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Polymeric surfactants based on the chemical modification of alternating aliphatic polyketones

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Document Version

Publisher's PDF, also known as Version of record

Publication date:

2019

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Araya Hermosilla, E. A. (2019). Polymeric surfactants based on the chemical modification of alternating aliphatic polyketones. [Groningen]: University of Groningen.

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Functionalization of polyketones: beyond the synthesis of polymeric surfactants

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6.1 Introduction

A functional polymer is a “polymer that exhibits specified chemical reactivity or has specified physical, biological, pharmacological, or other uses that depend on specific chemical groups”. [127] The functional groups (for instance hydroxyl, carboxyl or amine groups) can be part of the polymer backbone or grafted onto it. In some cases, these materials are sensitive to external factors such as temperature, pH, ionic

strength, chemical agents, electric field, and light. [293–295] Hence, polymers that bear those functional groups may change their properties in response to environmental changes. [293, 296–299] There are two approaches to synthesize functional polymers: direct polymerization of functional monomers, [300–302] or the chemical modification of synthetic polymer. [303, 304] In this respect, polyketones have been chosen for the synthesis of functional polymer through the chemical modification approach due to the presence of highly reactive 1,4-di-carbonyl moieties that react with primary amines yielding water-resistant pyrrole units. The Paal-Knorr reaction possess important qualities: it is carried out in one-pot; it is solvent- and catalyst-free; and it yields water as the only by-product. Furthermore, the number of primary amines that can be utilized to functionalize polyketones is countless, making this easy synthesis a fast, cheap, easy and versatile approach to create polymers with almost any desired pendant functional group. Functional polyketones have been used for different applications such as self-healing materials, [149–151] emulsions with adhesive properties, [152, 153] coating materials, [154] and water-insoluble resins for the absorption of Ca^{2+} and Mg^{2+} . [155, 156] During this thesis, it has been shown that they can also be used for the synthesis of polymeric surfactants with pH-responsive character by starting from aliphatic polyketones. These products were used in the encapsulation or dispersion of hydrophobic and active low-molecular-weight molecules. For instance, polyketones bearing aromatic amines as pendant groups were able to encapsulate hydrophobic antibiotics without the utilization of organic solvent. In addition, polyketones chemically modified with an aliphatic secondary amine modified the properties of 5,10,15,20-Tetrakis-(sulfonatophenyl) porphyrin such as aggregation patterns, acid-base behavior, and luminescence characteristics.

The goal of this chapter is to present the flexibility of the Paal-Knorr reaction in the synthesis of functional polymers via the chemical modification of aliphatic polyketones. Besides the products already presented in this thesis, it is worth noticing also the possibility to use functional polymers obtained in this way as catalysts as well as emulsifiers for the production of different kinds of emulsions. The first application discloses a novel research area interesting at academic level while the second one stems from the amphiphilic nature of these polymers and aims at suggesting possible industrial applications. In particular, we show here the synthesis of supported ionic liquids polymers based on aliphatic polyketones and their utilization as catalysts for the production of cyclic carbonates. Furthermore, the application of two amphiphilic polymers with a pH-responsive character, also based on aliphatic polyketones, in the formation of water in oil emulsions will be shown.

6.2 Polymeric emulsifiers based on polyketones

6.2.1 Introduction

Emulsions are a type of dispersion systems formed by two immiscible liquids. Usually, these colloids are constituted by water and organic liquids (oil). [305] By mixing these two liquids and an emulsifier, it is possible to obtain oil-in-water (O/W) and water-in-oil (W/O) emulsion. However, more complex emulsions can be formed such as multiple emulsions. [306] O/W emulsions are constituted by an oil dispersed as droplets in the aqueous phase, and O/W emulsions by water as the disperse phase and oil as the continuous phase. Emulsions in nature are thermodynamically unstable (with the exception of mini-emulsions) such that the presence of a third constituent is necessary for the creation of a kinetically stable or a sufficiently stable emulsion. In this respect, polymeric surfactants have been used to assist the production of emulsions. [307, 308] Their function is to stabilize the emulsion mainly by steric hindrance when they are adsorbed in the hydrophobic/aqueous solution interface. [112, 119, 309] The stabilization of emulsion against flocculation and coalescence involves an energy barrier meant to avoid the droplets coalescence, i.e. at relatively short distances where normally the attractive Van der Waals interactions become predominant. One mechanism to stabilize emulsion is the electrostatic stabilization (produce by ionic surfactants), which is based on charge separation and the formation of a double layer. [310] Polymeric surfactants, [119, 311] also known as amphiphilic polymers, [123, 136, 312] are macromolecules composed of lyophilic and lyophobic segments (called hydrophobic and hydrophilic segments if the solvent is water) which are responsible for their properties in solution. [118] In general, surfactants are characterized for reducing the free energy of surfaces and interfaces, and for the self-assembly as micelles aggregates when their concentration reaches a certain value, the so-called critical micelle concentration (CMC). [313, 314] Due to these properties, surface active polymers have been used in many applications such as paper coatings, dyestuff, drug delivery, [315] agrochemicals, detergents and oil recovery. [126] In the case that the water solubility of the polymer depends on external stimuli such as pH, [316] light, [307] redox reaction, [317] and temperature, [133] the polymer might show a stimuli-responsive behaviour. [121] For instance, pH-responsive polymers can accept or release protons when the pH is adjusted, resulting in an alteration of their hydrophilic-hydrophobic balance. [131]

As already mentioned in the other chapters, polyketones are a remarkable class of polymeric materials for the synthesis of functionalized polymers, in this specific case polymeric surfactants. Polyketones can be functionalized with primary amines via the Paal-Knorr reaction. [147, 149, 150] The amphiphathic architecture of these polymers is based on a hydrophobic backbone consisting of aliphatic 1,4-dicarbonyl units and N-substituted pyrrole moieties and the grafted hydrophilic pendant groups. In addition, the latter are pH-responsive moieties (Figure 6.1).

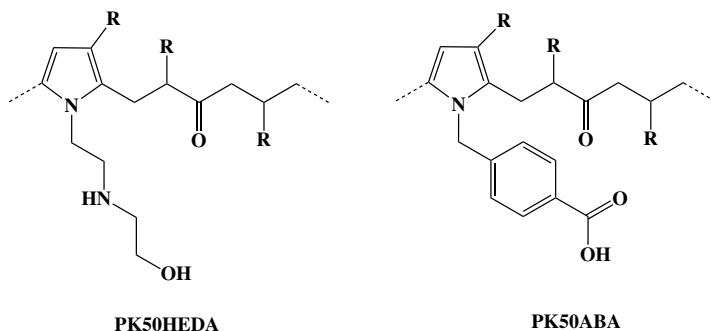


Figure 6.1: Polyketones modified with HEDA (left) and ABA (right).

