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NMR, FTIR AND KINETIC ANALYSES OF POLYURETHANES SYNTHESIZED WITH SUCROSE OF SUGAR CANE, CROTONIC ACID AND POLYCAPROLACTONE

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●Abstract

Polyurethanes (PU´s) are commonly used in a number of applications including catheter, hospital bedding, surgical material, as well as in a variety of injection molded devices. The PU synthesis is reported due to sucrose, crotonic acid and polycaprolactone (PCL). The PU´s synthesized were characterized using nuclear magnetic resonance (^{13}C-NMR) to determine the different spectrum and Fourier transform infrared spectroscopy (FTIR) to analyze the new bands formed and to confirm at 1637 cm^{-1} the sign of carbonyl group appears, indicating the formation of the urethane group in the different polymerization. Computational chemistry methods can be used to explore the theoretical chemistry behind reactive systems, to compare the relative chemical reactivity of different systems, and, by extension, to predict the reactivity of new systems. The reaction order was determined by means of the simulation with the Hyperkinetic software which corresponded to the first reaction order, because the speed constants are very similar to different periods of time.

Key words: polyurethane, NMR, FTIR.

●Resumen

Los poliuretanos (PU´s) normalmente se usan en varias aplicaciones, incluso el catéter, ropa de cama de hospital, material quirúrgico, así como en una variedad de dispositivos de moldeo por inyección. La síntesis del PU es reportada mediante sacarosa, ácido crotónico y policaprolactona (PCL). Los PU´s sintetizados fueron caracterizados utilizando resonancia magnética nuclear (^{13}C-RMN) para determinar los diferentes espectros y espectroscopía de infrarrojo por transformadas de Fourier (FTIR) para analizar las nuevas bandas formadas, y confirmar a 1 637 cm^{-1} la aparición de la señal del grupo carbonilo, indicando la formación del grupo uretano en las diferentes polimerizaciones. Los métodos de química computacional pueden ser empleados para explorar la química teórica entre sistemas reactivos, para comparar la reactividad química de diferentes sistemas, y predecir la reactividad de nuevos sistemas. El orden de reacción fue determinado mediante la simulación con el software Hyperkinetic el cual correspondió a una reacción de primer orden, debido a que las constantes de velocidad son muy similares a diferentes periodos de tiempo.

Palabras clave: poliuretano, RMN, FTIR.

Introduction

Polyurethanes (PU´s) represent a main class of synthetic elastomers applied for long term medical implants. They present tunable chemical properties, excellent mechanical properties and good biocompatibility can be designed to degrade in biological environment /1/. PU´s with poly(e-caprolactone) (PCL) blocks and diisocyanate in their structure have good elastomer properties and biocompatibility as well as high physical and mechanical properties /2/. Polyols are higher molecular weight materials manufactured from an initiator and monomeric building blocks.

They are most easily classified as polyether polyols, which are made by the reaction of epoxides (oxiranes) with active hydrogen containing starter compounds, or polyester polyols, which are made by the polycondensation of multifunctional carboxylic acids and hydroxyl compounds. They can be further classified according to their end use as flexible or rigid polyols, depending on the functionality of the initiator and their molecular weight.

Taking into account functionality, flexible polyols have molecular weights from 2,000 to 10,000 (OH number from 18 to 56). Rigid polyols have molecular weights from 250 to 700 (OH from 300 to 700). Polyols with molecular weights from 700 to 2,000 (OH 60 to 280) are used to add stiffness or flexibility to base systems, as well as increase solubility of low molecular weight glycols in high molecular weight polyols. Polyols for rigid applications use high functionality initiators such sucrose /3-4/.

Sucrose is a disaccharide (glucose more fructose) with the molecular formula $C_{12}H_{22}O_{11}$. Its systematic name is a-D-glucopyranosyl-(1↔2)-ß-D-fructofuranoside. PCL is biodegradable polyester with a low melting point of around 60 °C and a glass transition temperature of about -60 °C.

