Nanostructuring High Molecular Weight Isotactic Polyolefins via Processing with γ-Cyclodextrin Inclusion Compounds. Formation and Characterization of Polyolefin−γ-Cyclodextrin Inclusion Compounds

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ABSTRACT: The present paper deals with the formation and detailed characterization of the γ-cyclodextrin (γ-CD) inclusion compounds (ICs) formed with two different high molecular weight isotactic polyolefins, i.e., polypropylene (i-PP) and poly(butene-1) (i-PB). Wide-angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC), solid-state ^{13}C NMR, and FT-infrared (FTIR) observations were used to prove the inclusion of the guest polymer chains into the narrow channels provided by the stacks of the doughnut-shape CD molecules. The main aim of polyolefin inclusion into a solid host lattice like γ-CD is to extend and reorganize their conformations, with the hope of improving their commercial properties following their coalescence from their ICs. In the second part of the paper, both coalesced i-PP and i-PB obtained after the host γ-CD is removed reveal different characteristics as compared with the as-received or corresponding control samples.

Introduction

Since high molecular weight isotactic polypropylene (i-PP) was first synthesized by Natta et al.,[1] a huge effort has been made to elucidate and improve the properties of this valuable polymer. Isotactic poly(butene-1) (i-PB) was also first synthesized in 1954. Currently, both polyolefins are very important commercial polymers, with a great interest from a scientific point of view because of, among other factors, their complex crystalline polymorphic behavior. In particular, i-PP is becoming one of the most used thermoplastics, especially with the performance improvement attained in combination with other components in blends and composites. Isotactic poly(butene-1), despite its enhanced properties compared with other polyolefins (i-PP, PE, etc.), has a restricted market penetration due to its peculiar polymorphic transformation.

Natta and Corradini clarified that the chain conformation of i-PP is a 3-fold (3_1) helix, which can be either right- or left-handed, with a periodicity of 6.5 Å.[2] Depending on preparation procedures, i-PP can be crystallized in four different crystal forms—α, β, γ, and smectic—distinguished by the arrangement of the 3_1 helical chains in the unit cell.[3−11] The α form is the thermodynamically stable crystalline modification, which is usually obtained under common processing conditions. i-PB can crystallize in five different crystal phases, depending on the preparation method, which differ in helical conformation and chain packing.[12−23] One of these phases, named form III (orthorhombic unit cell and a 4_1 helical conformation), is rarely observed and can be obtained by crystallizing from various solvents. Of the remaining crystal phases, form II is unstable, converting over time to the most prevalent phase, form I. Form II (tetragonal unit cell and an 11_3 helical conformation) is commonly obtained by melt crystallization and transforms slowly and irreversibly to form I (hexagonal unit cell and 3_1 helical conformation) at room temperature without constraints. Form I′ and form II′ are formed upon crystallization from the melt under high pressure. Moreover, form I′ and form III crystals have been found to form on solution crystallization depending on the solvent, concentration, and crystallization temperature.

We have previously reported the formation of inclusion compounds (ICs) between cyclodextrins (CDs) and several hydrophobic as well as hydrophilic high molecular weight polymers.[24−28] CDs, having a doughnut shape with a hydrophobic cavity surrounded by a hydrophilic shell, act as host molecules. One might expect that only hydrophobic guest molecules would be accommodated into the hydrophobic cavity of the CD molecules. Different reports in the literature, however, show that CD molecules may also host hydrophilic, as well as ionic, guest molecules,[29−34] but CD molecules prefer to form an IC only with the more hydrophobic guest molecules from a multiguest solution.[24] The molecular recognition of CD host molecules can be successfully used in purification or separation processes.