Here we present the preparation of oil in water emulsions assisted by polymeric surfactants based on polyketones. The polymers were synthesized via the chemical modification of polyketones with N-(2-hydroxyethyl)ethylenediamine (HEDA) or 4-(aminomethyl)benzoic acid (ABA) using the Paal-Knorr reaction. These polymers were presented in the Chapters 3 and 5, respectively. The surface activity of the polymers was characterized through surface tension measurements. Moreover, emulsion stability tests were carried out in order to understand which factors may contribute to the stability of the emulsions.

6.2.2 Experimental

Reagents

For reagents, model compound and polyketones modification methods see chapter 3 and 5 for PK50HEDA and PK50ABA, respectively. In this chapter, the used polyketones are characterized by a carbonyl conversion of 0.63 (PK50HEDA) and 0.69 (PK50ABA).

Procedures

Surface tension studies. For PK50HEDA, the surface tension measurements were performed at 4 different polymer concentrations (0.5, 2.5, 5 and 15 mg/mL). The polymer was solubilized in acid conditions with HCl (1.0 M) and the pH was adjusted with aqueous NaOH (0.1 M). For PK50ABA, the measurements were performed at 5 different polymer concentrations (0.6, 3.0, 6.0, 18 and 30 mg/mL). The polymer was solubilized at basic conditions with NaOH (1.0 M) and the pH was adjusted with aqueous HCl (0.1 M). A 1 mL-plastic syringe was attached to a needle with a capillary radius of 1.65 mm. The temperature was set at 20 °C during the period of measurement and the water density was set to 0.997 g/mL.

Preparation of emulsions. The emulsions were prepared using a shaking machine (ABO ECH, IP 40). First, 10 mL of chloroform was added to 10 mL of the polymer solutions. Second, the solution (Chloroform and polymer solution) was shaken during 2 min. for the formation of the emulsions. Third, pictures were taken periodically to visualize the phase behavior.

Phases inversion in the prepared emulsions. Phase inversion experiments were carried out for PK50HEDA. First, emulsions with a polymer concentration of 2.5 and 15 mg/mL were formed. Second, the emulsion pH was adjusted to pH 7. Third, the pH of the emulsion was adjusted by adding a certain amount of NaOH (0.5M) and shaking the emulsion incite the phase inversion of the solution.

6.2.3 Results and discussion

Surface tension study of PK50HEDA and PK50ABA. Polyketones modified with HEDA and ABA displays an amphiphilic structure. The secondary amine and the hydroxyl groups provide the hydrophilic segments for PK50HEDA and the benzoic group the hydrophilic segments for PK50ABA. Furthermore, the hydrophobic segment is given by the backbone (Figure 6.1). The polymers are weak polyelectrolytes such that the solubility of the polymers can be altered by increasing or decreasing the pH. [131, 213] The polymers become less positively and negatively charged and, as consequence, the hydrophilic/hydrophobic polymeric balance changes in favor to hydrophobicity. This phenomenon was studied measuring the surface tension of the polymer solutions. Figure 6.2 shows the reduction of surface tension of the polymer solutions as a function of the pH and polymer concentrations. The polymers lose their charge as the pH increases or decrease and the hydrophobic blocks begin to be absorbed at the water/air interface. Consequently, the polymer lowers the surface tension of the solution. [214, 215] PK50HEDA displays a higher surface activity as the pH increases. This is expected since increasing the polymer hydrophobicity results in a higher polymer surface excess. [216] In addition, it is well known that increasing the concentration of surfactants causes an increase of surface activity. This is observed as the surface tension decreases with the increase of the polymer concentration at each value of pH (Figure 6.2 left).

PK50ABA displays a higher surface activity as the pH decreases and at high polymer concentrations (Figure 6.2 right). The surface tension measurements show a smooth curve such that is not possible to identify the critical micelle concentration. [147] Moreover, it is worth mentioning that the polymer is insoluble in water at concentrations higher than 6.0 mg/mL at pH 8; and the polymer cannot be dissolved in aqueous media at the concentrations of 18 and 30 mg/mL under pH 9.

Emulsion stability. At almost equal volume fractions (as in the present case), the polymer structure is most relevant factor to determine whether the continuous

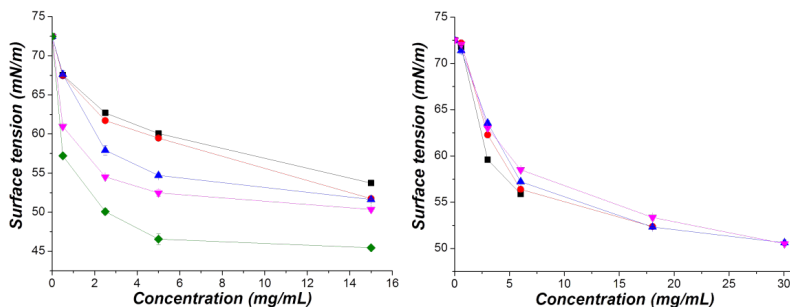


Figure 6.2: Surface tension graph of PK50-HEDA (left) and of PK50-ABA (right) as a functions of pH and concentration. PK50-HEDA (■) pH 3.0 (●) pH 4.0 (▲) pH 5.0 (▼) pH 6.0 (○) pH 7.0. PK50-ABA (■) pH 8.0 (●) pH 9.0 (▲) pH 10.0 (▼) pH 11.0.

phase is the water or oil in emulsions formed with the presence of polymer emulsifiers. [308] In addition, according to the Bancroft rule, the continuous phase is the phase where the emulsifier is more soluble. [318] As mentioned above, PK50HEDA can be dissolved in water under acidic condition. Therefore, it is possible to affirm that the emulsions formed by using water, PK50HEDA, and chloroform are O/W emulsions. There are two factors that may influence the stability of oil in water emulsions: the emulsifier concentration and the surface tension. [319] Figure 6.3 shows the stability of emulsions (measured here as the time needed for phase separation) as a function of pH and polymer concentration. It can be observed that the stability of the emulsions increases as the polymer concentration and the pH increase. The least stable emulsion is the one at a polymer concentration of 0.5 mg/mL. At this condition, the polymer displays a higher surface tension which means that more energy is needed to stabilize the emulsion. The polymer becomes more hydrophobic at higher pH values, which contributes to lower surface tension. Consequently, less energy is needed to obtain a more stable surface, raising the emulsion stability. In addition, the emulsions at higher polymer concentrations show higher stability, which is correlated to the low surface tension displayed by the polymer (Figure 6.2 right).

