Alternating aliphatic polyketones, produced by co- and terpolymerization of carbon monoxide and olefins (mixtures of ethylene and propylene) using palladium-based homogeneous catalysis represent a very promising class of polymers for a wide range of applications. This research focused on chemical product development of low molecular weight, alternating aliphatic polyketones (Mw 1500-5500) (Figure 1).

**Figure 1** Synthesis of CO-ethylene-propylene based low molecular weight polyketones.

Besides many interesting chemical and physical properties, alternating polyketones can act as excellent precursors for the preparation of functional polymers by chemical modifications owing to the presence of highly reactive carbonyl groups along the backbone. The most interesting reaction route is the Paal-Knorr reaction (i.e. the 1,4-di-carbonyl moiety of the polyketones reacts with a primary amine function yielding a pyrrole unit), since this reaction can be accomplished at mild conditions without the need of any catalysts and organic solvent (Chapter 2 and Chapter 4). By using this route, a great variety of functional groups can be attached to the backbone of the polyketones (Figure 2). This could open up pathways to new chemical products and lead to the discovery and development of new applications for alternating polyketones. In this thesis, the work focused primarily on amine- and furan-based polyketone derivatives.

**Figure 2** Preparation of functional polymers from polyketones via Paal-Knorr reaction.
Summary

The current market of wood adhesives is dominated by urea-formaldehyde or phenol-formaldehyde based thermosetting resins, which are known to be hazardous substances as formaldehyde is classified as a suspected carcinogenic chemical. In Chapter 3, water-based polyketone emulsions have been developed for the application as formaldehyde-free and environmental-friendly wood adhesives using a simple and cost-effective route. Polymeric amines derived from the polyketones were applied as polymeric surfactants for the self-emulsification of polyketones. All processing steps, including surfactant preparation, surfactant protonation, and resin emulsification can be performed in single one-pot reaction. Polyketone-based wood adhesives do not release any volatile toxic components during the manufacture nor during the application and end-use cycle. The byproduct obtained during the manufacturing and curing steps is only water. The prepared wood emulsions exhibit extremely long shelf-life at room temperature and were found to be stable and effective as wood adhesive even after a period of 2 years. The achieved submicron particle size (less than 500 nm) of the emulsions remained basically unchanged in time, thus demonstrating high kinetic stability of the emulsions. Cryo-SEM studies revealed uniform and spherical microstructures of the emulsion particles. The viscosity of the system decreases significantly in the first week which may be due to a rearrangement of the polymers at the surface of each particle (i.e. a kind of “arms”-free polymer chains retraction onto the surface of the polymer particle, causing the viscosity of the adhesive to level off quickly to a value less than 1 Pa s) and then remains constant over the storage time of 2 years. According to the European Standard (EN-314) for wood glue testing, the quality of the emulsions as adhesive was evaluated by measuring the shear strengths on the applied maple substrates (hard wood). Average shear strengths of 2.7 MPa could be achieved for both the fresh emulsions and the ones that were stored for 2 years. This by far exceeds the strength requirement of 1 MPa according to the EN-314 and the minimum shelf-life of some days for the currently applied commercial adhesives.