PCL is derived by chemical synthesis from crude oil. It can be prepared by ring opening polymerization of e-caprolactone using a catalyst such as stannous octanoate. PCL has good water, oil, solvent and chlorine resistance. PCL is degraded by hydrolysis of its ester linkages in physiological conditions (such as in the human body) and has therefore received a great deal of attention for use as an implantable biomaterial. In particular it is especially interesting for the preparation of long term implantable devices, owing to its degradation which is even slower than that of polylactide /5-6/.

HyperChem is a complete suite of modeling molecular for the chemical simulation, calculation and visualization of molecular properties. It includes wide selection of quantum mechanics methods, molecular mechanics and molecular dynamics. They are supplemented with capacities of visualization 3D and animation /7/. The main objective in this work similar PUs were prepared and characterized with different types of polyoles (sucrose, crotonic acid and PCL). The computational simulation of the PU synthesized by means of HyperChem to determine the behavior of the reaction.

Experiment section

Materials

Polycaprolactone diol (MW of 1250 g/mol, Aldrich Chemical Company Ltd), Dibutyltin dilaureate (MW 631, Aldrich Chemical Company Ltd), 1,6-hexamethylene diisocyanate (MW 168, purity 98%, Aldrich), PEG (Average Mn 570, Aldrich), DMSO (MW of 78.13 g/mol, purity 98%, BDH), TDI (MW of 174.16 g/mol, Oekanal), Crotonic acid (MW of 86.09 g/mol, purity 97%, Fluka), ethanol (MW of 46.07 g/mol, purity 99.5%, Aldrich).

Method

Polyurethane synthesis

Classic. The reaction mixture was agitated at 500 rpm. A sucrose PU (PUSAC) was synthesized in molar relationships of 1:2 (PSAC 1) and 0.06:2 (PSAC 2) of polyol (sucrose, crotonic acid and PCL) and isocyanate, respectively, at 70 °C. The reaction was taken during 15 min.

Ultrasonic. The PU´s were synthesized with equal molar relationships of the monomers that in the classic synthesis but in this case, the whole synthesis process was carried out in ultrasonic bath of 35 kHz, without agitation, the polymers were left at rest for 48 hr to polymerization. After, the polymers are precipitate with ethanol-water

(1:1) and water solutions, finally, the polymers were filtered to hole, being obtained the sucrose PU.

Nuclear Magnetic Resonante (NMR) The NMR analyses of the PU´s were carried out in a team of Brucker of 500 MHz Brucker apparatus and the tetramethylsilane (TMS) as standard internal /8/.

Fourier Transform Infrared Spectroscopy (FTIR) The FTIR analyses of the PU were determined by means of a Spectrometer FTIR 4 100 type TO, Julabo, of resolution 4 cm^{-1}, detecting TGS in range of 3 500 cm^{-1} and 600 cm^{-1} with addition of ATR. The assignments of the absorption bands main in the spectra were studied of agreement with the program for the assignment of spectra to GO to SEIZE version 2.0 /8/.

Computational study. Theoretical calculations of the electronic structure of sucrose, DMSO, TDI and PU were analyzed with the HyperChem suite /9/.The standard molecular mechanics method used was based on the Polak-Ribiere algorithm with a RMS gradient value of 0,1 kcal/mol/Å according to the HyperChem manual /9/.

Kinetic studies

The studies of the PU synthesis kinetic were carried out with the Hyperkinetic software, which is a program of biological application, which is used to determine the kinetic constants of the enzymatic reactions. It carries out quantitative analysis of the enzymatic activity as well as Michaelis - Menten calculations /10/.

● Results and discussions

Analysis of total energies and QSAR properties of PU

Table 1 shows the results of the analysis of the PU structure by means of DMSO, TDI, and PEG-600, using different types of polyols like sucrose, crotonic acid and PCL. It is appreciated that the total energy that represent the changes of the Gibbs free energy are determined through the geometry of optimization, which was used to locate a minimum energy in the potential energy surface, and this way to get the balance structure of a molecular system, while the option of molecular dynamic used numeric methods for represents an interface between the experimental and theoric laboratory, to determine this way the relationship among the molecular structure, movement and function of the reactions, it is appreciated that the energy values are negative they indicate that the reactions are carried out for both models.