The present work is focused on the formation and characterization of i-PP− and i-PB−γ-CD ICs. Although there is another report in the literature about the complex formation between methylated CDs and polypropylene oligomers ($M_w = 1600$),[35] this is the first paper that successfully proves the formation of CD IC crystals containing high molecular weight polyolefin guests (i.e., i-PP and i-PB). Harada and co-workers[35] demonstrated

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that oligo(ethylene)s and poly(propylene)s, in the liquid state, can be solubilized in water in the presence of methylated CDs by forming their corresponding soluble ICs. Here we demonstrate the formation of i-PP− and i-PB−γ-CD IC crystals and the modification of certain properties of the guest polyolefins following coalescence from their γ-CD ICs.

As we have demonstrated previously, the formation of polymer−CD ICs and subsequent coalescence of the guest polymer chain represents a novel way to manipulate the properties of different polymers.[27,36,37] As a result of segregation and extension of the guest polymer chains in the narrow CD channels, the final coalesced polymer can retain a distinct chain conformation. Both polyolefins represent high performance materials, and it is of great interest to modify their characteristics to develop materials with improved properties. Having this aim in mind, we first report the formation and characterization of the i-PP− and i-PB−γ-CD IC crystals, along with some preliminary results concerning the coalesced polyolefins, which will be followed by a future paper that will study in detail and compare the modified properties of the coalesced polymer samples with those of as-received or precipitated control samples.

Experimental Section

Materials. An i-PP sample with a weight-average molecular weight (M_w) of 12 000 g/mol and polydispersity of 2.4 was purchased from Aldrich and used without any further purification. The second i-PP sample used in this study was a commercial grade supplied by Repsol-YPF. The degree of isotacticity was determined by ^{13}C NMR at 125 °C in a 20% (w/v) 1,1,2,2-tetrachloroethane-d_2 solution and found to be 50 and 92% fractions of isotactic pentads ($P_m = 0.85$ and 0.98) for these i-PP samples, respectively. The viscosity-average molecular weight (M_v) of the Respol-YPF sample was obtained by intrinsic viscosity measurements using a modified Ubbelohde viscometer in decalin solutions at 135 °C. A concentration of 0.1 g dL^{-1} was used, and the measurements were carried out under a nitrogen atmosphere. The intrinsic viscosity-average molecular weight relationship is given by

$$[\eta] = 1.10 \times 10^{-4} M_v^{\ 0.80}$$

The intrinsic viscosity was found to be 1.64 dL g^{-1}, and the calculated M_v was 164 000. The abbreviations for these two i-PP samples, throughout the paper, will be i-PP1 and i-PP2, respectively.

i-PB samples were obtained from Basell and have M_w of 115 800 and 380 000 g/mol, respectively, as measured by GPC. The degree of isotacticity was determined by ^{13}C NMR at 90 °C in a 20% (w/v) 1,2-dichlorobenzene-d_4 solution as % fraction of isotactic pentads and were 85.7 and 87.5, respectively. These two i-PB samples are noted as i-PB1 and i-PB2, respectively.

Dimethyl sulfoxide (DMSO) (+99.6%) and 1,2,4-trichlorobenzene (TCB) (+99%) were used as received from Aldrich.

Formation of i-PP−γ-CD ICs. 0.3 g (7.14 mmol) of i-PP was dissolved in 200 mL of TCB to get a clear solution at 120 °C, with continuous vigorous stirring. 20 mL of hot (120 °C) γ-CD solution (9.26 g, 7.14 mmol) in DMSO was added dropwise to the polymer solution, while stirring was maintained at 120 °C for 3 h. The combined solution was allowed to cool to room temperature and stirred for another 24 h. The resulting white precipitate was collected by vacuum filtration, washed with hot TCB (120 °C) and water to remove uncomplexed i-PP and γ-CD, respectively, and vacuum-dried at 35 °C after an acetone rinse.

Formation of i-PB−γ-CD ICs. i-PB−γ-CD IC white crystals were obtained by the aforementioned procedure. Note that the molar feed ratio of polyolefin repeat units/CD is 1:1, which represents a 3-fold excess of CD, based on molecular modeling of the IC which suggests three repeat units of threaded and included polyolefin for each mole of CD.

