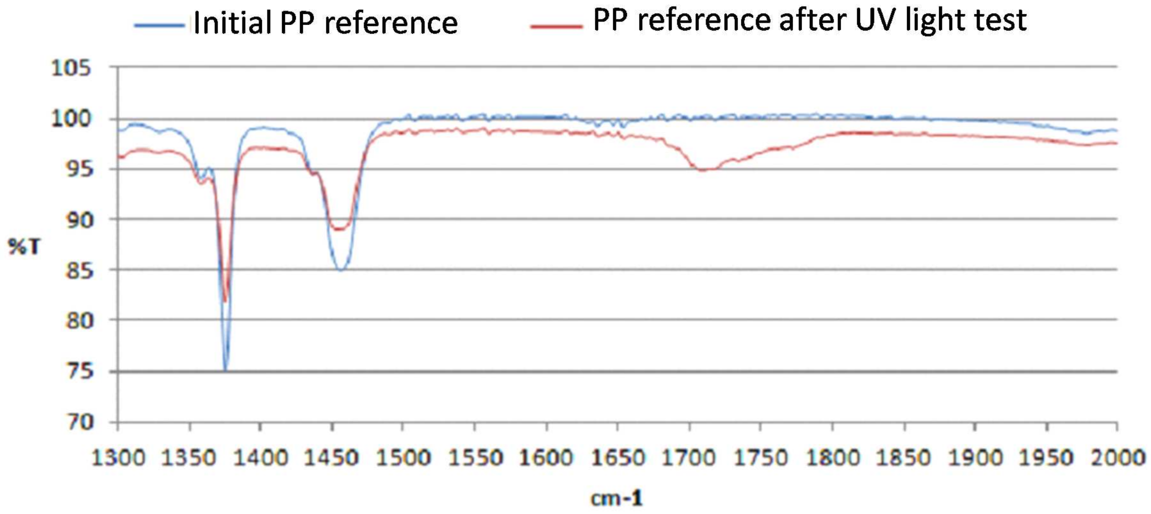
Figure 6.18 Polypropylene specimen tests after 1000 hours of UV light test exposition.

All samples exposed, doped or not with carbodiimide, presents high appearance degradation effects after 1000 hours of exposition to UV light test. Probably the exposition time needs to be reduced to observe differences. The most degraded specimen test part shows a white opaque appearance. Nevertheless, differences are observed in the terminal parts of the samples. In Figure 6.18 is observed that the reference material without carbodiimide addition presents the most yellow appearance on its terminal zones. Comparing specimen doped with R14 and R15, more yellowing appearance is observed once less functionalized carbodiimide is used. This situation shows that the UV light test can degrade this kind of samples. Moreover, carbodiimide addition has shown a good performance, decreasing yellowish processes in a larger scale than the observed in the climate cycles test.

In order to study how carbodiimides can avoid or decrease this kind of degradation processes, FTIR, SEM and mechanical assays has been also carried out.

6.2.2.2 FTIR study

FTIR spectra were recorded before and after the UV light ageing test in order to identify new functional groups generated by degradation processes. Figure 6.19 shows the registered spectra of the specimen tests. The spectra are focused in the range of 1300 to 2000 cm^{-1} because no changes were detected in other wave lengths.



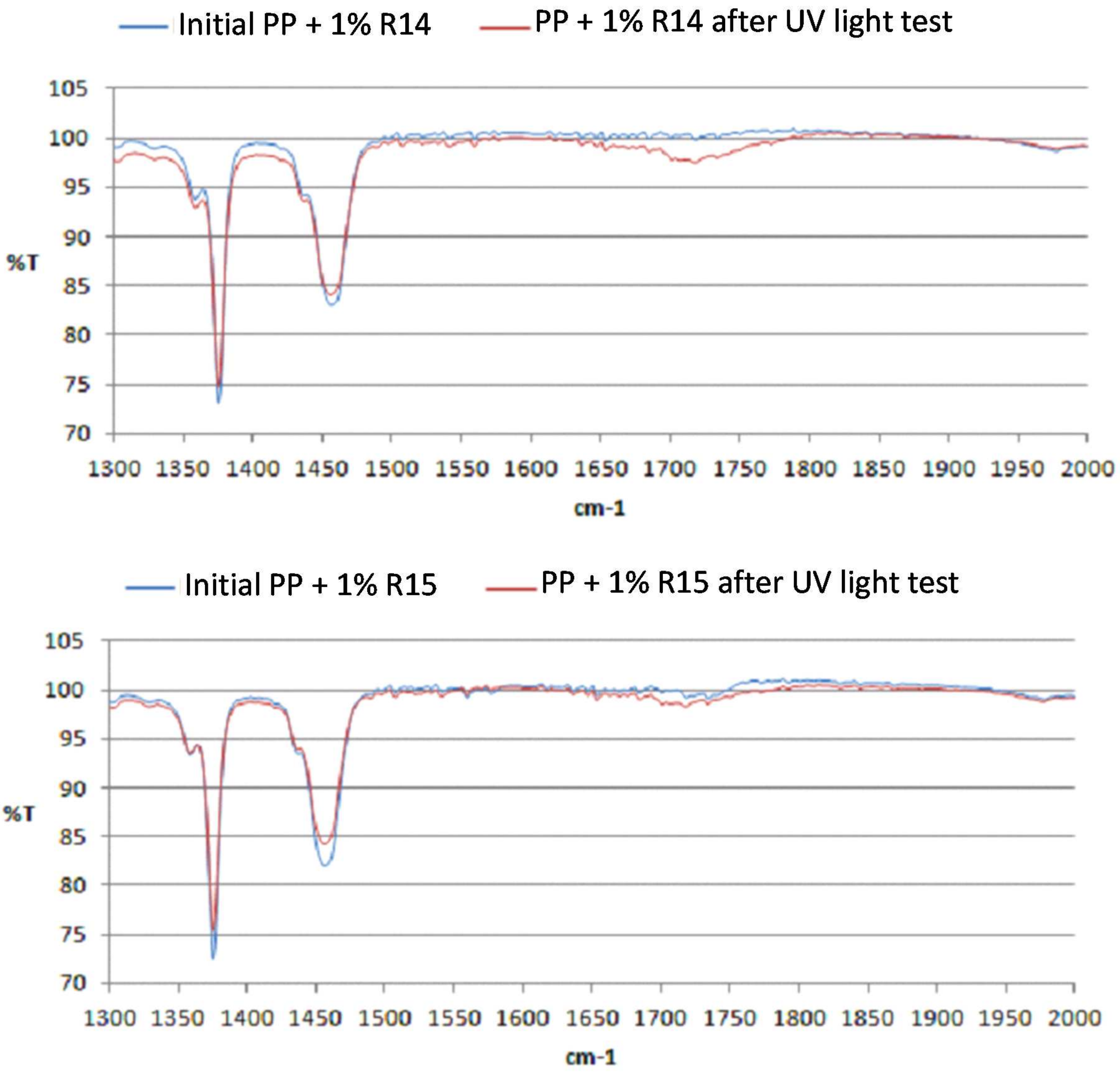


Figure 6.19 FTIR spectra of polypropylene specimen tests before and after being exposed to 1000 hours of UV light test.

FTIR study shows clear differences between all the specimen tests. As commented in the appearance evaluation, UV light can degrade the polypropylene samples. UV irradiation causes an oxidative degradation in the material. This kind of oxidizing processes are caused for the presence of tertiary carbons in the polypropylene structure which are finally oxidized in presence of UV radiation generating carbonyl groups which precede to form aldehydes and carboxyl groups. The study of the evolution of the carbonyl absorption band shows the evolution of the degradation processes in each sample test.

The FTIR spectra obtained shows a reduction in the absorption bands at 1400-1350 cm^{-1} and at 1500-1450cm^{-1} which corresponds to the groups (-CH_3) and (-CH_2-CH_3) respectively, indicates a reduction in the tertiary carbons. A new band appears after the UV light test exposition at 1720 cm^{-1} which is assigned to the carbonyl group generated by the degradation processes caused for the UV light incidence.

In the polypropylene reference specimen FTIR spectrum after UV light test exposition, are shown a higher carbonyl absorption band compared against the samples with carbodiimide included. In the specimens doped with carbodiimide, carbonyl band are also observed with less area contribution in the case of using the 50% functionalized sample (R14), and is practically inexistent in the case of using the 100% functionalized sample (R15).