TABLE 1 TOTAL ENERGY OF PU SYNTHESIZED BY MEANS OF DIFFERENT TYPES OF POLYOLES (SUCROSE, CROTONIC ACID AND PCL)

POLYOL	SUCROSE	CROTONIC ACID	PCL
OPTION	**TOTAL ENERGY (Kcal/mol)**	**TOTAL ENERGY (Kcal/mol)**	**TOTAL ENERGY (Kcal/mol)**
Geometry of optimization	- 958 91	- 964 89	- 943 27
Molecular dynamic	- 952 92	- 963 78	- 942 89

Table 2, shows the properties analysis of Quantitative Structure-Activity Relationships (QSAR) of the PU synthesis reactions by means three types of polyols (sucrose, crotonic acid and PCL) where it is appreciated that the psychochemical properties starting from the electronic structural parameters turned out to be very similar.

TABLE 2 QSAR PROPERTIES OF PU SYNTHESIZED BY MEANS OF DIFFERENT TYPES OF POLYOLS (SUCROSE, CROTONIC ACID AND PCL)

PROPERTIES	SUCROSE	CROTONIC ACID	PCL
Surface area (Å^2)	74 165,4	74 195,5	74 175,4
Volume	71 278,4	71 318,8	71 296,2
Log P	- 4,55	- 5,65	- 4,69
Refractivity (Å^3)	129,60	131,36	130,58
Polarizability (Å^3)	50,52	56,78	54,69
Mass (amu)	5 945,9	5 948,9	5 946,4

^{13}C- NMR Analyses

PU Synthesized due Sucrose

Figure 1 shows the NMR spectrum of PU. Signs between 5 to 9 ppm are representative that it is carried out the polymerization reaction. Sing to 11 ppm is attributed to the carbons of the glucose ring and the signs from 12 to 15 ppm are attributed to the methyl groups of the TDI, from 16 to 30 ppm and of 90 to 110 ppm are characteristic signs of the carbon together to the hydroxyl groups of the sucrose structure, to 52 ppm represented the characteristic sign of the C-O bond.

From 64 to 77 ppm are shown the sucrose signs, from 81 to 89 ppm and of 114 to 120 ppm are assigned to the different carbons that are of the reaction of the isocyanate (TDI) with the hydroxyl groups (sucrose), to 122 ppm the sign of the carbon of the isocyanate group is presented.

The sign assigned to HA of the glucose is characteristic of the o-glucosidic bond is presented to the 5 ppm and, therefore, it is proven that the sucrose structure stays during the polymerization reaction. In the aromatic area, the signs appear of 7 - 8,5 ppm due to the carbons of the aromatic ring (TDI). /11/

