Functional polymers from alternating aliphatic polyketones
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Chapter 1

Introduction

Abstract
During the past 40 years, the synthesis and application of functional polymers (i.e. polymers displaying the presence of functional groups along the backbone) has become a major research topic at both academic and industrial levels. Depending on the specific chemical structure, systems have been developed for electrical, biological, thermal, mechanical or medical applications. These functionalized systems are generally obtained by post-manufacturing modification of non-functionalized or pseudo-functionalized polymers. However, the functionalization pathways offer little flexibility and remain limited to a small class of readily available polymers. This thesis focuses on a new route to produce functional polymers, i.e. the use of the Paal-Knorr reaction applied to alternating aliphatic polyketones. The presence of 1,4-dicarbonyl units along the backbone constitutes an important chemical feature for these polymers. Indeed, it allows the post-manufacturing functionalization through the so-called Paal-Knorr reaction, which introduces N-substituted pyrrole units along the polymer backbone. The synthesis and application of several novel polymers prepared in this way is the topic of this thesis.
1.1 Aim and structure of the thesis

This thesis aims at offering a large perspective on the use of modified aliphatic polyketones that can be obtained by the Paal-Knorr reaction. In a brief history of polyketones, in particular, alternating ter-polymers of carbon monoxide, ethene and propene are reviewed. Next, the major modification methods available to produce functional polymers are presented, including an overview of the accessible polymer structures. Thereafter, the chemical modification schemes available for aliphatic polyketones are reviewed and discussed. In particular, the Paal-Knorr reaction is highlighted as an efficient tool for converting aliphatic polyketones to semi-aromatic backbones containing pyrrolic units substituted with a functional group.

1.2 Polyketones: a relatively new class of thermoplastic and thermosetting materials

Historically, polyketones have been attracting the attention of several scientists at both academic and industrial level due to the relative simplicity of the corresponding monomeric units, i.e. carbon monoxide and unsaturated hydrocarbons.

The first high pressure copolymerization of CO and ethylene by radical co-polymerization was discovered in 1941 by researchers of Farbenfabriken Bayer [1]. The applied process generated thermally instable, difficult to process, random olefin – CO copolymers with relatively low levels (10-20 mol %) of carbon monoxide.

In 1953, Reppe and Magin [2] discovered alternating aliphatic polyketones by using milder conditions (200°C, 200 atm) using K$_2$[Ni(CN)$_4$] as catalyst in aqueous solution. The catalyst and ligand choice were optimized in order to achieve high molecular weight ethene/CO copolymers (ECO) as a new class of semi-crystalline thermoplastics with a crystallinity degree in the range of 35-50 wt % [3]. However, these ECO polymers appeared to be unstable at high temperatures resulting in rapid decomposition just slightly above their melting temperature (around 268°C) [4], which hindered their processability. As a solution to this problem, propene has been incorporated in order to decrease the polymer melting point, thus decreasing the lower limit of the processing temperature window. In this respect, the design of such EPCO terpolymers (ethylene-propene-CO copolymers) was possible as a consequence of the discovery of new homogeneous catalytic systems based on Palladium (II) complexes with bidentate phosphine or nitrogen ligands [5]. In the 1980s, Shell researchers patented the use of the same catalyst coupled with a Brønsted acid, such as tri-fluoroacetic compound, and methanol as reaction solvent. Production yields high enough for a market launch were achieved, i.e. 6 Kg of polymer (g of Pd)$^{-1}$h$^{-1}$ under mild conditions (90°C, 4.5 MPa) [6], while in 2002 even higher productivities were reported (i.e. 11.2 Kg of polymer (g of Pd)$^{-1}$h$^{-1}$) [7]. Shell introduced a series of ethene/propene/CO terpolymers in the polymer market under the trade name of Carillon [8] but, due to changing business strategies, stopped the production of this engineering thermoplastic in 2001.