In a similar way, the emulsions assisted with PK50ABA are also O/W emulsions. Figure 6.4 shows the stability of the emulsions at a polymer concentration of 3.0 mg/mL. The emulsion stability decreases as the pH decreases which is the opposite as for the emulsions assisted by PK50HEDA. This is not surprising as the polymer becomes more soluble in water as the pH increases, which result in a lower surface activity. Concerning to the emulsions at concentration of 6.0 mg/mL, all of the emulsions at pH between pH 8 and pH 11 were stable for more than 6 hours. It is worth to mention that a polymer concentration of 0.6 mg/mL, the emulsion cannot be formed. This was mainly because the concentration of the polymer was very low and the surface tension was close to the value of water. On the other hand, the

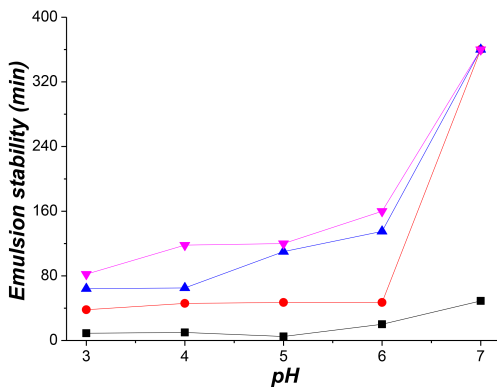


Figure 6.3: Emulsion stability in a function of the concentration of PK50-HEDA and pH. (■) 0.5 mg/mL (●) 2.5 mg/mL (▲) 5.0 mg/mL (▼) 15 mg/mL.

emulsions formed at a higher polymer concentration and lower values of pH display better stability and their life time was higher than 6 hours (data not shown).

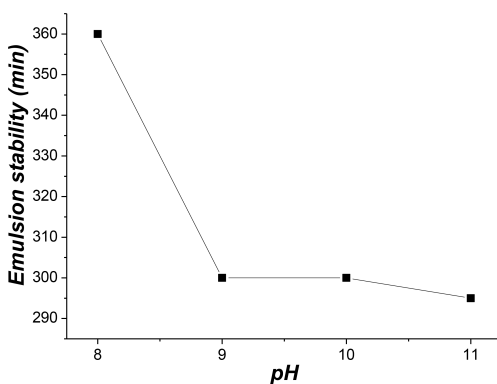


Figure 6.4: Stability of the emulsions produced with PK50ABA at a concentration of 3.0 mg/mL.

Phase inversion. For the polymers presented in this chapter, the ability to react to the external pH and change the hydrophilic/hydrophobic balance can be conveniently exploited to change the solubility of such polymers and thus, according to the Bancroft rule (*vide supra*) the kind of emulsion, i.e. O/W or W/O. PK50HEDA is soluble in water at low values of pH and it develops into a more hydrophobic macromolecule when the pH increases. It would be expected that by changing the pH from acid to basic of an O/W emulsion assisted by PK50HEDA, the oil may become the continuous and water the dispersed phase. Thus, a simple change in pH values might induce the formation of a W/O emulsion. Phase inversion experiments were conducted to emulsions formed with PK50HEDA at polymer concentrations of 2.5 and 15 mg/ml. In both cases, the initial pH of emulsions was 7 and the inversion point of the emulsions was around pH 8 for both concentrations (Figure 6.5). However, the polymer precipitated in time from the solution as probably its solubility in chloroform is not sufficient. Moreover, the stability of the inversed emulsion is low and the phenomenon of phase inversion was difficult to identify at a polymer concentration of 2.5 mg/ml. Indeed, phase separation was observed within 1 minute. However, when the concentration increased to 15 mg/ml the stability of the emulsion increased significantly.

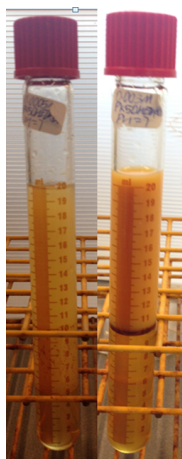


Figure 6.5: Phase inversion point of emulsions assisted by PK50HEDA at different concentrations. 2.5 mg/mL (left) and 15 mg/mL (right)

The occurrence of phase inversion is particularly interesting when considering industrial applications as the interfacial tension at the phase inversion point reaches a minimum. [320] In turn, this entails the possibility to produce emulsions with very little mechanical energy input by, on purpose, adjusting the pH values in order to “pass” the phase inversion point at least twice. Although the systems presented here

need still optimization for this purpose (e.g. in terms of solubility issues and stability as reported above), the fact that they can induce phase inversion is already positive. Obviously more research is needed in order to further study this possibility.

6.2.4 Conclusions

A series of new functional polymers were synthesized through the chemical modification of aliphatic polyketones with HEDA and ABA. It was illustrated that the resulting polymer perform interesting behaviour and they could act as polymeric surfactants, after protonation or deprotonation processes. Moreover, it was possible to form emulsions by using the derived polymer. The stability of the emulsions depended on the polymer concentration and the values of pH. Furthermore, the phase inversion experiments can indicate that the polyketones modified by HEDA behave as pH-responsive polymeric surfactants.

6.3 Catalysts Based on Polyketones¹

6.3.1 Introduction

Global warming is considered one of the main environmental problems of our times. [321] The gases that cause it are carbon dioxide (CO₂), nitrous oxide (N₂O), methane (CH₄), fluorocarbons (CFs) and chlorofluorocarbons (CFCs). [322] The control of the emission of CO₂ is desired since there is a near-linear correlation between the rise in global mean temperature and the carbon dioxide emission. [323, 324] Essentially, the natural carbon cycle (photosynthesis) may recycle 203 Gt of CO₂ each year, whereas the anthropogenic activities create around 7 Gt per year. Although it represents barely the 3.4% of the total CO₂ reused in the natural cycle, the natural carbon cycle cannot recycle the excess of CO₂. [325] Therefore, this phenomenon triggers the accumulation of this molecule in the atmosphere. The International Panel on Climate Change has projected that, by the year 2100, the atmosphere will be composed up to 570 ppm of carbon dioxide, which would produce a temperature rise of 1.9 °C and an increase of the sea level of 38 m. [326, 327] In order to prevent the risky reinforcement of the greenhouse effect, the industries that rely on fuel combustion might move to renewable energy technologies. Nevertheless, the latter is not able to supply the high demand of energy to power the global economy.

In this context, other initiatives have been created. They are directed to mitigate the emission of CO₂ through its capture and utilization. [323, 328–330] The transformation of CO₂ into valuable chemicals may stimulate the carbon capture and it also represents an excellent alternative for the substitution of non-renewables petrochemicals as chemical feedstocks. [331, 332] This gas displays excellent characteristics: it

¹This sub-chapter was performed in collaboration with A. J. Kamphuis and this work will probably appear in both theses.