Self-healing polymeric materials have the capability to repair or recover themselves when suffering mechanical and/or thermal induced damage, which can occur autonomously or be activated by external stimuli (e.g. heat) for once or multiple times. An easy-accessible and highly-efficient self-healing system was reported in Chapter 4. The system is based on the Diels-Alder (DA) and Retro-Diels-Alder (RDA) reaction applied to furan-functionalized polyketones (PK-furan) and bis-maleimide. PK-furan can easily be obtained under mild conditions by the Paal-Knorr reaction of alternating polyketones with furfurylamine. The degree of furan functionality can be well adjusted by varying the molar ratio of the 1,4-di-carbonyl functionality of the polyketones and furfurylamine. A highly cross-linked polymeric network can be achieved by the DA reaction of PK-furan with bis-maleimide. The final properties of this network can be tailored by tuning the structure of
the polyketones, the degree of furan functionalization, and the level of cross-linking (i.e. the ratio of furan-functionality to bis-maleimide). NMR, FTIR spectroscopy, and thermal analysis demonstrated ultra-fast kinetics of the present system (gel formation in 2 h at 50 °C and its reversal in 5 min at 150 °C) and 100% or complete thermal reversibility. Self-healing ability was evaluated by using dynamic mechanical analysis (DMA) and 3-point-bending mechanical testing. DMA shows that dynamic mechanical properties of the cross-linked PK-furan remain almost unchanged after 6 repetitive heating-cooling cycles. The thermal remendability of the cross-linked polymers was demonstrated by 3-point-bending testing which showed complete recovery in fracture loading, while the remending process could be repeated multiple times without any loss in mechanical properties. The simplicity of the synthesis and the striking healing ability of this system open the pathway to 100% recyclability and reworkability of thermoset materials.

Functionalization of carbon nanotubes via non-covalent or covalent attachment of chemical groups is essential to facilitate their manipulation for many further applications. Chapter 5 reported a new and simple approach to functionalize multi-walled carbon nanotubes (MWNTs) by applying an amidation-type grafting reaction with amino-functionalized alternating polyketones (polyamines). It is found that polyamines can act as cross-linking agents to interlink or cross-link individual carbon nanotubes to form carbon nanotube junctions or complex networks, which may be applicable in nano-scale electronic circuits. The covalent attachment of polyamines (around 40 wt% based on the total weight of the MWNTs) was testified by using thermogravimetric analysis (TGA), X-ray photoemission spectroscopy (XPS), elemental analysis, and Raman spectroscopy. In contrast to good solubility of carboxylic acid-functionalized MWNTs in water, the functionalized MWNTs after cross-linking are insoluble in any solvent (e.g. water, toluene, and chloroform). After functionalization, the polymer bridges within, as well as between the bundles of the MWNTs and the interconnects of the MWNTs (end-to-side or end-to-side) were observed by using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The processability of the cross-linked MWNTs was also studied by melt blending of cross-linked MWNTs into low density polyethylenes (LDPE). The resulting composites show similar dispersibility and comparable mechanical properties to those obtained by simple blending of “un-cross-linked” carbon nanotubes with LDPE.

Polymers containing amino functionality (e.g. polyethylenimine, chitosan, and polylysine) have been used as tissue scaffolds, polymeric carriers for drug and DNA delivery, medical devices, etc. Polyamines, derived from the chemical modifications of alternating polyketones, can be considered as a very promising class of polymers for biomedical applications (Chapter 6). Polyamines can be cross-linked at a high temperature
(140 °C) by the formation of either imine bonds or bis-pyrrole units, depending on the amount of amino groups grafted onto the polymer backbone. The cross-linking degree can be fine-tuned as a function of the cross-linking time. The surface wettability of polyamine films was found to become more hydrophobic with increasing cross-linking degree. Atomic force microscope analysis indicated that smooth and flat surfaces with the roughness less than 0.5 nm can be achieved for polyamine films before and after cross-linking. Interesting cell behavior of rat vascular smooth muscle cells (VSMC) and bovine arterial endothelial cells (BAEC) were observed on exposure to polyamine solutions and polyamine films in a *vitro* study. It was found that polyamines without cross-linking or at low cross-linking levels may induce apoptosis, i.e. a programmed cell death that is essential for tissue and organ development, physiologic adaptation, and disease. This was confirmed by activation of Caspase-3/7 assay and direct visual observation at the microscope. This valuable property of the polyamines can find application in the design of drugs or medical implants that require cytostatic properties. On the other hand, polyamines at high cross-linking levels display good biocompatibility with both VSMC and BAEC, which can be utilized to enhance cell adhesion and tissue integration for tissue scaffolds.