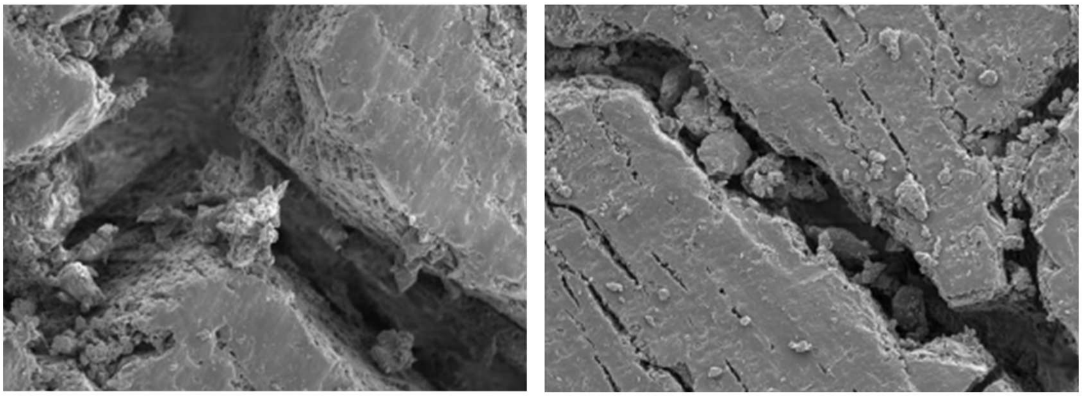
The FTIR results show that polypropylene can be stabilized against degradation by using carbodiimide. The inclusion of this functional group in the system allows to decrease the degradation by reacting the new groups generated. Carbodiimide acts as a connecting chain once polypropylene is degraded and chain scission is produced. For this reason highly functionalized carbodiimide sample produces a better stabilization, which has been confirmed by both appearance and FTIR study.

6.2.2.3 SEM study

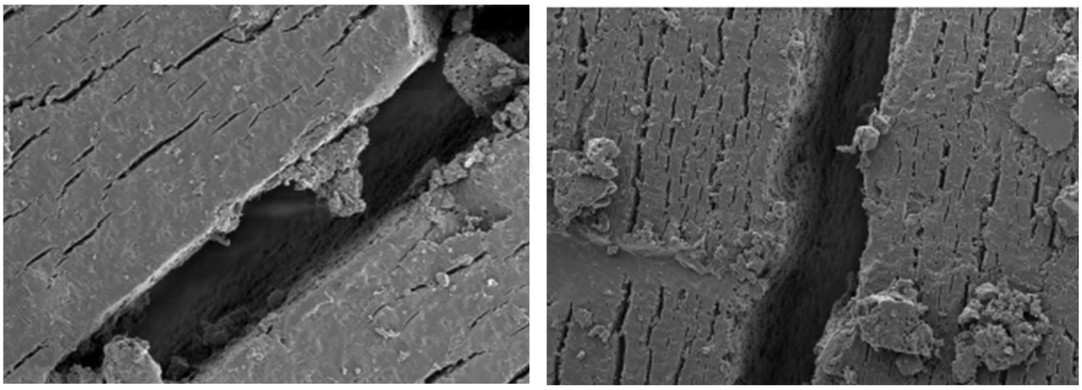
Once at molecular scale it is probed that there has been appreciable changes caused by degradation processes, the different specimen tests has been also characterized by SEM. The micrographs recorded shows the surface differences after 1000 hours of UV light tests exposition.

In Figure 6.20 are shown the micrographs acquired at 50 µm of the different polypropylene test samples after being exposed during 1000 hours to the UV light test.

PP reference material



PP + 1% R14



PP + 1% R15

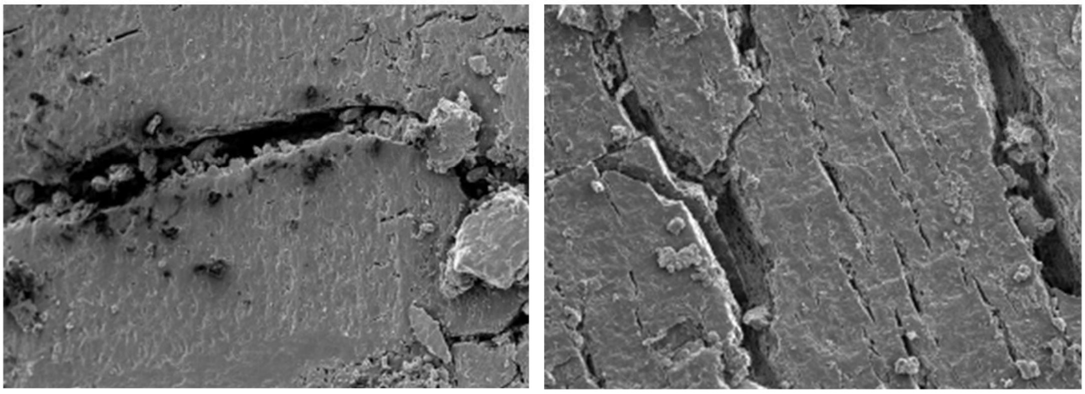


Figure 6.20 SEM micrographs of the different polypropylene specimen samples after 1000 hours of UV light test exposition.

The micrographs shows degradation points in the material surface. The polypropylene reference material which is the sample without carbodiimide addition, has the most degraded surface with a more irregular appearance and higher size of the degraded zones. Comparing the specimen with carbodiimide added, the sample with the 50% functionalized carbodiimide (R14) shows a higher degraded surface with larger and deeper cracks than the polypropylene sample prepared with R15 (100% functionalized carbodiimide). This last sample present slightly superficial degradation, as has been seen in the FTIR study.

Sample R15 has better compatibility with the polypropylene system than R14 due to its totally functionalization. The better incorporation to the final matrix improves the resistance to degradation caused for external agents as temperature, humidity and UV rays. The new compounds and groups formed during the degradation processes as had been seen in polyurethane system, are neutralized or reacted with the carbodiimide groups present decreasing the harmful effect and maintaining the polymer structure.

6.2.2.4 Mechanical properties study

Before and after expose the specimen test to the different ageing test, the same mechanical properties study than in the polyurethane system application were performed. The results are shown in Table 6.7.

Table 6.7 Traction test results of each polypropylene specimen test before and after being exposed to UV light test.

Sample	**Traction strength (MPa)**		**Traction elongation (%)**	
	Before	**After**	**Before**	**After**
Reference material	20.78	11.85	6.74	3.12
+ 1% R14	22.71	15.28	7.51	5.53
+ 1% R15	22.75	16.21	7.76	5.97

The introduction of 1% of carbodiimide into the polypropylene system decrease the Young Module and increase the traction resistance. The new compounds prepared, presents less rigidity than the un-doped polypropylene sample, which is also observed in the elongation percentage. The carbodiimide incorporation acts as a plasticizer and the functionalization degree of the used sample slightly affects to the mechanical properties, obtaining a less rigid product once the totally functionalized carbodiimide (R15) is added, which means that a better compatibility is achieved between sample and matrix.

The mechanical properties performance has shown that carbodiimides are compatible with the polypropylene system. This effect increases once the used carbodiimide is highly functionalized. Its addition produces an increase in the plasticizer properties.

After the UV light test exposition, specimen tests were characterized again and the values obtained show an improvement in the properties in the carbodiimide doped samples. As is shown in the FTIR and SEM studies, carbodiimide addition to the polypropylene matrix improve the degradation resistance producing a lower reduction in its mechanical properties. This effect increased once carbodiimide sample is 100% functionalized.

Analyzing all the studies done and the results obtained on the polypropylene specimen tests, it is noted the necessity to incorporate the carbodiimide oligomer in the polymer structure. Once better is the compatibility and the inclusion to the polymer chain, better resistance results are obtained against external agent exposition.

6.3 WATER BASED CARBODIIMIDE OLIGOMER

All the carbodiimide applications and functionalizations requires the use of organic solvents. Nevertheless, there is a wide variety of applications that requires water as solvent. The carbodiimide oligomer prepared by using TMXDI as starting diisocyanate monomer is not water soluble, even with the vinyl functionalization. For this reason, a specific functionalization is needed to obtain a water soluble carbodiimide oligomer.

There are many strategies and products capable to give the water solubility function, which basically dotes the final product of a certain level of polarity. The TMXDI monomer and its corresponding carbodiimide oligomer has a very low polarity, which makes it insoluble in water; Log Kow 4.76 [26]. In order to give some polarity to the final oligomer obtained, the most used way is to add an ethoxylated chain. Etoxylated products are produced by reacting ethylene oxide at high temperature and pressure [27]. The incorporation of this kind of products to fatty acids or similar hydrophobic products is a wide used technique to make them water miscible. Ethoxylated chains are polar structures miscible in water which can dote of some polarity the products reacted. This strategy is a very used way to obtain surfactants [28]. There are other techniques to obtain the same final result, for example the incorporation of some ionic charge in the polymer structure also dotes the structure of more polarity than before. This way is wide used to obtain water dispersible polyurethanes [29].

Ethoxylated alcohols can be used to functionalize the carbodiimide oligomer obtained. In this case, the alcohol group is the isocyanate reactive group and the ethoxylated chain is the final functionality of the oligomer which produces a polarity increase. Is important to note the use of monofunctional groups because the use of diols will act as a chain extensor and no functionality will be observed.

In Figure 6.21 is shown the chemical structure of this kind of products.

