THERMAL AND STRUCTURAL BEHAVIOR OF METALLOCENE-TYPE RANDOM PROPYLENE COPOLYMERS

R.G. Alamo*, Florida A&M University and Florida State University College of Engineering. Department of Chemical Engineering Tallahassee, Fl 32310-6046 J.R. Isasi, M-H. Kim, L. Mandelkern, Florida State University Institute of Molecular Biophysics Tallahassee, Fl 32306 D.L. VanderHart. National Institute of Standards and Technology Polymer Division. Gaithersburg, MD 20899-8544

Introduction

Fast advances in the development of metallocene-type catalysts allow polymerization and co-polymerization of olefins with a well-defined homogeneous molecular structure (1,2). These materials present narrow molecular weight and narrow comonomer composition distribution and, thus, present different properties compared to the classical copolymers polymerized with Ziegler-Natta type catalysts which are known to be very polydisperse (3). Metallocene propylene copolymers are commercially attractive as a means to improve consistency in the material and to expand into new areas of applications. From a more a academic point of view, the homogeneous copolymers permit the study of thermodynamic properties and the details of the lamellar structure as a function of increasing comonomer content and the type of comonomer or molecular weight as independent variables, without the need of lengthy fractionations.

We are interested in studying the effect of incorporating low concentrations of comonomer (up to 10 mol %) in the polypropylene chain on physico-chemical and structural properties of the copolymers. The properties of copolymers with four different types of comonomers, ethylene, butene, hexene and octene will be compared and discussed. These studies are relevant as a means to predict product performance since similar copolymers are produced industrially when highly crystalline polypropylene with somewhat lowered melting points or improved fracture toughness and transparency, are requested for special applications.

Previous studies have been carried out in samples characterized by a broad polydispersity in comonomer composition and molecular weight (4, 5) or in fractions obtained from heterogeneous propylene co-ethylene copolymers (3, 6, 7). While the melting temperatures are invariably reported to decrease with increasing ethylene content, however, the degrees of crystallinity obtained either by DSC or WAXS are found to decrease (4, 5) or to remain constant (6, 7) with increasing co-monomer content. Thus, there is no consensus on issues of fundamental basis such as the co-crystallizability of the comonomer unit. From x-ray diffraction and DSC data, Zimmermann (5) concluded that the ethylene units are completely rejected from the crystal phase. However, Avella et al. (8), Busico et al. (4) and Gedde et al. (6, 7) on the basis of unit cell volume, crystallinity and crystal thickness concluded that the ethylene units are partially incorporated in the crystal lattice.

In a recent work (9) the melting temperatures (Tm) of propylenebutene copolymers were found to be significantly higher than those of propylene/alpha-olefin copolymers with a comonomer length changing from 6 to 16 carbons. Small differences were found in the Tm of the propylene/higher alpha-olefin copolymers.

The issue of comonomer crystallizability is addressed in the present work from two different perspectives. First, the presence of comonomer units in the crystal is investigated by well-developed 13 C NMR methods (10). In a second approach, the properties of different types of propylene copolymers polymerized with the same catalyst, are compared at a fixed comonomer content and molecular weight. Both approaches require an initial detailed characterization by high resolution 13C NMR spectroscopy of the stereo, regio and comonomer fractions present in the polypropylene molecule. The properties studied include thermal behavior, phase structure, crystallite thickness, relative contents of the alpha and gamma polymorphs and an analysis of the linear growth rates. The kinetics of the development of the gamma polymorph are also studied and discussed on the basis of the requirements for the formation of the same polymorph in homopolymers (11).

Experimental

The copolymers studied are listed in Table 1. The samples are labeled M_xC_y with x as the length of the co-monomer (x=2 for ethylene, x=4 for butene ... etc) and y is the percentage of comonomer by mass. The number of misinsertions, stereo type of defects (based on NMR pentads) and comonomer units, per 1000 monomeric units in the chain are also listed. The molecular weight and polydispersity of these materials are also given.

The melting behavior was studied by differential scanning calorimetry using either a Perking Elmer DSC 2 or Perking Elmer DSC 7 both operated under nitrogen and calibrated with indium, wide-angle x-ray diffractograms were obtained at ambient and above ambient temperatures in a slit collimated Siemens D500 diffractometer. Long periods were obtained from the SAXS intensities collected in the 10 m Spectrometer of the ORNL. Optical microscopy was carried out in a Linkan hot stage fitted to an Olympus BH-2 microscope. The CP MAS spectra were collected either in a 100 MHz spectrometer or in a Bruker 300 MHz at the NHMFL facilities.