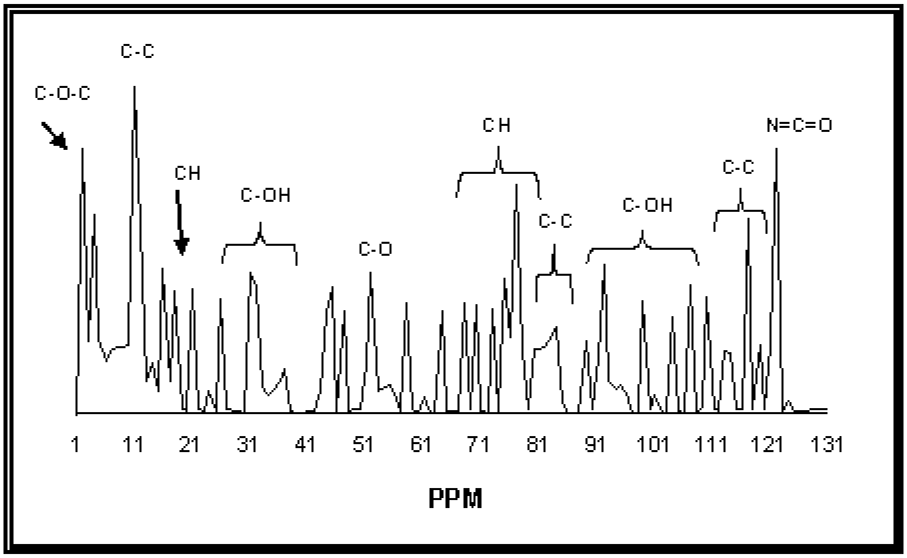


Figure 1. NMR Spectrum of the PU Molecule by Mean Sucrose.

PU Synthesized due Crotonic Acid

Figure 2 shows the NMR spectrum, where is appreciated that, the signs from 8 to 12 ppm and from 20 to 34 ppm correspond to the C-C bonds of the methyl groups (PEG). From 15 to 18 ppm are characteristic signs of the methyl groups of TDI, from 35 to 40 ppm the signs are attributed to C=C of the crotonic acid bond and from 42 to 46 ppm are attributed to the C-C of the crotonic acid chain.

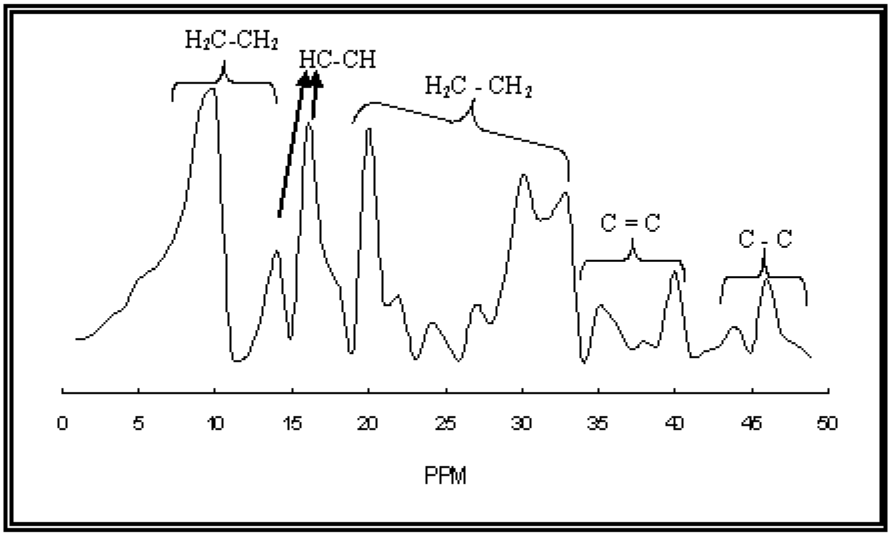


Figure 2. NMR Spectrum of the PU Molecule by Mean Crotonic Acid.

PU Synthesized due PCL

Figure 3 shows the NMR spectrum, where is appreciated that, the signs to 7 and 20 ppm correspond to the C-C bonds of the methyl groups (PEG), to 13 ppm are characteristic signs of the methyl groups (TDI), to 33 ppm the signs are attributed to C-C bonds of the methyl groups (PCL).