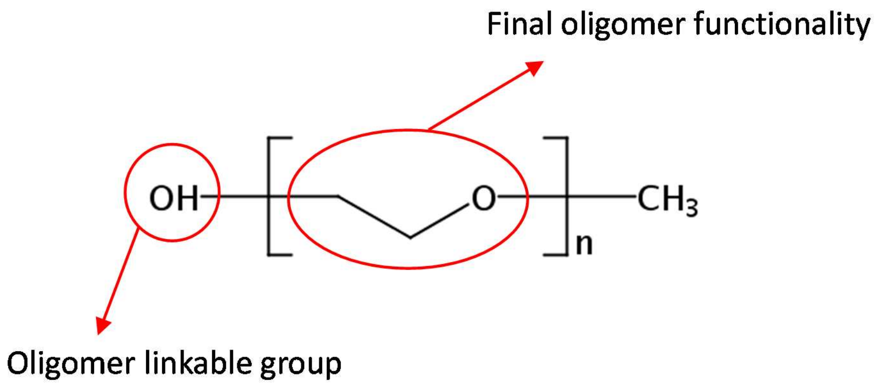


Figure 6.21 Ethoxylated alcohol chemical structure.

Depending on the number of ethylene oxide moles present in the functionalizing compound (n in Figure 6.21), we can get different products like MPEG 2000, MPEG 1000, MPEG 500 and MPEG 350 which contains 44, 22, 11 and 7.1 moles of ethylene oxide respectively. In addition, a wide variety of ethoxylated fatty alcohols which can vary both the ethylene oxide moles present and the length of the alkyl chain of the initial alcohol used can also be used.

High ethoxylated products contribute to the oligomer with a higher polarity than using less ethoxylated products. However, once more ethylene oxide moles are present in the final carbodiimide oligomer, less active content are obtained by dilution effect. For example, if sample R6 (1150 Da aprox.) was functionalized with 2 moles of MPEG 1000, a 3150 Da carbodiimide oligomer were obtained. It means a 66% dilution of the active content present in R6. Moreover, most of the MPEGs mentioned are waxes with a melting point between 45-60ºC [25], if more amount of this compounds is used to functionalize the samples, more solvent to make the sample workable were required, and it will cause an extra dilution. Similar problems are obtained with the ethoxylated alcohols.

Knowing these facts, 2 new samples are prepared, R16 and R17, by using the synthesis process optimized for sample R6, in order to obtain an average molecular weight close to 1150 Da.

Both samples were 100% functionalized by using MPEG 500, and lauryc alcohol with 3 moles of ethylene oxide. Table 6.8 shows the final results for both carbodiimide oligomer samples before ethoxylated functionalization.

Table 6.8 Characteristics of samples R16 and R17 before being functionalized.

Variables	R16	R17
NCN content (%)	15.21	14.97
NCO content (%)	4.82	5.04

Final values obtained for both R16 and R17 samples are in concordance with the synthesis process optimized for sample R6. Similar results are obtained by using the same process. The slightly differences between both samples are caused for the different conversion ratios reached.

Once the carbodiimide oligomer base was synthetized R16 was functionalized by using MPEG 500, and R17 by using lauryl alcohol with 3 moles of ethylene oxide. The ethoxylated functionalizing compounds amounts used were in a 1:1 molar ratio regarding to the isocyanate content. The functionalization reaction was carried out at 80ºC, which is the urethane synthesis optimum temperature. MPEG 500 and ethoxylated lauryl alcohol used are liquids at room temperature, for this reason is not necessary to warm it before the addition. At this temperature, the hydroxyl group reacts with the terminal isocyanates groups forming a new urethane group and polarizing the final carbodiimide oligomer.

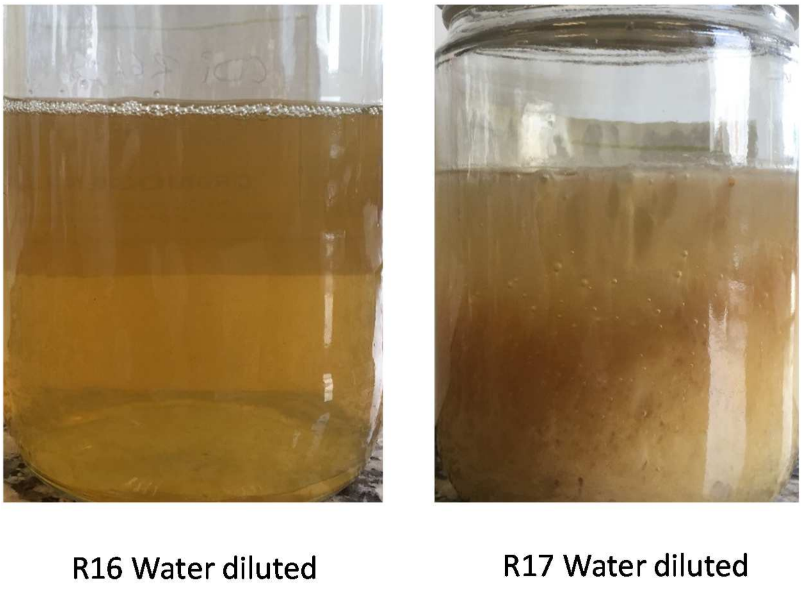
After functionalization reaction, the isocyanate content is again checked in order to confirm that the value is close to 0%. In Table 6.9 is shown the final isocyanate content and the functionalizing compound amount required for each 100 g of oligomer prepared.

Table 6.9 Characteristics of samples R16 and R17 after being functionalized.

Variables	R16	R17
Functionalizing compound	MPEG 500	C12 alcohol 3 MOE
Functionalizing compound amount (g)	57.38	36.96
NCN content (%)	9.66	10.93
NCO content (%)	0	0

Finally, the obtained polymers are diluted in the necessary amount of water to obtain a 45-50% solid content in the final product. The dilution can be performed by pouring the oligomer into warm water under stirring. To carry out this process, the carbodiimide oligomer needs to be kept at 80ºC to facilitate its manipulation and incorporation to the water.

Once dilution has been completed, R16 is completely water compatible and has a completely transparent appearance. Nevertheless, R17 did not accept the water and the sample is separated in two phases (see Figure 6.22). Same situation is observed with non-functionalized carbodiimide oligomer. This indicates that there is a minimum of ethylene oxide moles that is required to endow the polymer with enough polarity to be water-soluble. In this case, R16 has been prepared by adding 22 moles of ethylene oxide, while R17 only 7. To make the carbodiimide oligomer water soluble is required more than 7 moles of ethylene oxide to dote the product with enough polarity to be soluble. By using a lower molecular weight carbodiimide oligomer, less ethylene oxide moles are expected to be needed to obtain a water soluble product.


R16 Water diluted

R17 Water diluted

Figure 6.22 R16 and R17 appearance after water dilution.

The ethylene oxide functionalization process decrease the active content of the carbodiimide oligomer due to the high amounts of functionalizing compounds required (see Table 6.9). The necessity to increase the number of ethylene oxide moles, produces an increase in the molecular weight of the compound needed, and dilute the final carbodiimide active content in the final polymer. In addition to this initial dilution, the final water dilution also decreases more the final active content.

Another way to obtain water soluble products is to form ionic products. The formation of cationic or anionic compounds polarizes the final product and make it easy water soluble [29, 30]. This strategy is well known in the polyurethane industry, where water dispersible polyurethanes are prepared by including certain amount of dimethylolpropionic acid in the formulation, which is finally neutralized to give the anionic product. This neutralization allows to obtain water dispersed polyurethanes at 40-50% of solid content.

In addition, the formation of quaternary ammonium compounds is a wide used method to produce water soluble products, for example in the softener synthesis, where fatty acids are first esterified with triethanolamine and finally quaternized to obtain a water dispersible products [31]. This kind of polarity introduction produces a less active content reduction due to the lower molecular weight of the functionalizing compound.

In order to check if this kind of process also works by using carbodiimides, a new sample has been prepared. R18 was synthetized following the synthesis process used for sample R6 preparation, which uses 0.15%wt. of CAT 1 at 180ºC. The final carbodiimide and isocyanate values obtained for sample R18 are shown in Table 6.10.

Table 6.10 Characteristics of sample R18 before being functionalized.

Variables	**R18**
NCN content (%)	14.87
NCO content (%)	5.12

A new functionalizing compound to add ionic character was developed to be used in carbodiimide oligomers. This compound was named “CDI MODIFIER COMPOUND 2”. R18 was end-capped with two moles of CDI MODIFIER COMPOUND 2 for each carbodiimide oligomer. The functionalization reaction is carried out at 80ºC until the isocyanate content is close to 0%. In Table 6.11 is shown the final functionalized oligomer characteristics for each 100 g of final sample.

Table 6.11 Characteristics of sample R18 after being functionalized.

Variables	**R18**
Functionalizing compound	CDI MODIFIER COMPOUND 2
Functionalizing compound amount (g)	23.3
NCN content (%)	12.05
NCO content (%)	0

Once is checked the total isocyanate reaction, the resulting carbodiimide sample is diluted in water at 50% of solid content. The product is added over the water under high agitation conditions. R18 emulsify in water and creates a stable white dispersion water compatible. It is possible due to the ionic charges added to the carbodiimide oligomer.

The use of TMXDI as starting monomer to prepare carbodiimide oligomers is especially important to obtain water dispersible products due to the high steric hindrance obtained over the carbodiimide functional group. This steric protection, contributed by the four methyl groups, gives to these carbodiimide oligomers an extra stability in water preventing its own hydrolysis that other isocyanates and diisocyanates monomers do not have [14].