1.2.1 ECO and EPCO properties and applications

Two forms of crystalline structure ($\alpha$ and $\beta$) are known for ECO polymers. Lommerts et al. [9] calculated the dimensions of both cell types; for the $\alpha$-form $A = 6.91$ Å, $B = 5.12$ Å, $C = 7.60$ Å; cryst. density = 1.382 g/cm$^3$ while for the $\beta$- form $A = 7.97$ Å, $B = 4.76$ Å, $C = 7.57$ Å; cryst. density = 1.297 g/cm$^3$. Moreover,
DSC analysis allowed detecting the presence of small endotherms around 100°C associated with the transition from the α to the β phase. The choice of appropriate reaction conditions and the design of metal catalyst allow the tailoring of the EPCO copolymers structure and, as a result, the bulk properties of the material vary from highly crystalline thermoplastics to highly amorphous elastomers [10]. Indeed, when the ethene/propene molar ratio during the polymerization is less than 0.5, the materials exhibit properties typical of amorphous low molecular weight polymers, while above this ratio the terpolymers are crystalline thermoplastics [11]. Lagaron et al. [12] found that the α/β ratio of the two crystalline structures decreases with increasing propene content in ethene/propene/carbon monoxide alternating polyketones. Indeed, above 2.9 mol % of propene intake, EPCO polymers show exclusively the presence of the β phase. The heat of fusion (degree of crystallinity) and melting point decrease with increasing propene level. Accordingly, crystalline density (as determined by WAXS) and lattice inter-chain interaction (as determined by Raman) were also found to decrease with the propene intake. Crystallinity influences inter-permeability gas diffusion and therefore aliphatic polyketones were found to have relevant barrier properties [13] towards gases such as oxygen or water vapor. As a consequence, such materials were recommended for food packaging applications. These require biocompatibility, which has been positively assessed for aliphatic polyketones produced by CO and several dienes [14]. Moreover, the chemical resistance against hydrocarbons was higher than for other commodity polymers (e.g. PS, PVC), thus encouraging application of these materials in fuel tank production [15] or as fire-retardant materials, fibers [16, 17], adhesives [18], membranes (micro-porous materials) [19].

1.2.2 EPCO blends and composites
Many blends have been realized by mixing polyketones with commodity polymers, such as polyamides [20, 21], polyalkylene-terephthalates [22], polycarbonates [23], polyurethane [24], polycrylates [25], polyethylene and polypropylene. In particular, relatively high impact resistance and toughness has been found for blends of polyketone and polyamides [26] probably as consequence of the hydrogen bonding between carbonyl and amide groups.
Blends with polystyrene [27] as well as with PVC [28, 29] have been recommended for food packaging applications, with prominent oxygen barrier properties when used as multi-layered polymeric films [30].
Moreover, polyketones are also used in combination with fillers, such as hydroxyapatite and alumina [31], in order to improve the toughness and decrease the overall material cost.

1.2.3 Chemical modification of EPCO copolymers
Besides the previously described excellent properties of (high molecular weight) aliphatic polyketones and the number of fields in which these polymers have already been used, a main feature of these polymers is the presence of carbonyl groups, which makes them valuable starting materials for post-modification. Indeed, C=O groups are highly polarizable, thus displaying high reactivity towards nucleophilic addition [32].
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The introduction of functional groups as pendant moieties along the backbone, such as alcohols [33, 34], ketals [35, 36], thiols [37], oximes [38, 39], methylene [40], cyanohydrin [41, 42] (Figure 1.1), conceptually invites the manufacture of bulk materials (EPCO oligomers) with a large variation of physical, thermal and morphological properties.

![Figure 1.1. Chemical modification of carbonyl and dicarbonyl units](image)

Moreover, such reactivity can be also employed when using EPCO oligomers as starting material for thermosets in the presence of bi-functional cross-linkers (Section 1.4.2).