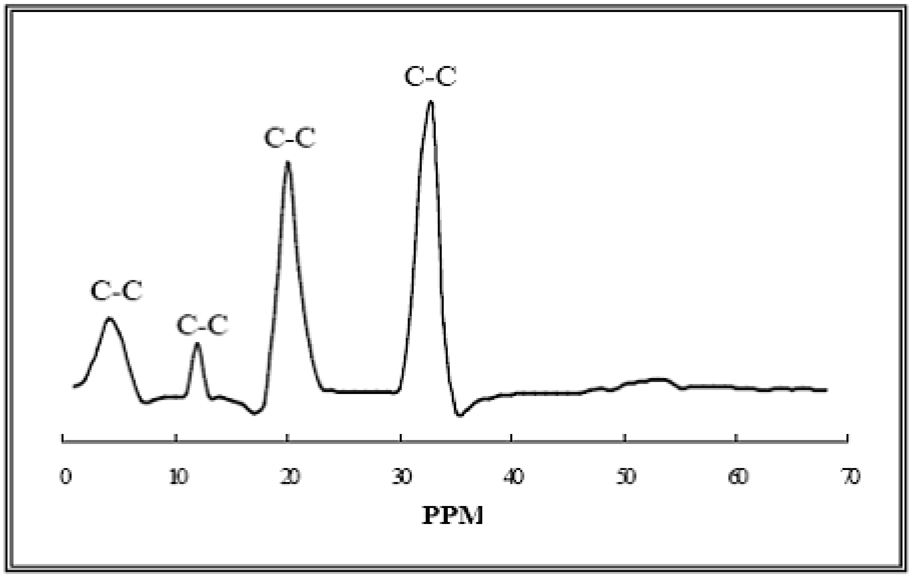


Figure 3. NMR Spectrum of the PU Molecule by Mean PCL.

FTIR Analysis

PU Synthesized by mean Sucrose

Typical FT-IR spectra of the polyurethanes are shown the absorption band of the OH disappears, during the reaction of sucrose and PEG and appears bands to 3274 cm^{-1} of NH with the same position of the OH bands, but with a very special characteristic, that the band is narrow and less intense. To 1637 cm^{-1} the sign of carbonyl group appears, indicating the possible formation of the urethane group. The PU bands are detected to 1600 cm^{-1} characteristics of the aromatic ring of the TDI, to 1218 and 1068 cm^{-1} attributed to C-O. /8/

PU Synthesized by mean Crotonic Acid

The infrared spectrum of PU by mean crotonic acid shows that the OH stretching band presents a shoulder to 3300 cm^{-1} that can be awarded to the asymmetric stretching vibrations (amine N-H bond) besides the symmetrical stretching of the H-N-H bonds appears to approximately 3290 cm^{-1} and the asymmetric stretching appears to 3300 cm^{-1}. A confirmation of the presence of the amine signs is the appearance due to the deformation type scissor, alone for primary amines that appears approximately to 1615 cm^{-1} /12/.

