In the second half of this century the use of polymers in our daily life has rapidly grown in volume as well as in the number of applications. However, the European chemical industry faces an ongoing maturization of the polymer business and the concurrent developments has sometimes led to the belief that the rise and decline of polymer science is already behind us.

During the last recession a number of companies have indeed reshuffled their product mix and have withdrawn themselves to core-activities. Obviously the market entry-barriers for new products have increased in time, however, this should not imply that there is no room left for further improvement of the present product portfolio. In view of the high entry-barriers for mature markets, the economical feasibility of new developments is of primary concern in order to gain insight into the viability of new polymer products.

1.1 Scope of the Thesis

New or modified polymerization catalysts have provided the opportunity to produce new polymer materials. Some of these developments either have been commercialized or have potential to enter the highly competitive engineering or commodity plastics markets.

The development of new metallocene based catalyst systems allowed synthesis of several new resins with some exciting properties. In 1985 chemists from Idemitsu Kosan synthesized syndiotactic polystyrene (sPS) for the first time. This process was later expanded by Dow Chemicals Company, which developed catalysts allowing
commercial production of sPS.\textsuperscript{5,6} sPS is a semi-crystalline polymer with a relatively high glass transition temperature and a high melting point (270 °C).\textsuperscript{7} In addition to these good thermal properties, sPS is both chemical and water/steam resistant, and the polymer can easily be formed and moulded.

Another important development was the use of metallocene catalysts to produce syndiotactic and isotactic polypropylene (sPP and iPP). Metallocene based iPP is being commercialized by Exxon Chemical Company under the trade name EXXPOL PP.\textsuperscript{8} This polymer has a narrow molecular weight distribution (MWD) and a narrow tacticity distribution. The formation of atactic chains is completely suppressed. During melt processing metallocene based EXXPOL PP is more easily extensible in fiber spinning than its broader MWD counterparts. The narrow tacticity distribution increases stiffness, which is useful in durable goods applications. sPP is being commercialized by the Fina Oil Company.\textsuperscript{9}

The most significant improvement in the area of polyolefins was the development of constraint geometry catalysts by the Dow Chemical Company.\textsuperscript{10} Single site metallocene based catalyst technology is known to produce homogeneous random olefin copolymers with very narrow molecular weight distribution and comonomer distribution, which together improve the physical properties. INSITE-Technology is unique among single-site catalyst technologies as it utilizes a constraint geometry catalyst, which creates long branches on narrow MWD polymers.\textsuperscript{11} It is found that this type of structure combines excellent processing and high performance, unusual given the conventional sacrifice of one for the other. Through INSITE-Technology, scientists at Dow Chemical have also been able to control the desired levels of long chain branches to meet customer performance and processing needs.

A recent approach to new polymer materials is the development of the group of cis-fixed palladium bidentate catalysts, which can be used for the production of alternating polyolefin ketones.\textsuperscript{12-15} In view of the chemical structure of this class of polymers, it was anticipated that these materials can be used for engineering plastic and fiber applications.\textsuperscript{16,17}
Introduction

The present thesis is devoted to the structure development in oriented perfectly alternating ethylene-carbon monoxide copolymers (polyketone; POK-C). Furthermore, a new polyalcohol (PAI) has been produced by reduction of this polyketone.

\[
\begin{align*}
\text{POK-C} & : \left( \text{CH}_2\text{CH}_2\text{C(O)} \right)_n \\
\text{PAI} & : \left( \text{CH}_2\text{CH}_2\text{CH(OH)} \right)_n
\end{align*}
\]

The aim of this thesis is to evaluate the potential of these materials for advanced industrial fiber applications.

1.2 Industrial or Technical Fibers

High modulus industrial or technical fibers find their application mainly in tyres and other mechanical rubber goods (e.g., V-belts, conveyer belts, hoses, ...). In view of the high demands of such end-uses the mechanical performance of industrial fibers at elevated temperatures is of paramount importance. Especially the dimensional stability (i.e., the retention of the tensile modulus and the fiber length at elevated temperatures) is an important parameter. Presently, poly(ethylene terephthalate) (PET), cellulose, poly(vinyl) alcohol (PVAI) and nylon-6,6 fibers dominate these market segments. An important feature of cellulose (viscose) fibers is an excellent retention of the tensile modulus at elevated temperatures, but the tensile strength [at room temperature] is lower than for PET or nylon-6,6 fibers. Nylon-6,6 fibers show a relatively low initial tensile modulus, whereas low-speed-spun PET fibers show a moderate high-temperature performance. The shrinkage in hot air of high-speed-spun PET fibers is strongly reduced relative to low-speed-spun material. This was an important break-through in the field of fiber science and these so-called high modulus/low shrinkage PET fibers are sufficiently dimensionally stable for many industrial fiber applications.
Traditionally PVA fibers are spun from aqueous solutions into an alkaline or sodium sulfate coagulation bath. Often a certain amount of boric acid is added to the spinning dope in order to reduce skin-core effects. These high-modulus PVA fibers, spun from aqueous solution, are commercialized mainly by Japanese companies. More recent developments involve the application of high-molecular-weight polymer and the use of organic solvents. The aim of these investigations was to improve both the tensile properties and the hot-water-resistance of PVA fibers. The latter approach was derived from the gelspinning concept developed for the production of high-strength polyethylene fibers. Indeed high-strength PVA fibers have been produced on bench-scale equipment, but the superior mechanical properties could not be reproduced at higher production speeds; the obtained mechanical properties were only slightly higher than those of commercially available PVA fibers spun from aqueous solutions. Also the fatigue behavior of these high-molecular-weight fibers is rather poor and a pronounced decline of the tensile modulus is observed at elevated temperatures, which can be attributed to the atactic nature of PVA.

1.3 Survey of this Thesis

To gain insight into the potential of the perfectly alternating ethylene-carbon monoxide copolymer (POK-C,) as a starting material for industrial fibers, this polymer has been spun from phenolic solutions. In a subsequent drawing stage the required molecular orientation has been induced. It is well known that the mechanical properties of polymer fibers are strongly governed by the degree of molecular orientation in the direction of the fiber axis. In Chapter 2 the structure of POK-C copolymers is described and the crystal structure of oriented POK-C fibers is presented. Based on the melting behavior of low-molecular-weight (symmetrical) POK-C homologs a first estimate for the crystalline heat of fusion is derived. In Chapter 3 the preparation of high-strength POK-C fibers is reported and the influence of the drawing conditions on the mechanical properties is discussed. The synthesis and structure of the polyalcohol prepared by reduction of POK-C is described in Chapter 4. The two polymers of interest show a pronounced difference in deformation behavior.
at elevated temperatures. The influence of the chemical structure, mainly polarity, and temperature on the topological constraints to the maximum attainable draw ratio of flexible polymer systems are discussed in Chapter 5. Oriented POKC₂ fibers exhibit polymorphism and the study into a structural transition at elevated temperatures together with the effect of the fraction of chain defects (i.e., propylene-carbon monoxide defects) on the room temperature crystal structure of polyketone terpolymers is presented in Chapter 6. Finally, in Chapter 7 the dimensional stability, creep resistance, and high-temperature strength of polyketone fibers are reported.

References and Notes

The central theme of the 8th Rolduc Polymer Meeting (1993), May 1993. Rolduc Abbey, Kerkrade, the Netherlands, was "The Rise and Decline of High Performance Polymers in Europe".

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