1.2.3.1 Paal-Knorr reaction

Among all possible modification pathways listed in the previous section, 1,4-dicarbonyl moieties present in ethene-propene-CO terpolymers have shown peculiar reactivity towards thiol, alcohol or amines. Indeed, through a multiple steps mechanism, 1,4-dicarbonyl groups can be easily converted into thiophene [43], furan [43] or pyrrole [44] respectively. This reaction is known as the “Paal-Knorr” synthesis and it is particularly interesting when applied on EPCO alternating terpolymers and amine-substituted compounds, since it yields N-substituted pyrrolic units with functional groups remaining anchored along the main chain [45] (Figure 1.2).

![Figure 1.2 Paal-Knorr modification of thermosetting ethene/propene/CO terpolymer.](image)

\[ R' = H, CH_3 \]
R can be any aliphatic functional group linked to at least a methylene unit, or an aromatic functional one. However, the latter has to be connected to the amine group by at least two carbon atoms. The Paal-Knorr reaction can be carried out without any solvent or catalyst and produces water as sole by-product under relatively mild experimental conditions (i.e. atmospheric pressure, 110°C) [46]. Up to date, the Paal-Knorr mechanism constitutes a unique example of a functionalization reaction for which the aromatic density along the backbone (i.e. the relative amount of the rigid component in comparison with more flexible alkyl chains) and the functionalization degree can be simultaneously adjusted. This represents, to the best of our knowledge, a unique feature that polyketones have in comparison with the other functional polymers (e.g. polyolefins, styrenics and acrylates). The increased backbone aromaticity obviously hardens the polymer backbone and it might have an added value for specific applications, especially in dispersion of dyes through hydrophobic interactions. Furthermore, the Paal-Knorr reaction is sensitive to steric hindrance, thus rendering primary amine groups connected with secondary carbons less reactive than the ones connected to primary ones [45]. Such limitation (sensitivity to steric hindrance) can represent an advantage since it renders the reaction regio-selective, hence allowing, upon appropriate choice of the reagents, the synthesis of polymeric aromatic amines. Although polyamines represent a class of polymeric materials particularly useful as chelating agents for metal ions [47], polymeric surfactants [48], polyelectrolytes [49], ion exchange resins [50], DNA carriers for gene delivery [51], controlled drug-release [52], and antibacterial coatings [53], their synthesis is generally rather complicated and it involves several synthetic steps [54]. Therefore, the Paal-Knorr modification of aliphatic polyketones might represent a valid alternative for the next generation of aromatic polyamines. Moreover, this synthetic pathway is also very flexible since it allows the synthesis of polymeric backbones with several different pendant N-containing groups (e.g. primary, secondary, tertiary and aromatic amine groups) [45]. The easiness of the modification reaction and its versatility are the key features of EPCO copolymers that might be appealing in the market of functional polymers. In the following section, a historical overview of functional polymer synthesis is presented in order to highlight the peculiar differences and advantages of the Paal-Knorr reaction on EPCO oligomers as compared to functional materials synthesized by using other modification strategies.

1.3 Functional polymer synthesis: an historical overview

Bulk polymers are chosen for their properties (e.g. mechanical strength, flexibility, chemical stability, and processability) and are used in the production of films, pipes, automobile parts, electric and electronic components, medical and sanitary products, toys, construction and agricultural materials. By functionalization of the bulk polymer, improvement of specific properties (e.g. compatibility in polymer blends) is observed with respect to the original ones.
A pioneering role in functionalization of bulk polymers was assumed, during the 1970–1980s [55, 56] (Figure 1.3), by the free radical-initiated post-modification of polyolefins (PO). This method involves the PO treatment with a peroxide as radical initiator and an unsaturated monomer (e.g. maleic anhydride and its derivatives) [57].