6.4 OTHER CARBODIIMIDE OLIGOMER FUNCTIONALIZATIONS

6.4.1 Dibutylamine functionalization

Some customers and applications, requires a carbodiimide product able to be used in different systems. In this case the final product is added as an additive. For this reason a product free of isocyanate groups is also demanded, due to its high reactivity with a lot of chemicals. In addition, a free solvent product, which is more ecological, and even increase the active content of the final product, is also required.

In order to achieve a free isocyanate oligomer carbodiimide, both terminal groups need to be reacted. In this case dibutylamine has been selected as a functionalizing compound due to both the faster reaction against isocyanate and the extra stability and rigidity acquired by both butyl groups. The addition of voluminous groups in different polymer structures produces a rigidity increase.

Dibutylamine can use both butyl groups to orientate the oligomer chains in the final system, reducing the intermolecular chain movement producing an increase in the rigidity of the product [32]. In addition, dibutylamine has the amine group which is very reactive against isocyanates and is capable to link it to the carbodiimide oligomer generating the corresponding urea. In Figure 6.23 is shown the dibutylamine structure.

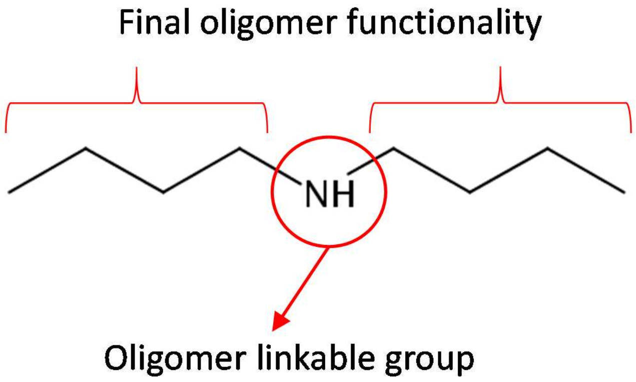


Figure 6.23 Dibutylamine structure.

There are other strategies to increase the rigidity and the thermal stability of the final oligomer synthestized such as the increase of the molecular weight average of the final carbodiimide oligomer prepared. Increasing the molecular weight generally causes an increase in the melting point [32]. However, the preparation of a higher molecular weight oligomer are linked to catalyst reduction or to an increasing in the conversion ratio. Both ways causes an increment in the reaction time needed, and the last way also decrease the final isocyanate content and the final functionalization ratio. Another option to increase the oligomer length is to functionalize the carbodiimide oligomer base with a high molecular weight functionalizing compound but this option decrease the active content of the final polymer which is one of the advantages to prepare a free solvent product.

For this reason, R19 sample was prepared to study the butyl chains of the dibutylamine functionalization effect on the thermal stability properties of the final carbodiimide oligomer. The R19 sample was synthetized by using the R6 sample optimized synthesis process. This is due to the necessity to obtain a higher molecular weight as possible. In Table 6.12 is shown the final isocyanate and carbodiimide values for the R19 sample carbodiimide oligomer base.

Table 6.12 Characteristics of sample R19 before being functionalized.

Variables	R19
NCN content (%)	15.45
NCO content (%)	4.76

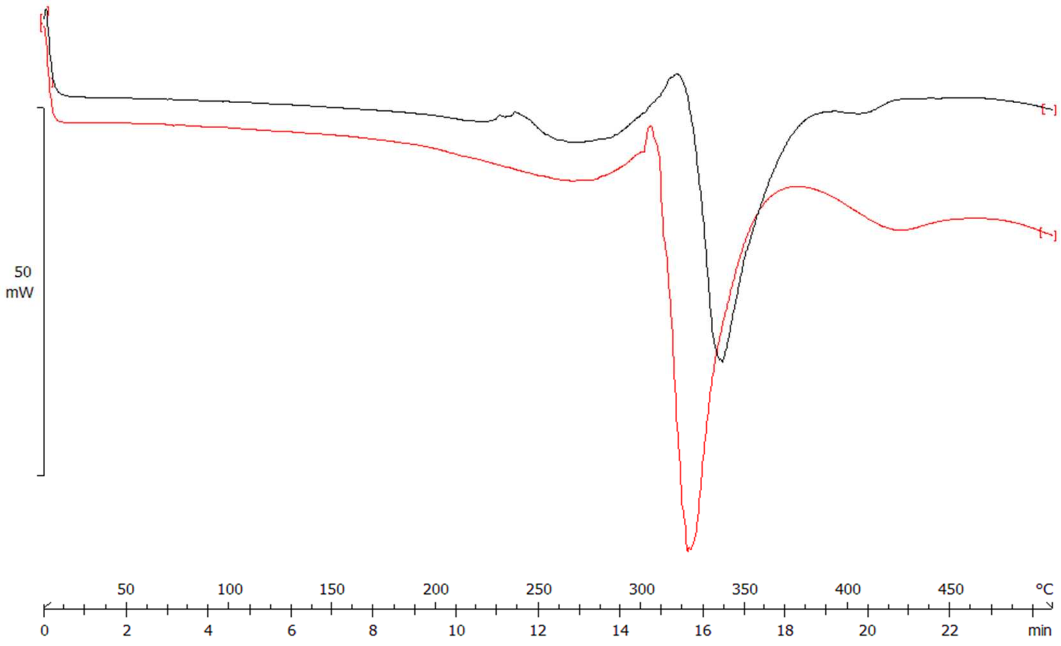
The dibutylamine functionalization reaction, due to its fast kinetics, can be carried out at room temperature [8], however, the high viscosity achieved by the oligomer at this point requires to run the reaction at 60-70ºC which is the minimum temperature to obtain an agitated product. The final values obtained after functionalization of R19 oligomer are detailed in Table 6.13.

Table 6.13 Characteristics of sample R19 after being functionalized.

Variables	R19
Functionalizing compound	Dibutylamine
Functionalizing compound amount (g)	14.76
NCN content (%)	13.46
NCO content (%)	0

As can be observed in the results shown in Table 6.13, the final product obtained has higher active content than the other functionalized samples prepared due to the lower dilution effect caused by the functionalizing compound.

In order to compare the thermal stability against the dibutylamine functionalized oligomer and the non-functionalized oligomer, its DSC spectra were performed. In Figure 6.24 are shown both DSC spectra.



Non-functionalized carbodiimide oligomer sample
Dibutylamine functionalized carbodiimide oligomer sample

Figure 6.24 DSC spectra of the dibutylamine and non-functionalized carbodiimide oligomer.

The DSC spectra show both thermal decomposition of dibutylamine functionalized oligomer and non-functionalized carbodiimide oligomer sample. The incorporation of 4 butyl groups in the oligomer chain increases the thermal stability in around 20 ºC, being 315ºC for the non-functionalized sample, and 337ºC for the dibutylamine functionalized sample. It is not a high improvement, but is confirmed that the inclusion of this kind of groups affects on the different chain movements, making it more difficult and making the final structure more stable.

6.4.2 Epoxy functionalization

Epoxide group is a cyclic ether formed by three atom ring, which makes it highly reactive. Ring opening reactions are the principal reactivity of this kind of compounds which are potent electrophiles. A wide variety of chemical such as alcohols, water, amines and other can serve as nucleophiles for the same reaction. Knowing the high potential reactivity of this chemical group another functionalization of the carbodiimide oligomer synthetized were designed.

In this case, as for the others a functionalizing compound with both the epoxy functionality and the isocyanate reactivity are needed to give the final epoxy functionality to the oligomer. Glycidol is the best option to carry out this step due to its hydroxyl functionality which can link the epoxy group to the carbodiimide oligomer. In Figure 6.25 is shown the glycidol structure.

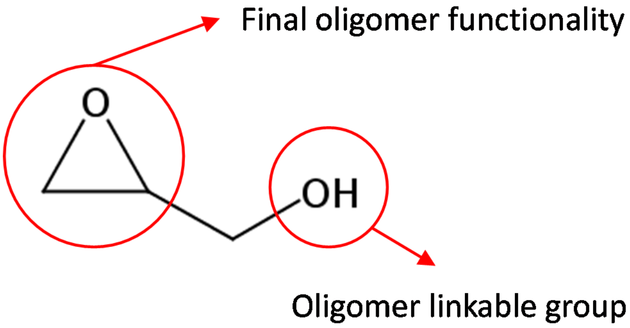


Figure 6.25 Chemical structure of glycidol.

The functionalization reaction is carried out in the same manner than the other detailed above, with a molar ratio between glycidol and isocyanate of 1:1. In this case, the correct functionalization should be checked by FTIR analysis because the epoxy group can react with the dibutylamine during the isocyanate titration method. For this reason absorption band of the isocyanate group are followed until no signal is detected.

Once the functionalization is complete the product can be diluted in many organic solvents depending on its final application.