γ-CD/TCB Control Sample. A γ-CD solution was generated by the dissolution of the solid γ-CD powder in DMSO at 120 °C with strong stirring. The resulting suspension obtained by the dropwise addition of the γ-CD solution to pure TCB was allowed to stir for 3 h at 120 °C and then cooled and stirred for about 24 h. Finally, the collected powder was vacuum-dried and analyzed. At first, a channel structure was observed by X-ray, but this crystalline arrangement was lost upon vacuum-drying.

Coalescence of Polyolefin−γ-CD ICs. IC-coalesced samples were obtained by washing the polyolefin−γ-CD ICs several times with DMSO. The control polymer samples were prepared by precipitation resulting from the dropwise addition of the nonsolvent DMSO to i-PP or i-PB solutions in TCB at 120 °C. This procedure was followed for the control polyolefin samples because it closely mimics the procedure used to make the polyolefin−γ-CD ICs and because it was realized that precipitation conditions (concentrations, solution to nonsolvent addition, etc.) can influence the accompanying crystallization process. After filtration and an acetone rinse, the coalesced and control polyolefin powders were vacuum-dried at about 35 °C for 48 h.

Characterization. *Wide-Angle X-ray Diffraction (WAXD).* Wide-angle X-ray diffraction (WAXD) measurements were performed with a Siemens type F X-ray diffractometer with a Ni-filtered Cu Kα radiation source ($\lambda = 1.54$ Å). The diffraction intensities were measured every 0.1° from $2\theta = 5-30°$ at a rate of $2\theta = 3°$/min. The supplied voltage and current were 30 kV and 20 mA, respectively. The diffraction peak intensities are all normalized.

Fourier Transform Infrared Spectroscopy (FT-IR). A Nicolet 510P FTIR spectrometer was utilized to obtain the infrared spectra of samples mixed into potassium bromide (KBr) and pressed into pellets. The spectra were taken over a range of 4000 to 400 cm^{-1}, with a resolution of 2 cm^{-1} using 64 or 128 scans.

Differential Scanning Calorimetry (DSC). Experiments were performed with a Perkin-Elmer DSC-7 under a nitrogen purge gas. Indium was used as a standard for calibration. All the ICs and i-PB samples studied in this work were investigated between 25 and 200 °C at a heating rate of 20 °C/min, held at 200 °C for 5 min, and followed by a second cycle to determine the change in thermal behavior. Melting temperature was consistently taken as the peak temperature. The thermograms of the as-received, precipitated, and coalesced i-PP were performed with a Thermal Analyst Q1000 modulated DSC (MDSC). Indium was used for the temperature calibration, and sapphire was used for the heat capacity calibration. i-PP samples were subjected to heating and cooling cycles (unless otherwise specified), consisting of 5.0 min hold at 50 °C, ramp to 200 °C at 5 °C/min, hold at 200 °C for 3 min, and ramping to 50 °C at 5 °C/min. A second cycle was run to study the changes in thermal behavior following the first heat.

Solid-State NMR. High-resolution solid-state ^{13}C NMR experiments were carried out at 50.1 MHz on a Chemagnetics CMX200 spectrometer using cross-polarization and magic angle spinning (CP/MAS) with high-power proton dipolar decoupling (DD). The spinning speed ranged from 4 to 4.2 kHz. The ^{13}C chemical shifts were referenced relative to TMS. The spectra were obtained with 1000 transients, 1.0 ms contact time, and 3.0 s pulse delay. The spectral width was 15 kHz with 2K data points, which were zero-filled to 8K before Fourier transformation.