**Figure 1.3** Chronological development of functional polymers according to the different functionalization strategies

These modified polymers showed enhanced affinity with polar organic molecules, metal and minerals, thus acting also as efficient compatibilizers for a large number of blends [58,59], composites [60] and nanocomposites [61, 62]. Such peculiar properties were obviously a consequence of the altered structure. However, the radical mechanism behind the functionalization process severely limits the kind (and amount) of functional groups which can be reacted with the polyolefin. This constitutes a relevant drawback if one takes into account that the degree by which a specific property (e.g. tensile modulus) can be improved is usually directly proportional to the functionalization degree. In order to increase the functionalization degree, several attempts have been carried out by changing the nature of the substrate, in particular by choosing a more reactive one with respect to the saturated aliphatic backbone of polyolefins. In this context, two basic strategies can be followed: post-functionalization or synthesis (and polymerization) of functionalized monomers. A typical example in this respect is constituted by styrenics and acrylates, which can be modified according to the routes described below (Figure 1.4).
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![Figure 1.4](image)

Figure 1.4 Routes for polymerization of functionalized monomers and post-modification of bulk polymers for styrene and acrylates. X represents a generic functional group.

Therefore, polymers which bear aromatic groups (such as polystyrenes [63]), unsaturation, heteroatoms, either along the backbone or pendant from the main chain, such as poly(acrylate)s and poly(methacrylate)s [64] or others, such as poly(vinyl ester)s [65], cellulose [66], chitosan [67], silica [68], poly(urethane)s [69], have been used in literature as building blocks for functional polymers.

While polymerization of functionalized monomers might present issues connected with side reactions and slower polymerization kinetics, post-modification of bulk polymers results generally in relatively low functionalization degrees. Both synthetic pathways have been used for the synthesis of several different kinds of functional polymers. However, all proposed strategies fail at fulfilling two precise and crucial requirements (in view of possible industrial applications): functionalization under mild conditions and with the minimum number of synthetic steps.

In particular, acrylates, methacrylates and styrene have displayed to better achieve the supra-mentioned requirement and several modifications have been carried out by using poly(4-chlorostyrene), poly(tert-butylmethacrylate) and poly(tert-butylacrylates) as precursors. However, this synthesis involves the use of solvents and catalysts, and it often occurs through several steps.

Against this backdrop, the Paal-Knorr reaction of EPCO oligomers represents an easy, original and alternative route in order to prepare functional polymers with relatively high functionalization degree (vide supra).

1.4 Functional polymers from chemically modified polyketones

1.4.1 Polymeric amines

Chemical modification of aliphatic polyketones by several kinds of di-amines (e.g. 1,2-di-amino-propane) has already been shown to constitute a simple synthetic approach towards the production of polyamines. The obtained materials have been tested as surfactants and the preparation of nano-sized emulsions (i.e. characterized by average particle size around 50 nm) with high stability (up to one month) has been reported [70]. Moreover, polymeric amines have been used as cross-linkers of multi-walled carbon nanotubes (MWNTs) by amidation-type reaction, with around 40 wt% polyamines grafted onto the surface of the
MWNTs [71]. The biological properties of polyamines synthesized by polyketone modification have also been assessed [72].

1.4.2 Thermo-reversible thermosets
Modified aliphatic polyketones bearing furan moieties (with a 1,4-dicarbonyl conversion around 80%) were found to undergo Diels-Alder/retro Diels-Alder reactions by employing 1,1’-(Methylene-di-p-phenylene)bismaleimide as the cross-linker. Because of the thermo-reversibility of this Diels-Alder cycloaddition, the resulting network displays typical thermoset properties but behave as a thermoplastic upon heating. Once cross-linked at 50°C, they can be re-processed at temperatures above 110°C. The results indicated 100% reversibility and recovery of mechanical properties as measured by the three-point bending test, DMA analysis and DSC [73]. The potential of using this reversible cross-linking and the modification of the polyketone backbone structure as tools to tailor the properties of the obtained materials will be investigated in this thesis.