6.5 REFERENCES

1. Laufer, W. and Eckert, A., *Method for stabilizing polymers containing ester groups*. 2013, Google Patents.

2. Wolfram, N., et al., *Stabilization of polyesters with polycarbodiimide*. 1965, Google Patents.

3. Ulrich, H., *Chemistry and technology of carbodiimides*. 2008: John Wiley & Sons.

4. Stloukal, P., et al., *Carbodiimide additive to control hydrolytic stability and biodegradability of PLA.* Polymer Testing, 2016. 54: p. 19-28.

5. Brown, D.W., Lowry, R.E., and Smith, L.E., *Hydrolytic degradation of polyester polyurethanes containing carbodiimides.* Macromolecules, 1982. 15(2): p. 453-458.

6. Hesselmans, L.C.J., Derksen, A.J., and Munneke, J.C., *Process for preparation of stable polycarbodiimide dispersions in water, which are free of organic solvents and may be used as crosslinking agent*. 2008, Google Patents.

7. Saeger, M., *Effect of Carbodiimide Functionalization Chemistry on Alginate Structure and Hydrogel Properties*. 2016, Tufts University.

8. Ulrich, H., *Chemistry and technology of isocyanates*. 1996: Wiley.

9. Sharmin, E. and Zafar, F., *Polyurethane: an introduction*. 2012: INTECH Open Access Publisher.

10. Ionescu, M., *Chemistry and technology of polyols for polyurethanes*. 2005: iSmithers Rapra Publishing.

11. Špírková, M., et al., *Novel polycarbonate-based polyurethane elastomers: Composition–property relationship.* European Polymer Journal, 2011. 47(5): p. 959-972.

12. Nikje, M.M.A., Garmarudi, A.B., and Idris, A.B., *Polyurethane waste reduction and recycling: from bench to pilot scales.* Designed Monomers and Polymers, 2011. 14(5): p. 395-421.

13. Smallwood, I., *Handbook of organic solvent properties*. 2012: Butterworth-Heinemann.

14. AKTIENGESELLSHAFT, B., *Carbodiimidas y procedimiento para su producción*. 2004.

15. Schollenberger, C. and Stewart, F., *Thermoplastic polyurethane hydrolysis stability.* Journal of Elastomers and Plastics, 1971. 3(1): p. 28-56.

16. Cauich-Rodríguez, J.V., et al., *Degradation of polyurethanes for cardiovascular applications*, in *Advances in biomaterials science and biomedical applications*. 2013, InTech.

17. DMITRICHENKO, M., et al., *Synthesis of O-Acetyl-N, N′-dimethylisourea and Its Phosphorylation with Phosphorus Pentachloride.* Chemischer Informationsdienst, 1986. 17(4).

18. Pretsch, E., *Determinación estructural de compuestos orgánicos*. 2002: Elsevier España.

19. Mark, H.F., *Encyclopedia of polymer science and technology, concise*. 2013: John Wiley & Sons.

20. Odian, G., *Principles of polymerization*. 2004: John Wiley & Sons.

21. Hageman, H., *Photoinitiators for free radical polymerization.* Progress in organic coatings, 1985. 13(2): p. 123-150.

22. Maier, C. and Calafut, T., *Polypropylene: the definitive user's guide and databook*. 1998: William Andrew.

23. Schnabel, W., *Polymer degradation, principles and practical applications.* W. Schnabel, Hahn-Meitner Institute, Berlin, ISBN 0-02-949640-3, 220 pages illus.,$ 32. 00, 1986.

24. Iakovlev, V.V., Guelcher, S.A., and Bendavid, R., *Degradation of polypropylene in vivo: a microscopic analysis of meshes explanted from patients.* Journal of Biomedical Materials Research Part B: Applied Biomaterials, 2015.

25. SciFinder, www.scifinder.cas.org.

26. Allnex. http://allnex.com.

27. Di Serio, M., Tesser, R., and Santacesaria, E., *Comparison of different reactor types used in the manufacture of ethoxylated, propoxylated products.* Industrial & engineering chemistry research, 2005. 44(25): p. 9482-9489.

28. Ullmann, F., et al., *Ullmann's encyclopedia of industrial chemistry*. Vol. 5. 1985: Vch Weinheim, Germany.

29. Najafi, F., Manouchehri, F., and Shaabanzadeh, M., *Synthesis and characterization of anionic polyester-polyurethane dispersion as environmentally-friendly water based resins.* J Chem Health Risks, 2011. 1: p. 23-26.

30. Zhang, M., et al., *High-load, soluble oligomeric carbodiimide: Synthesis and application in coupling reactions.* The Journal of organic chemistry, 2004. 69(24): p. 8340-8344.

31. Brock, M., et al., *Process for the quaternization of triethanolamine fatty acid esters and imidazolinamides and the use of the reaction mixtures in laundry softener compositions*. 1995, Google Patents.

32. Askeland, D.R., et al., *Ciencia e Ingeniería de los Materiales*. Vol. 3. 1998: International Thomson Editores.

Chapter 7

Pilot plant and industrial production scaling up

7. PILOT PLANT AND INDUSTRIAL PRODUCTION SCALING UP

The main objective in industry is the production of goods every day, all of which have some impact in the consumers. In the case of the chemical industry, such as Cromogenia Units S.A. the main objective is to produce chemical products and specialties to solve different existent customer and market necessities.

After the different trials and studies done during this work referred to polycarbodiimides based on TMXDI monomer, some customer orders have been received regarding to this kind of products. The product that has attracted more interest in the customers has been the functionalized carbodiimide oligomers that can be used in polyurethane systems, which has the reference R13 in previous sections.

The trials done in different customers by using sample R13 prepared at laboratory scale has been successfully for its use in solid polyurethane applications. Due to its good laboratory application, a first pilot plant order of 120 kilos was received to be used for industrial homologation.

This process is usual once a product homologation is required for a customer. Initially the product is tested at small scale (laboratory scale) comparing their properties with other similar products used. If the test performed has similar or even better results than the reference product, a pilot plant order for preparing around 100-500 kilos is required to test the product at the normal scale application. Once the product is correctly evaluated, the homologation is finished and the industrial orders and consequently the industrial production step is started.

7.1 PILOT PLANT PRODUCTION

A pilot plant is a pre-commercial production system that produces small volumes of new technology-based products, mainly for the purpose of learning about the new technology for the final application to industrial production. For this reason, this is a preliminary step needed before adjusting the process to the final industrial installation.

7.1.1 Pilot plant process design

For the pilot plant scale production, is necessary to well known the final requirements of the product and the facilities required to carry out correctly the designed process. In this case our interest is to scale up the protocol for the synthesis of the R13 sample.

The *installation facilities required:*

Temperature:	180ºC
Nitrogen:	Sparging is required during all the process.
Gas purge:	Scrubber is recommended.
Raw materials charge system:	A safe system to charge the raw materials is required to guarantee the security.
Sampling system:	A safe sampling system is required in order to follow the reaction kinetics.

The product specification is important in order to planning the process. All the steps and the raw materials involved need to be know before start the production.

The most important think to check in the facilities list is the high temperature required to carry out the carbodiimide synthesis. The rest of requirements are common necessities, for this reason the major part of the reactors are installed with the correct pumps for charging, raw materials addition and sampling systems. However, 180ºC is not a very usual working temperature and not all reactors and factories are equipped with thermic oil heating system. Due to the lower temperatures usually required, the major part of reactor are equipped with a jacket or a serpentine where steam or hot and cold water can be added. Hot water arrives around 70-80ºC and steam usually can heat the reaction system over 130ºC, which makes impossible to run the conversion of isocyanates to carbodiimide. The steam pressure can be modified in order to increase its temperature. Increasing the boiler pressure until 5-6 Bar, the system can be heated until 150-160ºC, but is really difficult to reach 180ºC by using this kind of heating systems because a pressure of 12-13 Bar are required [1].

Knowing this fact, a thermal fluid heating system is required. Thermal oil is a common heat transfer mediums for these systems. In Arteixo Química, the Galician factory of Cromogenia Units, we have this type of heating system that is used for production [2]. For this reason, the reaction has been carried out in Arteixo Química.

Once has been selected the emplacement, the reactor selection needs to be done. Knowing that the customer order is around 120 kilos, a reactor of around 350 L, as maximum, is required. The ratio between the wall reactor surface and the volume reactor used for the production (S/V) is a key factor to obtain a correct product appearance. If 100 kilos are charged and reacted in a 3 m^3 reactor, the probability to obtain a darker product than the expected are very high. This is caused for the extra heating generated in the reactor wall over the product. In addition, a very low charged reactor do not assure a correct stirring and homogenization.

This considerations are not decisive at laboratory scale, buy are of crucial importance in the pilot plant. The use of glass reactors, and electric heating systems from the bottom of the reactor, reduce the extra heating problems and the oxidation and contamination processes caused for the degraded reactor stain steel material [3, 4].

Finally, attending to all the determining factors commented, a 180 L reactor is equipped with all the required facilities. This smaller reactor is connected to the thermal oil system and also is equipped with a stirrer, a sampling valve and several entrances for the raw material. To carry out the optimized carbodiimide oligomer synthesis process, the following facilities are also installed:

- Nitrogen sparging tube
- Gas outlet connected to an alkali scrubber
- Vacuum system connection

The final equipped reactor used is shown in Figure 7.1 and Figure 7.2.