Results and Discussion

The high resolution 13C NMR analysis of the copolymers revealed an interesting feature of the propylene-ethylene copolymers, a significant amount of the 2,1 misinsertions had an ethylene unit added subsequently. This was taken into account when summing up the total number of units (defects) disrupting the isotacticity and is the reason for the lower contents of 2,1 misinserptions in the propylene ethylene copolymers listed in Table 1. The analysis also indicates negligible contents of comonomer blocks (diads, triads ...).

The degree of partitioning of each type of defect and of the comonomer was studied by analysis of the CP MAS ¹³CNMR spectra of slowly cooled samples obtained under two different spin-locking times (10). Besides the resonances associated with the three main types of carbons, the crystalline spectra of propylene-ethylene copolymers show sharp well defined resonances that appear at chemical shifts consistent with those calculated for the methine and methylenes carbons of the ethylene group.

In contrast, the crystalline spectra of propylene-hexenes and propylene-octenes copolymers did not show the characteristic resonance of the end methyl in the branch. The data allow us to conclude that ethylene units are partially incorporated in the crystal phase in agreement with the conclusions reached by other investigators from indirect studies (4, 6, 7). Molecular mechanics calculations of model compounds also indicated that isolated ethylene units may be incorporated into the polypropylene helix since they cause only a moderate disturbance of the crystal structure (12). Branches longer than two ethylene units such as butyl and hexyl branches do not accommodate as easily in the helix and the NMR results indicate that these branches are rejected to the interlamellar region.

In agreement with the NMR results, the melting temperatures and degrees of the crystallinity of propylene-ethylene copolymers are, especially in the higher ethylene content region, significantly higher than the melting temperatures of propylene hexenes or propylene-octenes copolymers. The differences in melting points range between 1 and over 10_C in the interval of comonomer content studied. Compared to a non-crystalline unit and for a fixed co-monomer content, the feasibility of inclusion of the ethylene unit in the crystal increases the number and the length of crystallizables sequences. As a result, propylene-ethylenes present thicker and better defined lamellae as seen by TEM. The long periods of the rapidly crystallized copolymers decrease slightly with increasing comonomer content for defect contents <3 mol% and remained invariant for higher contents of comonomer. This result was independent of the comonomer type except for propylene-butenes which show higher long periods. The crystal thickness of propylene-ethylenes and propylene-butenes were, however, significantly higher in the range of defects contents >2 mol%.

Other properties such as rate of crystallization and the relative concentration of crystals formed in the gamma polymorph are also affected by the partial inclusion of the comonomer in the lattice. Thus, propyleneethylenes have higher linear growth rates and lower concentrations of the gamma polymorph in the crystal phase than those found in propylene hexenes and propylene octenes copolymers. Moreover, in agreement with reported studies in homo-polypropylenes and propylene copolymers (11, 7), WAXS data of the melting process indicates that the gamma polymorph melts at lower temperatures than the alpha form. Kinetic studies in these metallocene copolymers also confirmed that the formation of the gamma form is favored with increasing defect units in the chain and at high crystallization temperatures. The thermodynamic and kinetic data will be discussed according to theoretical models.

Table 1. Characterization of Propylene Copolymers

Sample	2,1	Tacticity	Comonomer	Total Defects	Mw	Mw/Mn
		/1	000 units	/1000 units		
M2CO.51	2	6	8	16	233090	1.98
M2C1.1	4	7	17	28	221250	1.81
M2C1.4	5	7	21	33	209250	1.77
M2C1.75	5	7	22	34	214840	1.75
M2C3.4	3	8	46	57	251040	2.12
M2C4.5	4	8	75	87	188010	1.71
M2C4.8	5	7	70	82	185300	1.86
M4C2.3	8	9	17	34	216500	1.7
M4C2.8	7	9	20	36	202970	1.76
M6CO.6	7	10	3	20	244630	1.83
M6C1.1	7	9	6	22	-	-
M6C2.7	6	11	17	34	206930	1.71
M6C2.8	7	10	18	35	-	-
M6C3.0	7	9	15	32	-	-
M6C5.3	7	9	27	43	217130	2.53
M8Cl.6	7	9	6	22	184900	1.85
M8C3.4	7	9	13	29	202290	1.76

Conclusions

Direct evidence of the inclusion of ethylene units in the crystal phase of propylene ethylene random copolymers was obtained from the analysis of the 13C NMR spectra of the crystalline region. Similar spectra of propylenehexene and propylene-octene copolymers show no evidence of inclusion of butyl and longer branches. It is shown that thermodynamic, kinetic and structural properties of the copolymers are affected by the comonomer inclusion in the crystal lattice.

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