1.4.3 Wood adhesives
Another application for functional materials derived from polyketones resides in the glue industry. On the basis of an earlier investigation at industrial level on the use of aliphatic polyketones emulsions in wood-glue industry [74, 75, 76, 77], important results have been achieved by Y.Zhang et al. [45]. Highly stable emulsions (up to 360 days) were obtained by using a primary amine-modified polyketone derivative in combination with virgin polyketone. The effect of physical factors, such as temperature, time and rotor speed and chemical ones such as protonation level and polyamine/polyketone ratio on the performance of the final product as wood adhesive were studied. Comparable shear strengths were found compared to the main commercial products, urea-formaldehyde and phenol-formaldehyde. The use of an environmentally safe cross-linker (i.e. amine-modified polyketones vs. formaldehyde) and excellent adhesion strength values constitute the main advantage of this pathway. Moreover, the original polyketone-based formulation can be successfully combined with natural products (such as proteins [78, 79]), resulting in a more prominent “green” character of the glue and in better properties. Indeed, a broadening of the glue lines (i.e. improved glue penetration in the wood) in the presence of polyketone water-based emulsion and soy proteins has been reported [78]. The use of soy proteins does not alter the satisfying adhesive properties with all the prepared protein-containing emulsions passing the European standard (EN-314) wood test with higher shear strength (1 MPa) than required. The use of Jatropha proteins (only partially soluble in water as compared to the fully soluble soy ones) resulted in even better performance as wood adhesive [79].

1.5 Thesis outline
This study aims at studying novel polyketones derivatives able to expand the current number and kind of applications for modified aliphatic polyketones obtained by the Paal-Knorr reaction.
Chapter 2 deals with the dispersion behavior of a water-soluble photosensitizer (i.e. tetraphenyl sulfonated porphyrine, TPPS) in the presence of two modified polyketones bearing imidazole (PK-Im) and pyridine (PK-Pyr) moieties. UV-Vis studies of aqueous solution TPPS with PK-Im and PK-Pyr were recorded at different pH and TPPS/polymer ratios. Two commercial polyelectrolytes, one aliphatic (polyallylamine) and one aromatic (poly(4-vinylpyridine)) were employed as reference systems. Finally the dispersion of TPPS induced by PK-Im and PK-Pyr were investigated when an acceptor polymer (Poly(viologen), PV10) is introduced in the system.

In Chapter 3, furan-modified polyketone by Paal-Knorr reaction are synthesized at different 1,4-dicarbonyl conversion levels and the thermal reversibility behavior is investigated at different furan/aromatic bismaleimide molar ratios. DMTA and DSC studies were used to investigate the differences between the prepared materials in terms of macro- (i.e. mechanical properties) and micro- (i.e. Diels-Alder reaction) reversibility achieved by varying the cross-linking density. Chapter 4 describes the use of cyclopentadiene-functionalized polyketones in the synthesis of thermally reversible thermosets. In analogy to the previous chapter, DMTA and DSC analysis were carried out in order to study the recovery of mechanical properties upon several different thermal cycles.

Chapter 5 describes the synthesis and use of three cross-linked modified polyketones bearing piperazine, glycine-like and primary amino groups as pendant units, and their application as macromolecular chelating agents for metal ion removal (e.g. Cu(II), Ni(II), Co(II), Fe(III), Cr(III), Ag(I) and Hg(II)) from water solutions. The role of each functional group contained in these polymers (i.e. primary, secondary and tertiary amine, carboxylic acid, carbonyls, pyrrole, imine) in the interaction with different metal ions has been qualitatively established by FT-IR studies. Metal ion uptake at different contact times and temperatures, as measured by atomic adsorption spectroscopy (AAS), allows quantification of the material absorption and capacity for the selected polymer-metal ion combinations.

Finally Chapter 6 shows the use of aliphatic polyketones as cross-linkers for amine-modified epoxy resins in electro-deposition coatings for automotive applications. An earlier study reported excellent adhesion, mechanical and anti-corrosion properties for the same cross-linking system, but low bath stability due to a high system reactivity. As the rate of the Paal-Knorr reaction was found to be sensitive to steric hindrance, 4-aminopiperidine (AP) and 4-aminoethyl piperidine (AMP) were selected as components to control the reactivity of the resin system. Several factors were considered, such as electrode distance, potential, and electro-deposition time. In order to optimize the annealing stage, temperature and curing time were varied too.
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