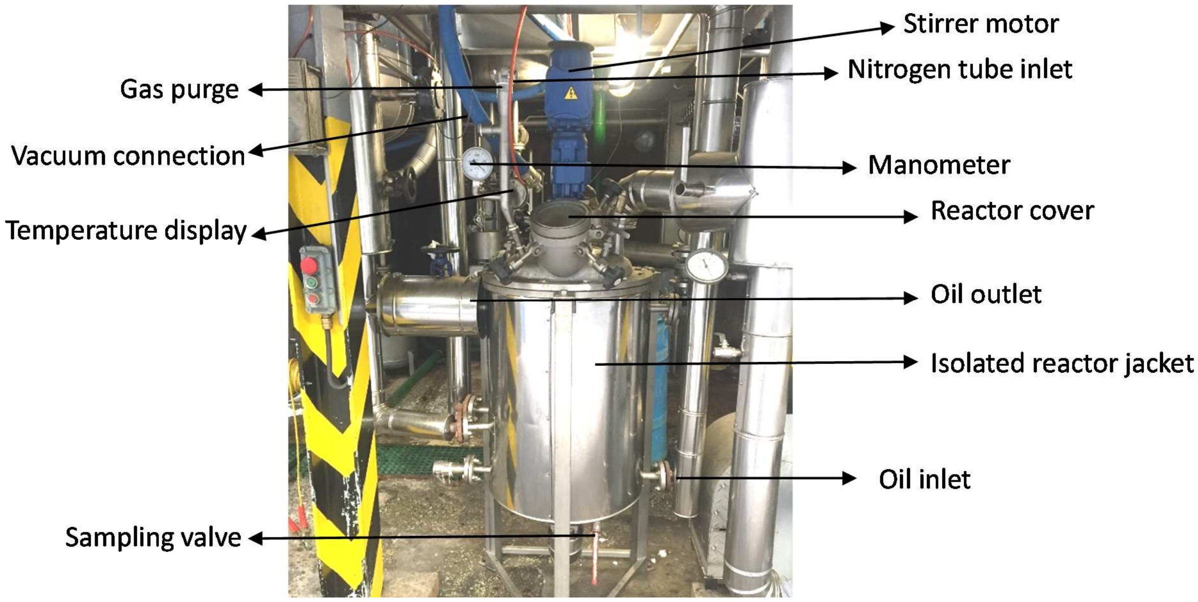


Figure 7.1 Pilot Plant reactor used.

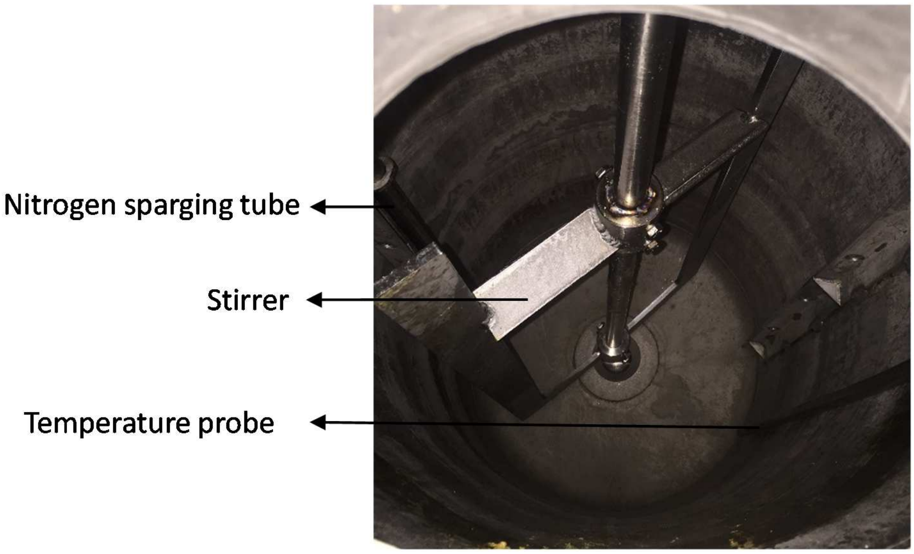


Figure 7.2 Internal part of the reactor of the Pilot Plant.

Once the reactor is completely equipped, the synthesis process is performed.

Knowing that the product is very sensitive to excessive heat, which could affect to the final oligomer structure and to the final colour appearance of the product, an initial monomer charge from about the 65% of the total volume of the reactor is done. This high initial charge, knowing that the final product is diluted until 45%; decreases the ratio S/V and the possibility to obtain a darker product caused for this kind of reasons.

7.1.2 Pilot plant process

The process followed to obtain this first pilot plant R13 product was the synthesis process optimized for sample R10. After the different application tests done, no performance differences between carbodiimide oligomers with different molecular weight were observed. For this reason the optimized synthesis process, which use potassium tert-butoxide as alkali to isomerize CAT 1, was selected.

As described in section 4, the CAT 1 purchased has a low concentration of isomer I. Its isomerization allows to decrease the reaction time. Lower reaction times increases productivity and can helps to improve the final color appearance.

Before starting the production is necessary to ensure that the pumps and pipelines that will be used for the raw materials charge are completely clean and dry. The presence of water in the pipelines or pumps can react with the TMXDI monomer used, causing an obstruction in the system. For this reason all the facilities, included the reactor inside, should be cleaned with acetone or toluene [5].

Once all the facilities are clean, and the raw materials charged (TMXDI by using the vacuum system), the nitrogen sparging and heating are started. Nitrogen proceeds directly from the liquid nitrogen deposit, which ensure a 99.999% purity. Once the reaction mixture reach 180ºC, which is the optimized reaction temperature for the conversion of TMXDI to its carbodiimide oligomer, sampling is done in order to control the reaction kinetics. The isocyanate content reduction versus the reaction time spent is shown in Table 7.1 and Figure 7.3.

Table 7.1 Isocyanate content during the pilot plant production.

Reaction time (h)	Isocyanate content (%)
0	34.46
3	25.92
6	21.33
9	16.76
12	13.12
15	10.19
17	8.25
19	7.31
21	6.68
22	5.72

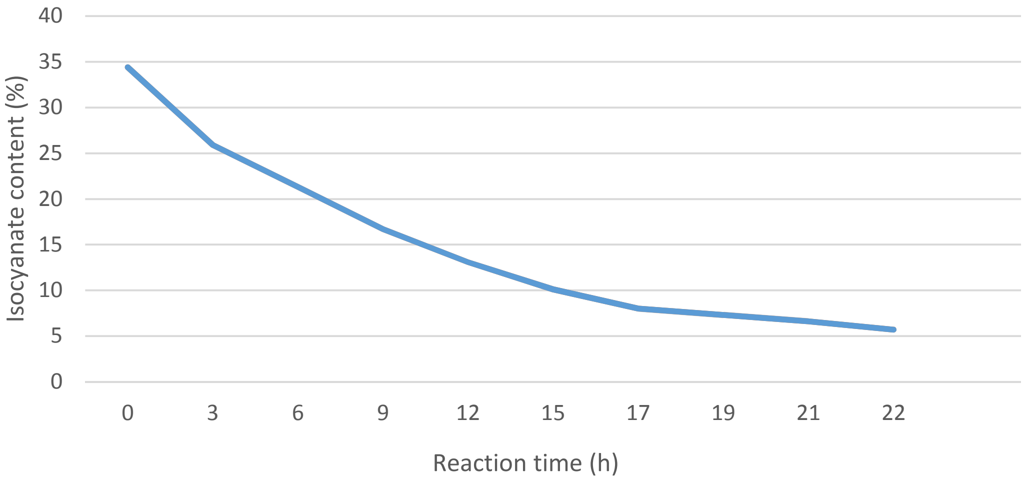


Figure 7.3 Pilot plant TMXDI conversion kinetics.

In the kinetic of TMXDI conversion is shown that the initially isocyanate content before start the conversion is 34.4%, which is the monomer theoretical isocyanate value. The time spent to reach an isocyanate content around 5% was of around 22 hours, which is around 1.5 hours more than the reaction time needed at laboratory scale. This difference is not important because is lower than the time spent if non isomerized catalyst was used. In this experiment has been also confirmed the extra activity achieved by CAT 1, once it is isomerized.

As was optimized at laboratory scale for all prepared samples, once an isocyanate content close to 5% is achieved, 30 minutes of vacuum are applied to the reaction system to remove the free monomer presence. Finally, the resulting carbodiimide oligomer is functionalized by using the "CDI modifier compound" and diluted until 45% of solid content by using Lauryl benzoate. In Table 7.2 are shown the final characteristics of the pilot plant product obtained versus the original R13 sample.

Table 7.2 Final characteristics of pilot plant product compared versus sample R13.

Properties	**R13**	**Pilot plant product**
Appearance	Light orange	Dark orange
Isocyanate content (%)	0.02	0.04
Viscosity 25ºC (cps)	670	380
Solid content (%)	45.1	46.7
Carbodiimide content (%)	8.63	8.75

Observing the final obtained values for the pilot plant production, the main characteristics such as isocyanate and carbodiimide content are accordingly to the original sample. However, some differences are also observed.