Results and Discussion

Proof of Polyolefin−γ-CD IC Formation. To demonstrate that a real γ-CD IC was obtained with both polyolefins (i-PP and i-PB), several analytical techniques were employed. DSC was run to make sure that the IC powder did not contain any unincluded polymer. WAXD is a valuable tool for CD-IC characterization because it

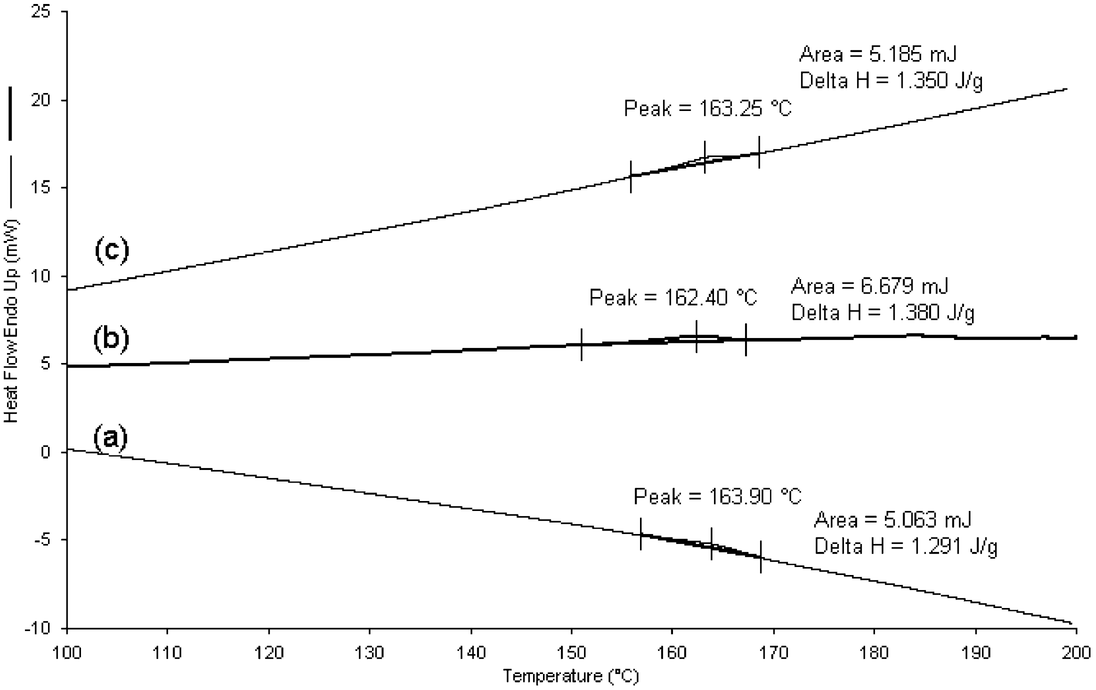

Figure 1. DSC thermograms of i-PP2−γ-CD IC washed once (a), twice (b), and three (c) times with TCB.

helps to monitor the crystal transition between the cage structure of as-received CD molecules and channel structure of polymer−CD ICs. FTIR spectra of the CD ICs prove the presence of both guest and host components in the sample. Moreover, solid-state ^{13}C NMR spectroscopy was used to characterize the structure of all CD ICs and indicate the presence of the included polymer chains.

The DSC thermogram of the i-PP1−γ-CD IC samples shows no thermal event between 25 and 200 °C. Lack of an endothermic peak at ~158 °C corresponding to the i-PP1 melting indicates that the polymer chains are all included and segregated by the CD walls. In other words, each polymer chain is separately included in one individual γ-CD channel, and therefore the i-PP sample is not able to form crystalline regions. In contrast, DSC curves, in Figure 1, recorded for i-PP2−γ-CD IC exhibit a small endothermic peak at 164 °C, which may suggest the presence of a certain small amount of uncomplexed i-PP2. However, we anticipated that washing the i-PP2−γ-CD IC crystals with hot TCB (130 °C) for several hours would remove most of the free i-PP2. Even after the second and third TCB washings, the endothermic peak is still observable, as we can see in parts b and c of Figure 1, respectively. The fact that the fusion peak remains constant after two consecutive washings leads us to conclude that the endothermic event at 164 °C does not correspond to the fusion of free i-PP2, but rather the fusion of the crystalline regions formed by uncovered portions of i-PP2 chains. Because i-PP2 chains are much longer than i-PP1 chains, it may be more difficult to have them fully included in the γ-CD channels. Instead, blocks of γ-CD molecules in channel structure cover only extended portions but not all of the i-PP2 macromolecules.