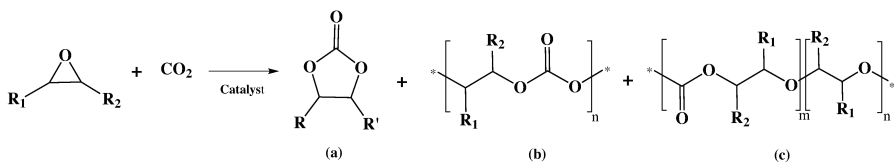


Figure 6.6: Possible products of the reaction CO₂ with epoxides. (a) Cyclic carbonates. (b) Polycarbonate. (c) polycarbonate containing ether linkages. [336]

is non-toxic, inexpensive, renewable and extensively available. [333, 334] Nevertheless, the usage of carbon dioxide as reagent is limited due to its high thermodynamic stability. [334, 335] This difficulty is overcome by reacting CO₂ with compounds that possess high free energy. [332, 336] One option is the reaction of epoxides with CO₂ to synthesize cyclic carbonates and polycarbonates (Figure 6.6). [337–340] Although the utilization of carbon dioxide as monomer in the synthesis of carbonates is a promising approach for the production of valuable chemicals, it should be noted that the potential yearly market of the obtained products implies that this route does not contribute significantly to the decrease of atmospheric CO₂ concentration. Cyclic carbonates are the thermodynamic product of this reaction. They have been used as aprotic polar solvents, [341] electrolyte solvents and electrolyte additives for lithium batteries, [342, 343] and intermediates in the production of polymers, drugs and pesticides. [344–348]

The reaction between CO₂ and epoxides is carried out in the presence of a catalyst due to the thermodynamic and kinetic inertness of the former. [344] The chosen catalyst can initiate the reaction by either activating the epoxide or CO₂, or both at the same time. [336] Most of the systems that have been investigated possess Lewis acid sites for the electrophilic activation of the epoxides and/or CO₂ and a nucleophile (Lewis base) for the ring opening of the epoxide (Figure 6.7). [333, 336, 348] In addition, this reaction can also be achieved only with a Lewis base.

Ionic liquids have been used as homogeneous catalyst for the cycloaddition of carbon dioxide and epoxides. [345, 350–353] However, its separation from the products involves distillation or extraction with organic solvents, which do not satisfy the concepts of green chemistry. [327, 345] To solve this problem ionic liquids can be immobilized on suitable supports, therefore, can be separated readily from the mixture. [354–358] For instance, ionic liquids have been immobilized onto amorphous silica, [359] mesoporous materials [356, 360], mlc-SILP materials [344, 357], graphene oxide [358] and magnetic nanoparticles. [361] An alternative to these types of systems are the polymer-support ionic liquids (PSIL). [362, 363] These systems combine the features of ionic liquids (thermal stability, low volatility, and non-flammability) with improved mechanical stability and process ability. [364] As mentioned above, homogeneous and heterogeneous catalysts have been used to initiate

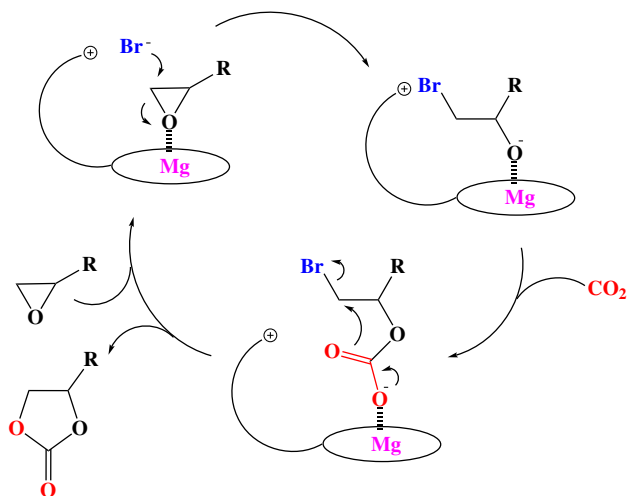


Figure 6.7: Scheme of a catalytic cycle via the cooperative activation of epoxide with a Lewis acid (Mg) and a nucleophile (Br⁻ ion). [349]

the cycloaddition of CO₂ to epoxides. [334, 365] Homogeneous catalysts display interesting characteristics. For instance, all the catalytic site are accessible for the reaction (active systems), and in addition, the chemoselectivity, regioselectivity, and enantioselectivity of the catalyst can be tuned. [332, 366] However, they are undesirable for the industry because their separation methods are cumbersome, energy consuming, and the catalyst may decompose if high temperature is needed for the separation (for instance distillation). [367] Moving to heterogeneous catalyst can solve this problem as they can be separated readily from the mixture after the reaction. [359] Nevertheless, this type of catalyst shows lower activity and reaction product yield in comparison to homogeneous catalyst. [332, 346] The generation of a system that combines the advantages and eliminates the disadvantages of homogeneous and heterogeneous catalyst is of paramount interest.

Due to the cheap synthesis and easy chemical modification of aliphatic polyketones via the Paal-Knorr reaction, they represent an interesting class of polymeric materials for the synthesis of polymer-supported ionic liquid catalysts. In this thesis, it has been shown the facile modification of polyketones with 1-(3-aminopropyl)-imidazole (Chapter 4), which can be easily quaternized with ethylene iodine (Figure 6.8). Besides, polyketones have been easily modified with furfurylamine yielding furan derivatives (PKFU). This type of polymer can be crosslinked with bis-maleimide via the Diels-Alder reaction (DA). [149–151] This results in a highly cross-linked polymeric network and can be disconnected at elevated temperatures through the Retro-Diels-Alder reaction (RDA). This system is a great approach for

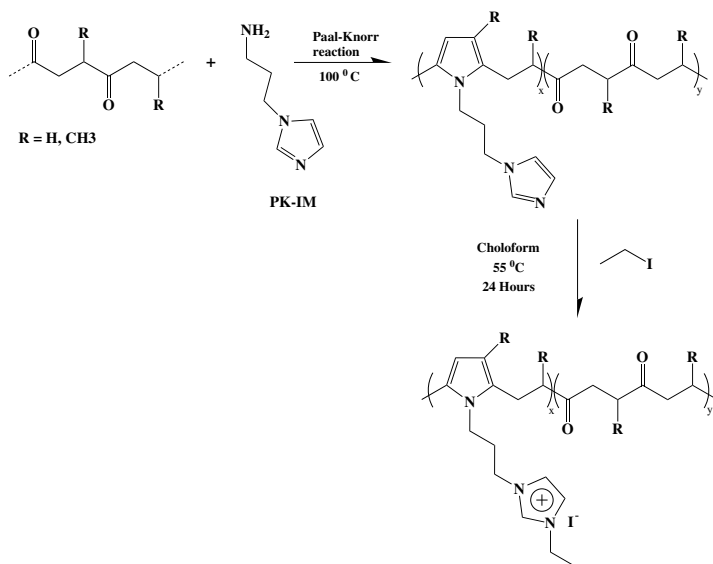


Figure 6.8: Schematic representation of a polyketones about to undergo a Paal-Knorr reaction with IM and the alkylation of imidazole group.

producing homogeneous catalysts and can also act as heterogeneous catalysts whether the polymer is crosslinked using the DA. Therefore, the synthesis of polymer supported ionic liquid with furan functional groups might permit its utilization as a hybrid catalytic system that can act as a homogeneous catalyst at reaction conditions and crosslinks via DA after, allowing easy catalyst separation.

