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Polymerisation and structure–property relationships of Ziegler–Natta catalysed isotactic polypropylenes

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ABSTRACT

Polypropylene homopolymer samples were prepared with a Ziegler–Natta catalyst using two different external donors, namely diphenyldimethoxysilane (DPDMS), and methylphenyldimethoxysilane (MPDMS). Each donor was used in varying molar ratios to the catalyst in order to prepare samples for physical testing. The polymers were fully characterised and also fractionated by preparative TREF with characterisation of the fractions. In terms of the polymerisation reactions the DPDMS external donor exerts greater influence at the active sites than the MPDMS and produces polymer of higher molar mass and lower polydispersity. The physical properties of the polymers were investigated using microhardness measurements. It is revealed that the microhardness is strongly dependent on the stereoregularity of the samples.

1. Introduction

The correlation of physical properties with molecular characteristics is vital in order to further the development of a polymer and improve on the properties attainable by the polymer. Polypropylene is one of the materials which has experienced a huge growth in consumption over the last few decades [1]. This has not materialised without significant contributions from the development of new catalyst systems and the increased understanding of why the material behaves as it does under a variety of conditions and testing methods.

In recent years there have been a number of studies which have contributed to the overall understanding of the effect of molecular characteristics on polymer properties. A series of papers by De Rosa et al. [2–5] have revealed much in terms of the effect of copolymerisation, and stereo- and regio-defects on the crystallisation and properties of polypropylene. Busico et al. [6,7] have made considerable contributions to the understanding of the polymerisation mechanism of Ziegler–Natta catalysis with the proposal of the 3-sites model. These developments have provided much assistance to the investigation of the structure–property relationships of these materials since one can better understand the manner in which the chains are produced. Therefore, one can tailor-make polymers with certain properties, especially if one also understands the effect of the microstructure on the crystallisation, and ultimately the mechanical properties of the materials.

The microhardness technique has developed into an important method to characterise the visco-plastic deformation in polymer samples [8]. The technique has proven to be able to detect very small transitions in polymer materials such as the glass transition temperature (T_g) [9], differences in the crystal phase [10–14], material anisotropy [8,15], thermal history [16,17], as well as polymer composition [18,19]. It is generally accepted that the principal factor affecting the microhardness of semi-crystalline polymers is the crystallinity of the material, although the rate of hardness increase with crystallinity is different for different materials [9]. Factors such as the crystal thickness have also been found to influence the hardness [19]. It is therefore apparent that the molecular characteristics affecting polymer crystallisation also affect the final properties of the material.

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Whereas it is quite simple to evaluate the changes in molecular composition as a function of polymerisation conditions, the link between the polymerisation conditions and the final properties of the polymer is not as simple to explain and predict. The aim of the current study is to tailor the polymerisation conditions such that polymers can be produced with controlled differences in microstructure for the investigation of structure–property relationships of polypropylene. Polymerisations were conducted with and without external donors, in order to produce samples with larger differences, and also with varying Si/Ti ratios to invoke small changes in the microstructure. Microhardness measurements were used as a tool to probe the physical properties of the polymers.

2. Experimental

2.1. Materials

Propylene of research grade (99.9%), triethylaluminium (TEA) as a 1.0 M solution in hexane, diphenyldimethoxysilane (DPDMS), and methylphenyldimethoxysilane (MPDMS) were obtained from Aldrich and used as received. The $MgCl_2$-supported Ziegler–Natta catalyst, containing diisobutylphthalate (DIBP) as internal donor, was obtained from Star Chemicals and Catalysts co., China. Toluene was obtained from Merck and was first distilled and dried over sodium and benzophenone before use. The commercial PP sample designated as PPH (Himont, Italy) has a M_w of 690 kg/mol, polydispersity of 5.2 and *mmmm* pentad content of 90.5%.

2.2. Polymerisations

Polymerisations were conducted in a 300 mL, stirred, stainless steel reactor. Preparative work with the catalyst and co-catalyst was performed under argon atmosphere using standard glove box and schlenk techniques. The Al/Ti molar ratio was maintained at 80 and the temperature was maintained at 40 °C for all reactions. Hydrogen was used to control the molar mass of the polymer in all reactions. The two different external donors were each used in Si/Ti molar ratios of 0, 4, 8, 16, and 40. Reactions were quenched by the addition of acidic methanol and the isolated polymers were dried under vacuum. Characterisation data for the polymer samples are given in Table 1.

2.3. TREF

Fractionation of the polymers was performed using preparative TREF. The standard fractionation procedure and set-up used has been previously published [20], however, the fractionation temperatures used in this study were different. The polypropylene samples were fractionated at temperatures of 25, 60, 80, 100, 105, 110, 115, 120, and 140 °C.

2.4. HT-GPC

Molar mass distributions were determined using a PL-GPC 220 high temperature chromatograph (Polymer Laboratories) equipped with a differential refractive index detector. The measurements were performed at 160 °C at a flow rate of 1 mL/min. The columns used were packed with a polystyrene/divinylbenzene copolymer (PL gel MIXED-B from Polymer Laboratories). The solvent used was 1,2,4-trichlorobenzene, stabilised with 0.0125% 2,6-di-*tert*-butyl-4-methylphenol (BHT). BHT was used as a flow rate marker. Calibration of the instrument was done with monodisperse polystyrene standards.

2.5. Thermal analyses

Crystallisation and melting temperatures were determined by a TA Instruments Q100 DSC system, calibrated with indium metal according to standard procedures. Heating and cooling rates were maintained at a standard 10 °C/min. The samples of the fractions and original polymers were first subjected to a heating ramp up to 220 °C, after which the temperature was kept isothermally at 220 °C for 5 min to remove thermal history. The cooling cycle followed the isothermal stage, with the subsequent second heating scan being recorded for analysis. A value of 209 J/g [21] was used as the enthalpy of fusion for the ideal 100% crystalline polypropylene for determining the percentage crystallinity.

2.6. NMR

^{13}C NMR spectra were recorded at 120 °C on a Varian VXR 600 MHz spectrometer in 1,1,2,2-tetrachloroethane-d_2, using δ 74.3 as internal secondary reference. The pulse angle was 90 degrees, the relaxation delay 15 s, and the acquisition time was 1.8 s.

2.7. Microhardness

Microhardness measurements were performed on a UHL microhardness tester equipped with a Vickers indenter. Samples were prepared by melt pressing at 200 °C at 3 MPa followed by quench cooling of the mould in an ice/water mixture. Measurements were obtained using an indentation speed of 25 μm/s and a dwell time of 15 s. Samples were analysed at indentation loads of 5 gf (48 mN) and 10 gf (98 mN), with the data presented being the average of 20 indentations.

3. Results and discussion

3.1. Bulk polymers

Table 1 contains the characterisation data for all the polymers synthesised. The presence or absence of an external donor in the polymerisation medium proved to be the basis for the most significant differences brought about for the manipulation of the polymer microstructure as was expected. The NO ED sample has a much lower degree of crystallinity, molar mass, and *mmmm* pentad content compared to the samples produced using an external donor. Extraction of the internal donor from the active sites [22–25] and a corresponding reduction in the stereospeci-