DSC thermograms of the i-PB−γ-CD ICs exhibit no thermal events between 25 and 200 °C (not shown). The melting point of pure i-PB appears at 125 °C and corresponds to the fusion of the form I crystalline polymorph. In correlation with the other analytical results, we may conclude that all existing i-PB chains in the corresponding γ-CD IC samples are fully covered by the host γ-CD molecules.

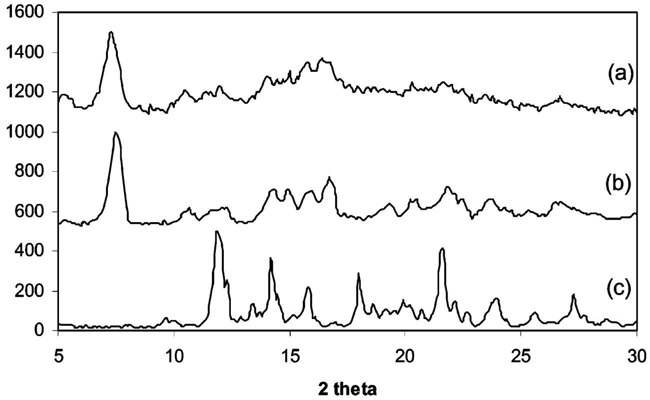

Figure 2. WAXD patterns of i-PP1−γ-CD IC (a), i-PP2−γ-CD IC (b), and as-received γ-CD (c).

Wide-angle X-ray diffractograms (WAXD) of the i-PP1− and i-PP2−γ-CD ICs, along with the as-received γ-CD cage structure, are presented in Figure 2. There it is apparent that the two IC crystals present similar X-ray patterns, which are completely different from that of pure γ-CD with a cage structure. The as-received γ-CD cage structure has a “herringbone” arrangement in which the cavity of each molecule is blocked by neighboring molecules.[38] This structure converts to a channel structure in the presence of a proper host molecule. The channel structure consists of a column obtained by stacking CD molecules on top of each other and having the polymer chain included in the inner cavity. Two theories are available in the literature concerning the mechanism of polymer threading to form channel structure CD ICs: (1) CD molecules are being threaded one by one from the polymer ends and slide toward the center of the polymer chain[29] or (2) preformation of a soluble “empty” columnar structure of CD molecules, which rapidly swallows the polymer chains in solution.[39] The latter theory is more likely, as it is supported by our observations that demonstrate the