In this chapter, we present the easy synthesis of catalysts by the chemical modification of aliphatic polyketones with 1-(3-aminopropyl)-imidazole and furfurylamine. Their imidazole groups were quaternized with ethylene iodide, yielding a series of polymer-supported ionic liquid catalysts (Figure 6.8 and 6.9). They were tested as homogenous catalysts for the synthesis of cyclic carbonates from carbon dioxide and epoxides under supercritical CO_2 conditions. The catalyst recovery through the polymer crosslink using the DA reaction is under investigation.

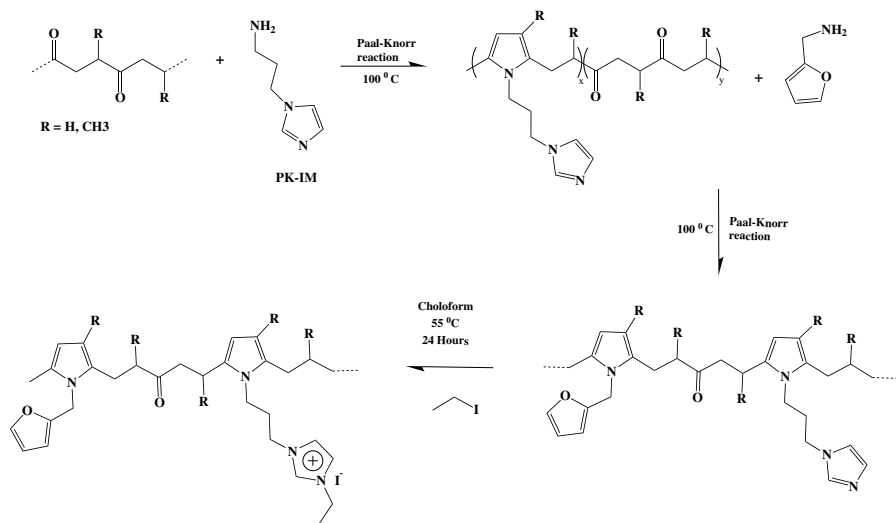


Figure 6.9: Schematic representation of a polyketones about to undergo a Paal-Knorr reaction with IM, FU and the alkylation of imidazole group.

6.3.2 Experimental

Reagents

1-(3-aminopropyl)-imidazole (IM) (Mw 125.17, 97% Sigma-Aldrich), ethyl iodide (EI) (Mw 155.97, 99% Sigma-Aldrich), 2,5-hexanedione (HD) (Mw 114.14, 98% Sigma-Aldrich), 1,2-epoxyhexane (Mw 100.16, 97% Sigma-Aldrich), styrene oxide (Mw 120.15, 97% Sigma-Aldrich), mesitylene (Mw 120.19, 98% Sigma-Aldrich) and tetrabutylammonium iodide (TBAI) (Mw 369.37, $\geq 99\%$ Sigma-Aldrich) were used as received. Furfurylamine (FU) (Mw 97.12 Sigma-Aldrich) was freshly distilled before using. Aliphatic polyketones made of ethylene, propylene, and carbon monoxide were synthesized according to a reported procedure [190, 210] yielding a polyketone with the aliphatic part comprised of 50 mol% ethylene and 50 mol% propylene (PK50, Mw 3636) and polyketone comprised of 30 mol% ethylene and 50 mol% propylene (PK30) (Mw 2930). DMSO (Aldrich) and CDCl_3 (Sigma-Aldrich) were used as solvents for $^1\text{H-NMR}$ analyses.

Procedures

Paal-Knorr reaction. A model compound (Pyrrole-IM) was synthesized as a reference for the characterization of the polymers, after the polyketone modification through the Paal-Knorr reaction. The reaction between the 1-(3-aminopropyl)-imidazole (IM) and 2,5-hexadione (HD) was performed in a round-bottom flask

equipped with a magnetic stirrer and a reflux condenser. First, 4.57 gr (0.04 mol) of HD and 5.0 gr (0.04 mol) of IM were dissolved in 30 ml of 1-propanol and transferred to a microwave (CEM Discover). The reaction was carried out during one hour at 100 °C (100 W). Secondly, the sample was placed in an oven for 48 h at 50 °C, in order to evaporate the solvent. Finally, the product was analyzed by ¹H-NMR (Varian Mercury Plus 400 MHz spectrometer), using (CD₃)₂SO as solvent. After the reaction between 1-(3-aminopropyl)-imidazole and 2,5-hexanedione (pyrrole-IM), it was performed the alkylation of the imidazole group (pyrrole-IMA). First, 0.4 gr. of pyrrole-IM (0.002 mol) and 0.31 gr. of iodoethane (0.002 mol) were dissolved in 50 ml of chloroform and placed in a round-bottom flask equipped with a magnetic stirrer and a reflux condenser. The reaction was carried out during 24 hours at a temperature of 50 °C. Secondly, the product was placed in an oven for 48 h at 50 °C, in order to evaporate the solvent. The product was characterized by ¹H-NMR (Varian Mercury Plus 400 MHz spectrometer) using (CD₃)₂SO as solvent.

Polyketone modification. The reaction was performed in a glass flask (100 ml) equipped with a magnetic stirrer and a reflux condenser. First, 19 gr. of PK50 (0.13 mol di-carbonyl group) and 15.9 gr. of IM (0.13 mol) were transferred to a microwave apparatus (CEM Discover). The reaction was carried out during 4 hours at 100 °C (100 W). Second, the products were further purified by solvent extraction technic, using as solvents water (the water was saturated with NaCl) and chloroform. Chloroform was evaporated using an oven at 50 °C for 48 hours. Third, the product was placed in an oven for 48 h at 50 °C, in order to evaporate the solvent. The product was characterized by ¹H-NMR using (CD₃)₂SO as solvent and elemental analysis. In the reaction between PK30 and IM, the same procedure as for PK50 was used. In this reaction, 11.5 gr. of PK30 (0.07 mol di-carbonyl group) and 8.75 gr. of IM (0.07 mol) were used (Table 6.1). The PK50 modification with IM and FU was carried out using the same procedure mentioned before. First 11.811 gr. of polyketones reacted with 4.69 gr of IM (PK50-IM40, Table 6.1). To calculate the conversion 1.37 gr of the product were remove and purified. Secondly, 10.442 gr of the converted polyketones were reacted with 3.21 gr of FU (PK50-FU40, Table 6.1). The carbonyl conversion was defined as the molar fraction of 1,4-dicarbonyl units converted via the Paal-Knorr reaction (x). It was calculated by elemental analysis (Euro EA elemental analyzer) by the following formula [157]:

$$x = \frac{NM_c}{nM_N + NM_c - M_p} \quad (6.1)$$

where N is the nitrogen content per g, M_N represents the atomic mass of nitrogen (14 g/mol), n is the number of nitrogen atoms of the converted 1,4-dicarbonyl segment, M_p is the molecular weight of the converted 1,4-dicarbonyl segment (215 g/mol PK50IM, 221 g/mol PK30IM80 and 187 g/mol PK50FU), and M_c is the molecular weight of the non-converted 1,4-dicarbonyl segment (126 g/mol for PK50

and 131.6 for PK30). M_p and M_c were calculated taking into account the incorporation of ethylene and propylene in the copolymers at ratio of 1:1.