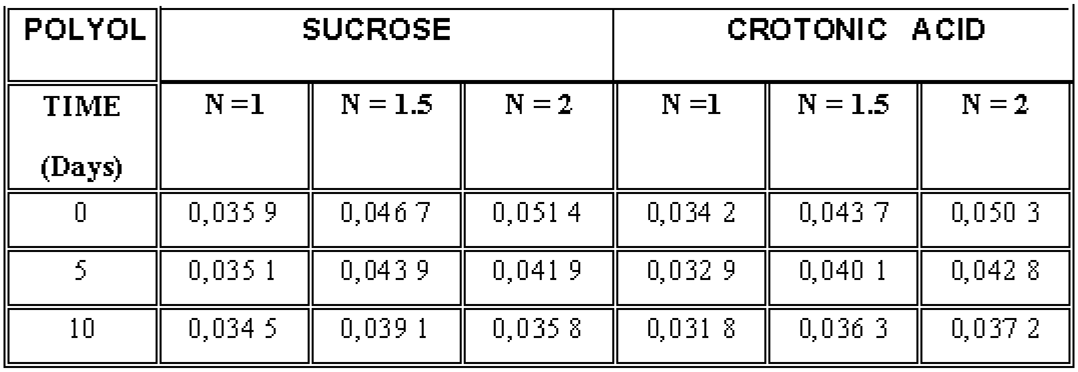
PU Synthesized by mean PCL

The PU spectrum shows that the region from 3420 to 3380 cm^{-1} of the hydrogen bonds of urethane coincide with the main band of the OH group from 2950 to 2830 cm^{-1} attributed to the CH stretching bands of methyl groups, to 1720 cm^{-1} is due to carbonyl (C=O) band. The confirmation of urethane group settles down with the presence from 1627 to 1545 cm^{-1} due to the deformation vibration of the NH bond and C-N stretching. Also, to 1525 cm^{-1} it is attributed to the amide NH flexion related with the urea formation, from 1187 to 1015 cm^{-1} are attributed to the stretching of the C-N, C-C and C-O bonds, and finally from 820 to 666 cm^{-1} NH vibration in fan outside of the plane. The characteristic peak of the PU to 3330 cm^{-1} is due to the vibration of the way NH stretching vibration, to 1730 cm^{-1} of the C=O stretching vibration without hydrogen, to 1535 cm^{-1} corresponds to the way NH stretching and the peak to 1222 cm^{-1} is assigned to the CN stretching bond.

Kinetic Studies

Tables 3 and 4 show the comparison of the different reaction orders (1, 1.5 and 2) of the PU synthesized due to sucrose, crotonic acid and PCL, respectively) where, the application of the differential method determines that the mechanism reaction is adjusted to a first order, because the speed constants to the different days are very similar, while for the order 1.5 and 2 the constants present important changes in the constants. Table 5 shows the results of the analysis due to Hyperkinetic software which allows the visualization with bigger speed of the kinetic parameters, which confirms that the enzymatic reaction mechanism was adjusted to a first order, for the different PU´s synthesized.

TABLE 3 COMPARISON OF REACTION ORDER OBTAINED BY MEANS OF THE DIFFERENTIAL METHOD FOR THE PU´S SYNTHESIZED WITH SUCROSE AND CROTONIC ACID, RESPECTIVELY.



POLYOL	SUCROSE			CROTONIC ACID		
TIME (Days)	N =1	N = 1.5	N = 2	N =1	N = 1.5	N = 2
0	0,035 9	0,046 7	0,051 4	0,034 2	0,043 7	0,050 3
5	0,035 1	0,043 9	0,041 9	0,032 9	0,040 1	0,042 8
10	0,034 5	0,039 1	0,035 8	0,031 8	0,036 3	0,037 2

TABLE 4 COMPARISON OF REACTION ORDER OBTAINED BY MEANS OF THE DIFFERENTIAL METHODTFOR THE PU´S SYNTHESIZED WITH PCL

POLYOL	PCL		
TIME (Days)	N =1	N = 1.5	N = 2
0	0,027 9	0,038 8	0,040 6
5	0,027 4	0,025 8	0,027 8
10	0,027 1	0,012 8	0,015 0

TABLE 5 REACTION ORDERS OBTAINED OF THE SIMULATION IN THE HYPERKINETIC SOFTWARE

POLYOL	REACTION ORDER
Sucrose	1,043
Crotonic acid	1,012
PCL	1,054

Conclusions

Computational chemistry methods can be used to explore the theoretical chemistry behind reactive systems, to compare the relative chemical reactivity of different systems, and, by extension, to predict the reactivity of new systems.

Through the analysis of the diverse structures, was possible to determine that the reaction of PU synthesis is carried out because the energy free of Gibbs of the sucrose, crotonic acid and PCL, are negative, which were obtained by means of the Geometry optimization and Molecular dynamic. Also, it was possible to confirm that the positive coupling constants indicate that the energy of the levels increases when the spin disposition is the same in the nuclei and it spreads to diminish when the spines are different, while when the coupling are negative, the behavior is contrary.

The nuclear magnetic resonance (NMR), the characteristic signs of the sucrose, PEG-600 and PU were determined, respectively, being proven that in the region of 4-7 ppm are appreciated the carbonyl bond of the urethane group and in the area of 2 to 5 ppm are proven that all hydroxyl groups of the sucrose reacted, and finally, the reaction happened totally with the TDI. The infrared spectrum shows that the hydroxyl and diisocyanate groups disappeared and NH and carbonyl groups appear what indicates that the reaction happens through the groups OH and the isocyanate of the TDI.

The kinetic analyses by means of the differential method were proven with the simulation of the Hyperkinetic software which was adjusted to reaction of first order for the PU´s synthesized with sucrose, crotonic acid and PCL, respectively.

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