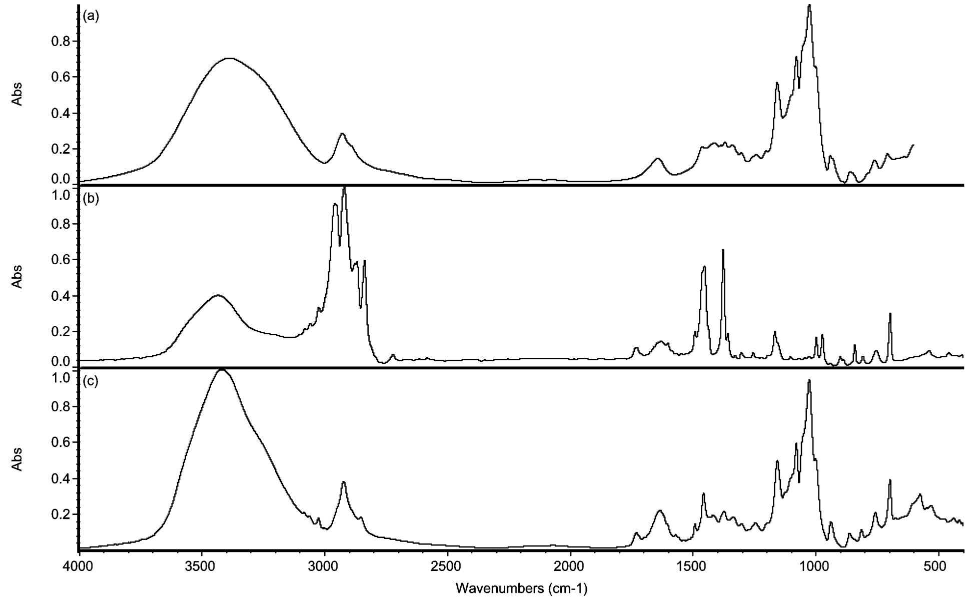

Figure 3. FTIR spectra of as-received γ-CD (a), pure i-PP1 (b), and i-PP1−γ-CD IC (c).

possibility to precipitate CDs from their saturated aqueous solutions into columnar structures, with no guest molecules but water.[40] γ-CD in columnar structure, with or without a guest polymer inside, shows a characteristic pattern in the WAXD. The most intense diffraction peak in the diffractogram of γ-CD columnar structure appears at around 7.5°, which represents the (200) planes of the hydrated crystals.[41] This is a fingerprint in the X-ray diffractograms for all γ-CD IC crystals obtained with long guest molecules. The crystalline regions formed by the uncomplexed portions of i-PP2 chains represent just a small fraction of the entire sample; therefore, no diffraction peaks corresponding to free i-PP2 are expected in the corresponding X-ray pattern.

The X-ray results obtained for i-PB−γ-CD IC samples are very similar to those discussed above for i-PP−γ-CD IC crystals. A sharp peak at $2\theta = 7.5°$ in the pattern of i-PB−γ-CD IC crystals (not shown) is strong evidence that γ-CD is hosting i-PB in a channel structure IC. The diffraction pattern for the TCB/γ-CD control sample (not shown) was recorded in order to make sure that the solvent molecules do not form an IC with γ-CD. This pattern is distinctly different from that of γ-CD IC in the channel structure. Apparently, TCB solvent molecules are not suitable as guest competitors for polyolefins chains in the process of γ-CD IC channel formation.

FTIR spectra of the as-received γ-CD, pure i-PP1, and i-PP1−γ-CD IC are presented in Figure 3. The most intense peaks of i-PP1 at 2960, 2920, 1454, and 1377 cm^{-1} are attributed to the antisymmetric stretching vibrations of the CH_3 and CH_2 groups and to the antisymmetric and symmetric bending vibration of CH_3 groups, respectively, and are almost invisible in the IC FTIR spectrum. The fact that guest polymer peaks are very weak and overlapped by the CD vibrational bands is not surprising because the expected weight ratio of guest/host molecules is around 1:10. In the case of γ-CD, among the various vibrational bands, a group of three most intense peaks can be identified as a contribution of coupled C−C/C−O stretching vibrations at 1079 and 1026 cm^{-1} and an antisymmetric C−O−C stretching vibration at 1158 cm^{-1}.[42] The pure γ-CD and TCB/γ-CD control samples, obtained by the same procedure used in IC formation, but in the absence of polymer, display identical spectra, indicating no complexation between γ-CD and the solvent molecules. FTIR spectra were also recorded for i-PB−γ-CD IC samples and compared with those of pure γ-CD and i-PB. The main vibrational bands of i-PB appear at 2960 and 2916 cm^{-1} due to the antisymmetric stretching vibrations of the CH_3 and CH_2 groups and at 1464 and 1380 cm^{-1} for the antisymmetric and symmetric bending vibrations of CH_3 groups, are very weak, and are overlapped by the CD bands in its IC FTIR spectrum. Up to this point there is no evidence of the existence of the polymer component in their corresponding IC crystals. Therefore, CPMAS ^{13}C NMR spectroscopy was used to further analyze the IC powders.