In order to adjust the stoichiometry of the functional groups when the polyketones derivatives are used as catalyst, it was considered the polymer molecular weight (Table 6.1) given in g/mol of functional groups (FG). This is calculated by the following formula (the formula was slightly modified from the formula used by Toncelli et. al [157]):

$$FG = \frac{xM_p + yM_c}{x} \quad (6.2)$$

Where y is the fraction of non-converted 1,4-dicarbonyl groups, provided that $x + y = 1$.

POLYKETONE DERIVATIVE	PK50 (G)	MOLES OF DI-CARBONYL GROUP	AMINE (G)	MOLES OF AMINE	N (%)	x	FG (G/MOL OF BASIC GROUPS)
PK50-IM80	19.10	0.121	15.18	0.121	15.12	0.67	268
PK30-IM80	11.5	0.07	8.75	0.07	13.9	0.62	302
PK50-IM40	11.81	0.037	4.69	0.037	9.965	0.38	438
PK50-FU40	11.44	0.033	3.21	0.033	1.165	0.11	

Table 6.1: Functionalization of PK50 and PK30 with IM.

Alkylation of PK50-IM with ethyliodide. The catalysts were synthesized through the alkylation of polyketones imidazole groups. First, 2 and 4 gr of functionalized polyketones were dissolve in 50 ml of chloroform and place in a round bottom flask equipped with a stirrer and a reflux condenser; stoichiometric amounts of ethyliodide were added to the reaction mix (Table 6.2). The reaction was carried out during 24 hour at a temperature of 50 °C. Second, the polymers were filtrated to use the products which have all the imidazole alkylated. Third, the product was placed in an oven for 48 h at 50 °C, in order to evaporate the solvent. Finally, the products were characterized by $^1\text{H-NMR}$ (Varian Mercury Plus 400 MHz spectrometer) using $(\text{CD}_3)_2\text{SO}$ as solvent.

POLYKETONE DERIVATIVE	PK50 (G)	MOLES OF IMIDAZOLE GROUPS (M)	EI(g)	MOLES OF EI (M)
PK50-IM80	2	0.0072	1.12	0.0072
PK30-IM80	2	0.0066	1.03	0.0066
PK50-IM40-FU40	4.0	0.0091	1.42	0.0091

Table 6.2: Alkylation of PK50IM and PK30IM.

General catalytic experimental procedure. The catalytic experiments were conducted in an ILS-462 10 Parallel Batch Reactor constructed by ILS-Integrated Lab Solutions GmbH. This parallel batch reactor allows ten separate reactions that can be performed simultaneously in a temperature range of 20–200 °C and a pressure range of 1–200 bar. For each reaction sample an appropriate amount of catalyst and epoxide, and 3.0 mmol of mesitylene (internal standard) were weighed into a glass vial equipped with a magnetic stirring bar and a screw cap containing a silicone/PTFE septum. The glass vials were then transferred to the high-throughput batch reactor. The reactor was subsequently closed in accordance with the standard closing procedure. The parallel batch reactor was first purged three times with 5 bar of N₂, after which it was pressurized to 10 bar of CO₂. Five minutes were waited before depressurizing the reactor to atmospheric pressure in order to prevent damage to the Viton O-rings; after reaching atmospheric pressure another five minutes were waited. Subsequently, the reactor was pressurized to 50 bar CO₂. After reaching this pressure, the reactor was heated to the desired reaction temperature. Upon reaching the reaction temperature, the reactor was further pressurized to 80 bar of CO₂. The process of purging, pressurizing and heating the reactor takes approximately between one and a half and two hours. The start of the reaction was defined as the moment at which the magnetic stirring was switched on after reaching the desired reaction temperature and pressure. The reactions were carried out at 900 rpm stirring speed for 3 hours. At the end of the reaction the magnetic stirring and the reactor heating were switched off and the reactor water cooling was turned on. Upon reaching room temperature, the reactor was depressurized according to standard depressurization procedure. Cooling down and depressurizing the reactor took approximately between two and two and a half hours. After reaching atmospheric pressure the reactor was opened and the vials were removed. ¹H-NMR (Varian Oxford 300 MHz) was employed to determine the conversion and yield of the reactions. The calculations are based on a comparison of the protons marked in Figure 6.13 (A) and (B) (support information). The selectivity of the reactions was determined with ¹H-NMR and FT-IR (Shimadzu IRTracer-100 with ATR). As expected, no polycarbonate signals were observed with ¹H-NMR (Figure 6.13 (A) and (B), support information). Additionally, the lack of a polycarbonate C=O stretch signal in the FT-IR spectra confirmed a reaction selectivity of >99% (Figure 6.14 (A) and (B), support information).

6.3.3 Results and discussion

Model compound synthesis. Model compound using 2,5-hexanedione and IM was synthesized to better assign the signals in ¹H-NMR spectroscopy and to demonstrate the feasibility of the Paal-Knorr reaction (Figure 6.10 left). The resulting product after the Paal-Knorr reaction shows the signal corresponding to the pyrrole group at 5.8 ppm (protons 1). Pyrrole-IM model compound also displays 3 peaks on the aromatic zone which are attributed to the imidazole group at 6.9, 7.1 and 7.5 ppm corresponding to the protons 6, 7 and 8, respectively. The peaks at 3.9 (proton 3)

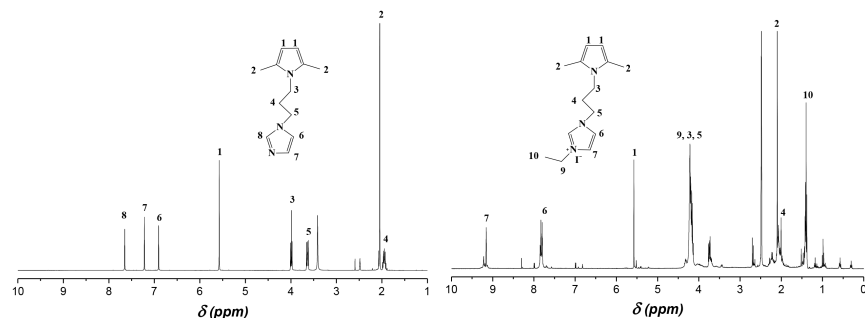


Figure 6.10: $^1\text{H-NMR}$ spectrum of pyrrole-imidazole model compound and after the alkylation of the imidazole group.