The viscosity obtained at pilot plant scale is lower than the obtained at laboratory scale due to the difference in the synthesis process used which causes differences in the molecular weight of the oligomer prepared.

One of the most important commercial characteristic is the product appearance. The obtained product is darker than the original one, it has a higher Gardner color than expected; around 17 and the expected was 15-16. The production of a darker product is caused by three reasons.

The first one is the use of not fresh TMXDI monomer. Once the drum is opened, the nitrogen atmosphere present inside changes. If it is stored again under oxygen atmosphere the product starts to yellowish, and the color could change from totally colorless to a Gardner color of 5-6 in few weeks [6].

The second reason is the use of alkali to isomerize the catalyst. This isomerization reaction increases the Gardner color of the catalyst used which is fast transferred to the reaction mixture, as has been commented section before.

The last reason, and not the less important is the use of the whole wall reactor to heat the reaction mixture. The reactor volume that is not full is still heated with the thermic oil during all the process. This situation can produce extra heating situations during the process that can affects to the color.

All scaling up processes needs to be optimized to obtain better results after first trial. In spite of all these improvable situations, the production has been carried out successfully. Similar activity and characteristics than for the original product have been obtained. In addition, adapting all the required facilities to the factory, a similar reaction kinetics than the expected have been registered, which means that the pilot plant is working correctly.

7.2 INDUSTRIAL PRODUCTION

After the first pilot plant production of the carbodiimide oligomer CDI modified, the product had correct application results, and it was homologated for the customer.

After the industrial customer homologation, a first industrial order or 1000 kilos was received.

7.2.1 Industrial process design

For the first industrial batch production is important to correct the difficulties observed during the pilot plant production. To produce the 1000 kilos of product ordered, a 1 m^3 reactor is selected to carry out the synthesis. The use of this reactor volume maximize the initial volume charge.

After the pilot plant batch, CAT 1 and TMXDI stock were practically finished. Due to the big production required, a new raw material purchasing was done. As was described in section 5, once new catalyst is purchased an isomer ratio analysis needs to be done in order to modify the amount of this raw material in the process. The new CAT 1 isomer ratio was analyzed by using the single scan ^{31}P NMR technique and $CDCL_3$ as solvent. In Figure 7.4 is shown the initial isomer ratio (a) and the isomerized isomer ratio after the potassium tert-butoxide addition (b).

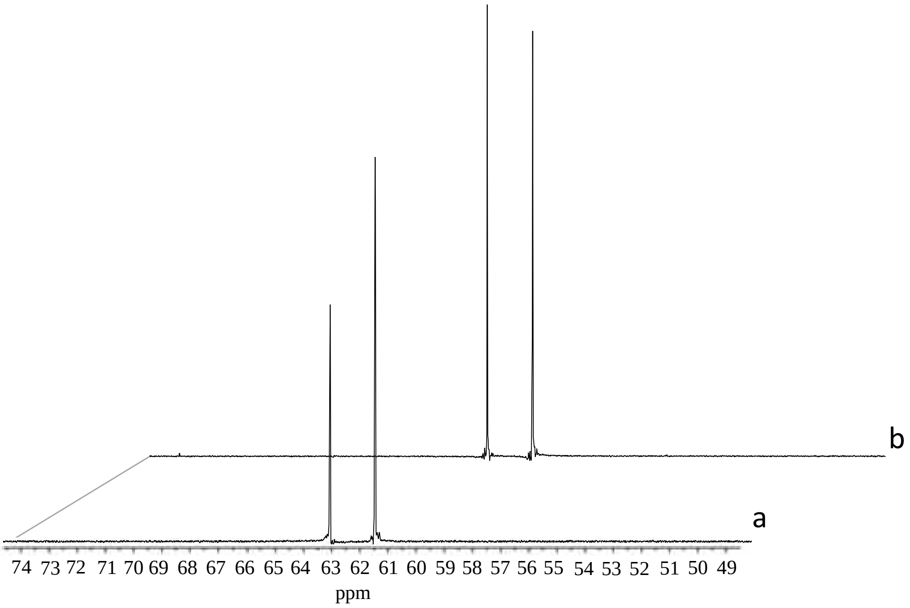


Figure 7.4 ^{31}P NMR spectra of the new CAT 1 purchased before (a) and after being isomerized (b).

The spectra shows the same two phosphorus isomers than the first CAT 1 purchased. In addition, these isomers have the same displacements, 63.39 and 61.42 ppm for isomer I and isomer II respectively. Nevertheless, its ratio in the catalyst mixture is not the same than the first batch purchased. In this case the initial isomer ratio is 42.1:57.9 for isomer I and II respectively. Once the alkali is added, the isomer I ratio increases until 51%. The isomerization arrives to similar values than the first CAT 1, even starting from a higher initial concentration.

Taking into account these results, and knowing how the alkali addition affects to the final color product, a process with no alkali addition was carried out in this first industrial process. The increased isomer I concentration of the new CAT 1 allows to run the conversion reaction in a similar time than using the old CAT 1 isomerized.

In addition to the use of the new more active CAT 1, the use of the fresh TMXDI will also improve the color appearance of the final product.

During the first pilot plant production the wall of the reactor were completely full of the thermal oil during the reaction. This time, only 1/3 of the reactor jacket will be heated with the thermal oil in order to avoid this kind of extra heating situations in the non-filled volume reactor. Additionally, the temperature of the thermal oil will be reduced from 220ºC to just 190ºC. This reduction temperature only affects to the time necessary to reach 180ºC in the reaction mixture. The use of colder oil has achieved a more clear color product production during the manufacturing processes of products such as polycaprolactones and polycarbonates. Similar performances are expected to be obtained during the polyTMXDI production.

To carry out the industrial production, the 1 m^3 reactor was selected. This reactor is the most versatile reactor that Cromogenia Unit has because is widely used to scaling up processes. For this reason, this reactor is equipped with all the facilities necessary to carry out correctly and safety the reaction conversion of TMXDI to its polycarbodiimide. In Figure 7.5 and Figure 7.6 are shown the 1 m^3 reactor used.

Figure 7.5 Top of the 1 m^3 reactor used.

Figure 7.6 Bottom of the 1 m^3 reactor used.

Once al the facilities are checked and cleaned, the industrial scaling up can be started.

7.2.2 Industrial process

First of all, the initial raw materials are charged into the reactor. The TMXDI was charged by using the vacuum system, and the rest (antioxidant additive and catalyst) are charged from the top of the reactor. Then stirring, nitrogen sparging and heating were started. Once the reaction mixture reached 180ºC, a constant sampling is done during all the process to study the conversion kinetics. In Table 7.3 and Figure 7.7 are detailed the conversion kinetics by the isocyanate content reduction during the reaction.

Table 7.3 Isocyanate content during the industrial production.

Reaction time (h)	Isocyanate content (%)
0	34.31
3	27.37
6	22.92
9	18.28
12	14.65
15	11.81
17	9.33
19	7.79
21	7.14
23	6.46
24	5.8

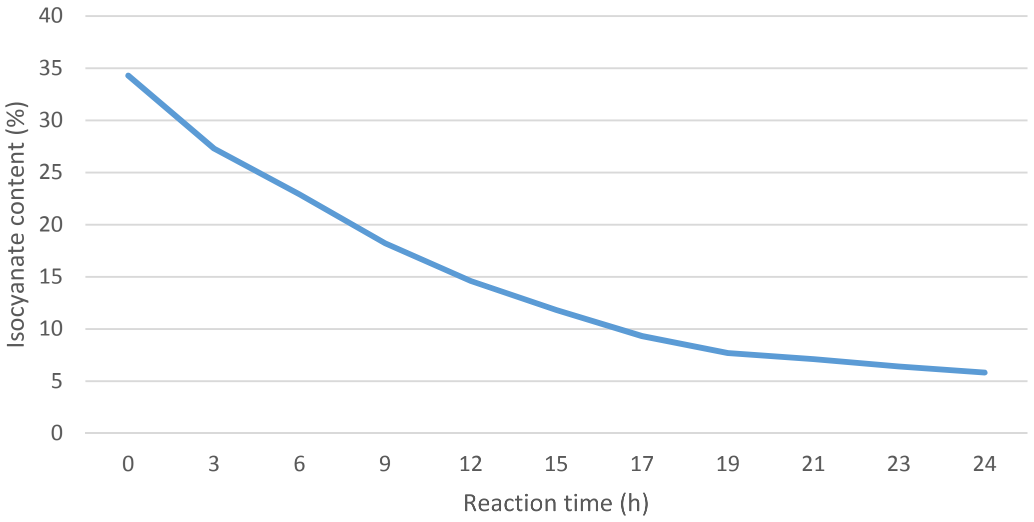


Figure 7.7 Pilot plant TMXDI conversion kinetics.