Figure 4 shows a comparison of CPMAS ^{13}C NMR spectra of pure i-PP, γ-CD, and i-PP−γ-CD IC. Significant changes can be observed in the carbon spectrum of γ-CD upon IC formation. The hydrated γ-CD cage structure exhibits a high-resolution NMR spectrum with several lines observed for each carbon resonance resulting from rigid, nonequivalent glucose units in the unit cell of the crystal structure. The lines for γ-CD in the IC spectrum are considerably broader and less split, reflecting a more mobile and disordered environment. Similar results were obtained for all previous CD IC crystals in channel structure or hydrated CD in columnar structure.[40] The signals for i-PP are easily identified and all are resolved in its bulk sample. The carbon resonances of the i-PP at 22.4, 26.9, and 44.8 ppm corresponding to the methyl, methine, and methylene carbons, respectively, can be clearly distinguished in its γ-CD IC spectrum. This is strong evidence that supports the formation of i-PP−γ-CD IC and the presence of included guest i-PP chains, which most likely are isolated in the narrow channels of the host CD crystalline lattice.

CPMAS ^{13}C NMR results obtained for i-PB−γ-CD IC crystals (not shown) also indicate the presence of guest i-PB chains included in the γ-CD channel structure. Detailed NMR analyses of the conformations and dynamics of the isolated polyolefins included in the narrow channels of the host γ-CD, as well as those of the

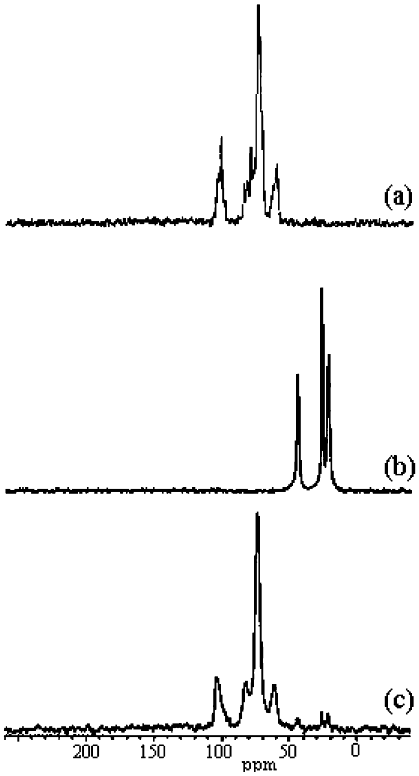

Figure 4. CPMAS ^{13}C NMR spectra of pure γ-CD (a), pure i-PP1 (b), and i-PP1−γ-CD IC (c).

coalesced, precipitated, and as-received polyolefins samples, will be reported shortly.

Coalescence of the Polyolefins from Their γ-CD IC Crystals. Preliminary characteristics of the coalesced polyolefins were obtained from DSC and X-ray diffraction observations. Once γ-CD IC crystals were proved to be formed with the polyolefins chains included inside the lattice γ-CD channels, the coalescence process was pursued in order to extract and solidify polymer chains with potentially modified conformations and morphologies. This was done by suspending CD IC powder in DMSO at room temperature. It should be mentioned that DMSO is a very good solvent for the host CD molecules but is a nonsolvent for both i-PP and i-PB. The coalesced polymers were first investigated by FTIR spectroscopy to make sure that no CD or solvents were left in the samples. The similarities between the IR spectra (not shown) recorded for the coalesced and precipitated i-PP and i-PB samples led us to conclude that no impurities remained in the coalesced samples.