and 3.7 ppm (proton 5), are assigned to methylene protons next to pyrrole ring and imidazole group. The methylene protons (proton 4) positioned between the methylene groups next to pyrrole ring and imidazole are assigned at 2.1 ppm. Finally, the protons of the methyl groups adjacent to the pyrrole group appear at 2.2 ppm (proton 2). The quaternization of the imidazole group can be confirmed by the appearance of new peaks in the $^1\text{H-NMR}$ spectra. In the Figure 6.10 (right), it is noticed the appearance of the proton signals of the methyl (proton 10) and ethyl (proton 9) groups which belong to ethyl iodide. In addition, the protons signals of the imidazole group shifted to down field (proton 7 and 6) and proton 8 disappears.

Polymer synthesis. The success of the PK50 and PK30 modification can be confirmed $^1\text{H-NMR}$ spectroscopy. Figure 6.6 shows the $^1\text{H-NMR}$ spectra of PK50-IM (A) and PK30-IM (B). The polymers display the formation of the pyrrole with a signal between 5.5 and 6 ppm that correspond to protons 1 from the ethylene and propylene 1,4-dicarbonyl segments, respectively. When the Paal-Knorr reaction takes place on the propylene 1,4-dicarbonyl segment a peak appears at around 2.0 ppm corresponding to the methyl group (proton 2). The polymers display the methylene protons, which are close to the pyrrole ring and imidazole group (proton 3 and 4) at 3.9 and 3.6 ppm, respectively. In addition, it is possible to assign the protons of the imidazole group at 6.9, 7.1 and 7.5 ppm corresponding to the protons 5, 6 and 9, respectively. When PK50 is modified with IM and FU, it can be seen the peaks of the IM plus the peaks of FU. In the Figure 6.11 (C), it can be identified the aromatic peaks (position 5 and 6) and the ethylene peaks (position 3) of the furan groups.

Synthesis of supported ionic liquid catalysts. Here, we present the synthesis and characterization of new catalysts consisting of ionic liquids supported on polymers (Figure 6.11). The imidazole groups of the polymers mentioned above were quater-

nized with ethylene iodine. As expected, the quaternization of the imidazole groups produces the appearance of the methylene (proton 7 PKIM and 13 PK50-IM40-FU40) and ethyl (proton 8 PKIM and 12 PK50-IM40-FU40) proton signals which belong to ethyl iodide; they can be assigned around 1.5 and 4 ppm, respectively. In addition, the protons signals corresponding to imidazole group shift downfield (proton 5 and 6 PKIM and 9, 10 PK50-IM40-FU40) and proton 9 disappears (11 in the case of PK50-IM40-FU40).

Cyclic carbonate synthesis assisted by supported ionic liquid catalysts. The cycloaddition reaction of epoxides with CO₂ was carried out in the presence of three different supported ionic liquid catalysts (SILC) (PK50-IM80, PK30-IM80, PK50-IM40-FU40). It has been proposed that the synthesis of the cyclic carbonate may be commenced by the coordination of the epoxide with the ionic liquid (quaternary amine and the oxygen of the epoxide) followed by nucleophilic attack by the halide counterion. This opens the epoxide, which can generate a five-member cyclic charge intermediate with the ionic liquid (Figure Figure 6.12). Afterwards, the CO₂ approaches the charged system and is inserted into the molecule. The last step is the ring closing that generates the final cyclic carbonate. [356, 360, 368] The SILC display activity in the conversion of the two epoxides (Table 6.3), with a complete selectivity towards cyclic carbonate product (>99%) for the three temperatures (100, 120, 150 °C). It is well known that reactions with ionic liquids as catalyst without the assistance of metal centres require relatively high temperature in order to obtain an acceptable product yield, and these conditions favor the formation of the thermodynamically stable cyclic carbonate. [344] Moreover, the selectivity is almost 100% to cyclic carbonate since the catalyst systems do not present a Lewis acid moiety, which is necessary for the growing chain of a polycarbonate. The solubility of the reaction component is an important variable in this type of reaction. [337, 369] A higher carbonate yield was found for styrene oxide than for 1,2-Epoxyhexane. That can be explained by a better solubility of the polymer in styrene oxide (which is acting as reagent and solvent) due to the aromaticity of both molecules. In addition, styrene oxide possess a higher polarity, therefore it favors the interaction with the polar supported ionic liquid, where the catalytic reaction occurs. [344] The carbonate yield also depends on the catalyst concentration and the reaction temperature. [351, 359, 370, 371] As expected, increasing the temperature improves the yield of the carbonates synthesis. It can be seen comparing the entry 4 and 9, where it was used PK30IM as catalyst and the temperature increases form 120 to 150. It also occurs with PK50IMFU at the same temperatures (entry 6, 7, 11, 12). In general, lowering the amount of catalyst decreases the carbonate yield. However, for PK50IMFU and PK30IM (at 150°C), lowering the concentration in 50% affects the cyclic carbonate yield only by 14% and 20%, respectively (entry 8, 9, 10 and 11 respectively).

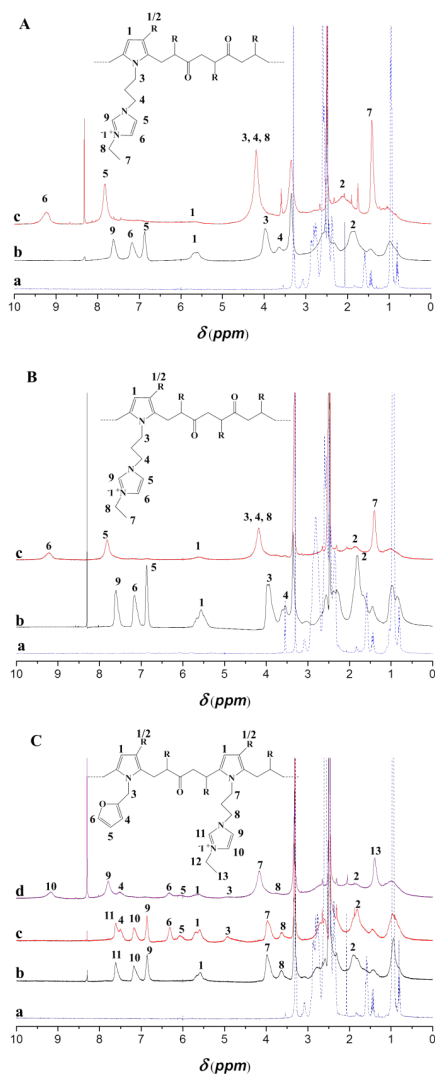


Figure 6.11: $^1\text{H-NMR}$ spectrum of PK50 (A), PK30 (B) modified with IM and PK50 modified with IM and FU (C). The alkylation with ethylene iodine. PK before modification (a). PKIM (b). PKIM after the alkylation of the imidazole group (c). PK50-IM40-FU40 after the alkylation of the imidazole group (d).