In the industrial batch it is observed that two more hours are needed to reach an isocyanate content close to 5%. This extra time is caused by non-alkali isomerization of the catalyst. In the pilot plant batch an isomerized CAT 1 with a 52% content of isomer I, was used. In the industrial process, CAT 1 with 42% isomer I concentration has been used to carry out the conversion. The reaction time needed are dependent of the more active isomer concentration. Despite spent 2 hours more than the pilot plant production, the reaction time is lower than if the first CAT 1 non-isomerized were used (see section 5). It is again demonstrated that the isomer I is the most active. Once more isomer I concentration are present in the catalyst, the conversion reaction is carried out faster.

After the conversion reaction, vacuum is applied to remove the free monomer un-reacted, which also decrease the isocyanate content until 4.82%.

To finish the industrial production, the obtained carbodiimide oligomer based on TMXDI is functionalized with “CDI modifier compound” and is finally diluted until 45-50% of solid content by using the same solvent than in the pilot plant production. In Table 7.4 are shown the final characteristics of the industrial product obtained versus the first pilot plant batch produced.

Table 7.4 Final characteristics of industrial product compared versus the pilot plant batch.

Properties	Pilot plant product	Industrial product
Appearance	Dark orange	Light yellow
Isocyanate content (%)	0.04	0.05
Viscosity 25ºC (cPs)	380	456
Solid content (%)	46.7	45.6
Carbodiimide content (%)	8.75	9.15

Observing the final values obtained for the industrial batch product, a correct scaling up has been performed. A correct product very similar to the pilot plant product, which was homologated has been obtained.

The use of the catalyst without alkali, has improved the viscosity and the final carbodiimide activity. This is caused for a slightly higher molecular weight of oligomer.

The process modifications, and the use of new raw materials, has been improved the final color product, which has reach a color Gardner of 8-9. This color appearance is even better than in laboratory scale. In Figure 7.8 are shown both the pilot plant and the industrial final product appearance.

Pilot Plant Industrial

Figure 7.8 Final pilot plant and industrial products appearance.

One important difference between industrial production and laboratory scale preparations is the 24 hours supervision. At laboratory scale, due to safety instructions, the reaction needs to be stopped overnight. It causes overheating situations in the wall reactor due to the high viscosity of the polyTMXDI prepared at room temperature that affects to the final color appearance. A continuous production process allows to maintain completely inert and stirred the reaction system which is also another key point to obtain a better product.

Analyzing both the pilot plant and the industrial productions, the problems appeared has been solved, and correct products has been obtained which have been homologated by the costumer. A very repetitive process was optimized which guarantee further correct productions. The modifications and precautions done has been improved the initial synthesis process optimized at laboratory scale, and it will be applied in future productions.

7.3 PRODUCTION COSTS

The final production cost is the most important commercial factor. Industry needs good products with good application results, and costs as low as possible.

The final production cost is determined basically by three different factors. The raw materials prices, the production cost and the packaging price. All this variables are always directly related to the total amount that is intended to be manufactured.

The raw materials price are always lower once more amount is purchased, and also depends on the suppliers. The cost per kilo of 1 drum of TMXDI monomer, is more expensive than the cost per kilo of one TMXDI tank (24Tn). The supplier can do this price reduction because it causes an increase on its production, and a reduction cost on its transportation to the customer.

The production cost includes the energy cost and the directly involved staff and facilities use cost. Usually this cost is calculated depending the annual manufacturing and factory cost produced. If more production are expected, a production cost reduction is achieved.

Finally the packaging is the last cost to be added to final cost production. Depending on the packaging needed by the customer, different costs are added to the final product. As commented above, higher packaging like tanks, or full container load, decrease the packaging and transport cost which is also included to the final price.

Regarding to the CDI modified functionalized carbodiimide oligomer diluted at 45% of solid content product manufactured at pilot plant and even at industrial scale, has a not cheap cost. This product uses specialties as raw materials such as the monomer and the catalyst, which increases the final price. In addition, the final product is a specialty chemical, which is used for very technical applications.

In the industry field, the commercial sector is focused to reduce production costs in order to increase the final business benefits, and to make easier to enter in certain difficult markets such as the automobile sector for example. In the Carbodiimide oligomer production, the raw material that most affects to the final cost is the TMXDI monomer, which is the 78% of the final cost. Other raw materials like the catalyst are more expensive, arriving to more than 1000 euros/kilo, but its low amounts required, do not affects too much to the final cost production. For this reason is important to pay attention not only to the catalyst, but also to the monomer.

Nevertheless, the catalyst is a strategic raw material because its use is exclusive to carry out the isocyanate conversion to carbodiimide. A good market position to purchase the catalyst and the study of its synthesis is another key point in the final production of carbodiimide products.

7.4 REFERENCES

1. Haar, L., *NBS/NRC steam tables*. 1984: CRC Press.

2. http://www.cromogenia.com/.

3. Lozano-Perez, S., et al. *Understanding surface oxidation in stainless steels through 3D FIB sequential sectioning*. in *Journal of Physics: Conference Series*. 2012: IOP Publishing.

4. Okamoto, G. and Shibata, T., *Stability of passive stainless steel in relation to the potential of passivation treatment.* Corrosion Science, 1970. 10(5): p. 371-378.

5. Ulrich, H., *Chemistry and technology of isocyanates*. 1996: Wiley.

6. Louis, S., *Stabilization of organic isocyanates*. 1959, Google Patents.

Chapter 8

Conclusions

8. CONCLUSIONS

The present doctoral thesis has been dedicated to the synthesis and characterization of polycarbodiimides based on TMXDI as starting monomer and to its final application and industrial production.

This research study has increased the knowledge about this kind of products especially how they work on the final applications.

The main conclusions derived from this research study are as follows:

- The structure of the catalyst used for the isocyanate conversion to carbodiimides needs to have an activated phosphoryl bond which acts as a nucleophile against the isocyanate group. The activation of this phosphoryl bond is favored by the presence of alkyl substituents instead of aromatic groups. In addition, the presence of aromatic groups, as substituents in the catalyst structure, increase the steric hindrance reducing even more the activity of the catalyst. For this reason, the most active catalyst used has been CAT 1.

- The structure of the isocyanate monomer used to carry out the conversion determines the optimum reaction temperature required. Aromatic isocyanates are more electrophilic, consequently increases the reaction rate. The steric hindrance, such as in the catalyst, also affects the reaction rate.

- The reaction mechanism postulated for the first time by Campbell and Monagle in 1962 has been confirmed by NMR technique. The intermediate structure formed by the interaction of the phosphor catalyst and the isocyanate monomer has been identified for first time by NMR. This technique also allows a correct identification of all the raw materials involved in the process. It has been also demonstrated that the catalyst is recovered after the isocyanate conversion.

- A correct process design allows to optimize the reaction time and the final color appearance. For this reason a process with nitrogen sparging, the presence of an anti-oxidizing additive and the application of vacuum step at the end of the process is the best way to maximize reaction yield improving the product appearance.

- MALDI TOF mass spectrometry is a very useful technique to determine the molecular weight of polycarbodiimides. Linear carbodiimide and branched uretonimine structures have been identified in all the sample prepared.

- The catalyst dose used to run the process determine the final molecular weight and the structure of the oligomer produced. High doses reduce the molecular weight due to the major chains initiated and also decrease the branched structures formed by increasing the initiation polymerization step and decreasing the propagation step.
- Isomer I has demonstrated to be the most active isomer present in the commercial CAT 1 mixture. This isomer increases the polarization of the phosphoryl bond and force it to react.

- CAT 1 can be alkali isomerized to increase the isomer I concentration. This change in the isomer concentration decreases the reaction time and the molecular weight of the oligomer. In addition, the alkali isomerization reaction produces an increase of the color Gardner, which affects to the final color appearance.

- Two new CDI modifier compounds, 1 and 2, have been developed to functionalize the carbodiimide oligomer prepared. The first one produces an activity increase, and the second one polarize the oligomer to make it water soluble.

- Carbodiimide oligomers prepared have demonstrated to work as good polymer stabilizers in different polymer systems.

- Carbodiimide oligomer addition to polyester based polyurethanes improve the resistance to ageing and hydrolysis. Carbodiimide groups react with the carboxylic acids formed during the degradation decreasing the degradation activity and rebuilding the polymer structure by forming O-Acylisourea structures. Carbodiimide addition also prevents yellowing caused for external agents. FTIR spectrometry allows to identify this kind of degraded and rebuilding structures.

- Carbodiimide doped polyester based polyurethanes has shown an increased fastness 50% higher in leather applications.

- Carbodiimide addition to vinylic systems such as polypropylene improves the degradation resistance. Better color, surface structure and mechanical properties are achieved after UV exposition.

- The molecular weight of the carbodiimide oligomer do not affects to the application. The key factor is the amount of carbodiimide units added to the system. In addition, once better is the functionalization of the oligomers used, better compatibility and applications results are obtained.

- The developed synthesis process is repetitive and can be scaled up. Better results are obtained by using fresh raw materials and using the reactor bottom heating system. Continuous process has demonstrate to obtain better product appearance.

This study has demonstrated that Cromogenia Units is able to design and to produce polycarbodiimides for its use as polymer stabilizers. Most of the acquired knowledge of this work can be applied in the industrial and process design of other kind of polymers.