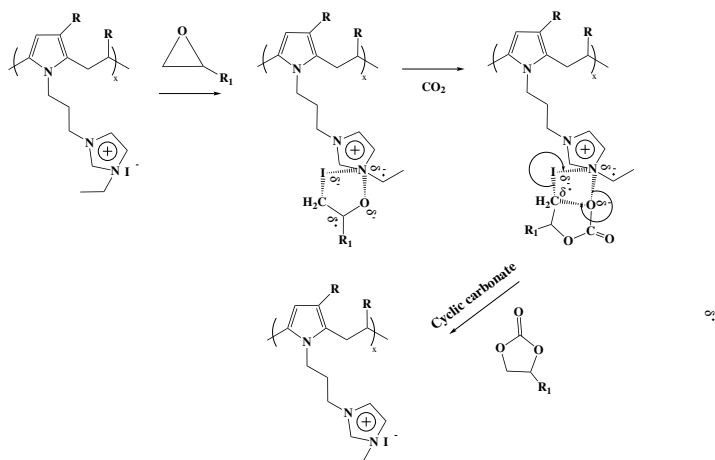


Figure 6.12: Mechanism proposed for synthesis of cyclic carbonates through the cyclic intermediate using ionic liquids immobilized onto polyketones. [356]

ENTRY	SUBSTRATE	AMOUNT SUBSTRATE (MMOL)	CATALYST	WEIGHT CATALYST (MG)	CATALYST (ODDE MMOL)	MESITYLENE (MMOL)	CONVERSION (%)	TEMPERATURE (°C)	CYCLIC CARBONATE SELECTIVITY (%)
1	Styrene oxide	30.0	PK50IM	42	0.12	3.0	8.7	200	>99
2	1,2-Epoxyhexane	30.0	PK50IM	42	0.12	3.0	8.9	100	>99
3	Styrene Oxide	50.0	PK30IM	76	0.2	5.0	36.6	120	>99
4	Styrene Oxide	50.0	PK30IM	38	0.1	5.1	20.2	120	>99
5	1,2-Epoxyhexane	50.0	PK30IM	38	0.1	5.0	0.57	120	>99
6	Styrene Oxide	50.0	PK50IM40FU40	55	0.13	5.1	26.4	120	>99
7	1,2-Epoxyhexane	50.0	PK50IM40FU40	55	0.13	5.0	3.8	120	>99
8	Styrene Oxide	30.0	PK30IM	45	0.12	3.0	96.2	150	>99
9	Styrene Oxide	30.0	PK30IM	23	0.06	3.0	75.3	150	>99
10	Styrene Oxide	30.0	PK50IM40FU40	66	0.15	3.0	98.2	150	>99
11	Styrene Oxide	30.0	PK50IM40FU40	33	0.075	3.0	84.8	150	>99
12	1,2-Epoxyhexane	30.0	PK50IM40FU40	66	0.15	3.0	65.4	150	>99
13	Styrene Oxide	30.0	TBAI	56		3.0	95.9	150	>99
14	1,2-Epoxyhexane	30.0	TBAI	55		3.0	82.5	150	>99

Table 6.3: Cyclic carbonates conversion by PK50IM and PK30IM.

6.3.4 Conclusions

The functionalization of polyketone with IM and FU was successfully achieved by the Paal-Knorr reaction. Their structures were confirmed by elemental analysis and $^1\text{H-NMR}$. We have also demonstrated the readily synthesis of support ionic liquids polymers based on aliphatic polyketones via the quaternization of the imidazole group with ethylene iodine. They are effective catalysts for the synthesis of cyclic carbonates through the cycloaddition of epoxides with CO_2 . We obtained nearly complete conversion of styrene oxide to cyclic carbonate and excellent yields with 1,2-Epoxyhexane at a temperature of 150°C with PK30IM and PK50FUIM in a solvent-free and CO_2 -rich environment. In addition, the materials might combine the assets of a homogeneous and heterogeneous catalyst if they will undergo the crosslinking process with maleimide compounds via the DA and be reused by de-crosslinking the network through the RDA. The latter is currently under investigation.

Supporting information

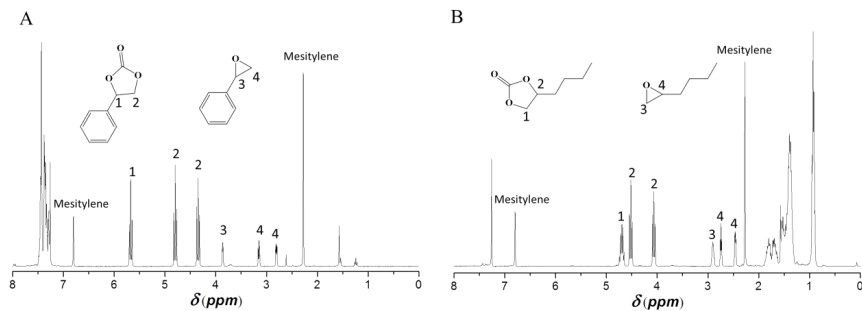


Figure 6.13: $^1\text{H-NMR}$ spectrum of a reaction aliquot from the reaction of CO_2 with styrene oxide (A), CO_2 with 1,2-epoxyhexane (B).

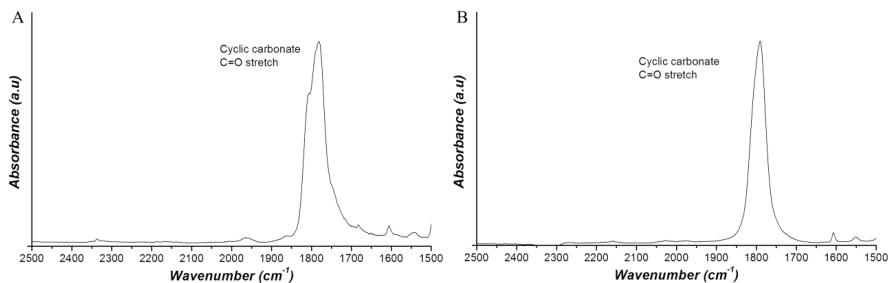


Figure 6.14: FT-IR spectrum of a reaction aliquot from the reaction of CO_2 with styrene oxide (A), CO_2 with 1,2-epoxyhexane (B).