1. Coalesced i-PP Samples. Wide-angle X-ray diffractograms of the as-received, precipitated, and coalesced i-PP1 in Figure 5 clearly indicate that only the α-form is present in the as-received and coalesced samples and a very poor α-form or almost a smectic form is obtained in the precipitated one.[43] The α-form is characterized by strong diffraction peaks at 13.9° (110), 16.9° (040), 18.6° (130), and 21.8° (041). No peaks are evident at 16.0° or 20.1° corresponding to the β or γ phase, respectively.[44] Careful analysis of all diffractograms reveals that the γ-CD inclusion/coalescence process does not modify the crystalline form of the included i-PP but yields a higher crystallinity for the coalesced i-PP. γ-CD IC formation isolates the included i-PP chains, and the narrow host γ-CD channels force them to adopt a highly extended conformation.[45] Since the coalescence is a rapid process, the polymer chains do not have enough time to reorganize and readopt their more entangled and randomly coiling conformations. Consequently, the first heating run MDSC data show an increase of about 27% in the crystallinity of coalesced i-PP1 in comparison with that of as-received i-PP1.

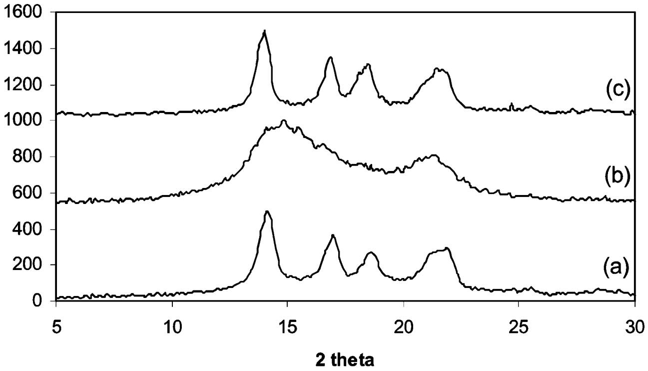

Figure 5. X-ray diffractograms of as-received (a), precipitated (b), and coalesced (c) i-PP1.

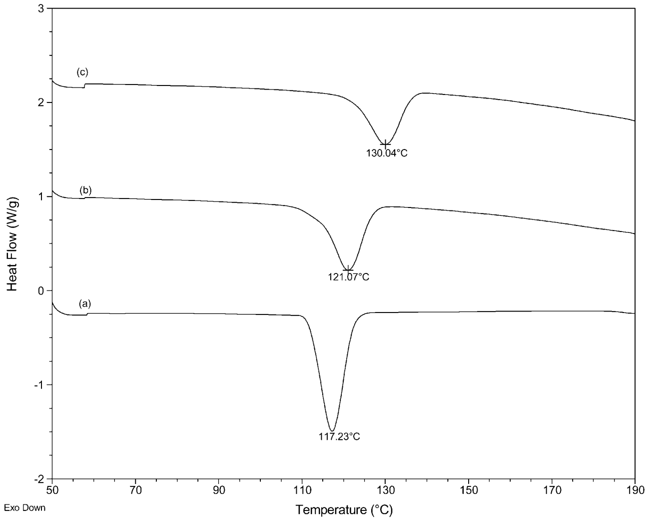

Figure 6. MDSC cooling scans of as-received (a), precipitated (b), and coalesced (c) i-PP1.

MDSC thermograms were run for as-received, precipitated, and coalesced i-PP1 at a heating rate of 5 °C/min. First heating scans of all three samples exhibit a single melting endotherm peak near 157 °C. However, on cooling from their melts at a rate of 5 °C/min, crystallization peaks occurring at different temperatures can be noticed in Figure 6. A significant increase in the crystallization rate was obtained for coalesced i-PP1, which crystallizes at 130 °C compared with crystallization temperatures of 117 °C for the as-received i-PP1 or 121 °C for the precipitated i-PP1. This behavior has been observed in other semicrystalline coalesced polymers, such as PET, and can be explained by considering that the included polymer chains retain a certain degree of their extended and untangled natures even after coalescence, facilitating their rapid crystallization.[36,37] All i-PP samples were kept in the melt at 200 °C for 3 min. However, the melt-phase memory effect in i-PP is very well-known and leads to crystallization rates highly conditioned by thermal history.[10,44,46] In a previous study, heating in the melt at 210 °C for 10 min was determined to be sufficient for investigating the nonisothermal crystallization of i-PP2 in the absence of melt-phase memory effects.[47]

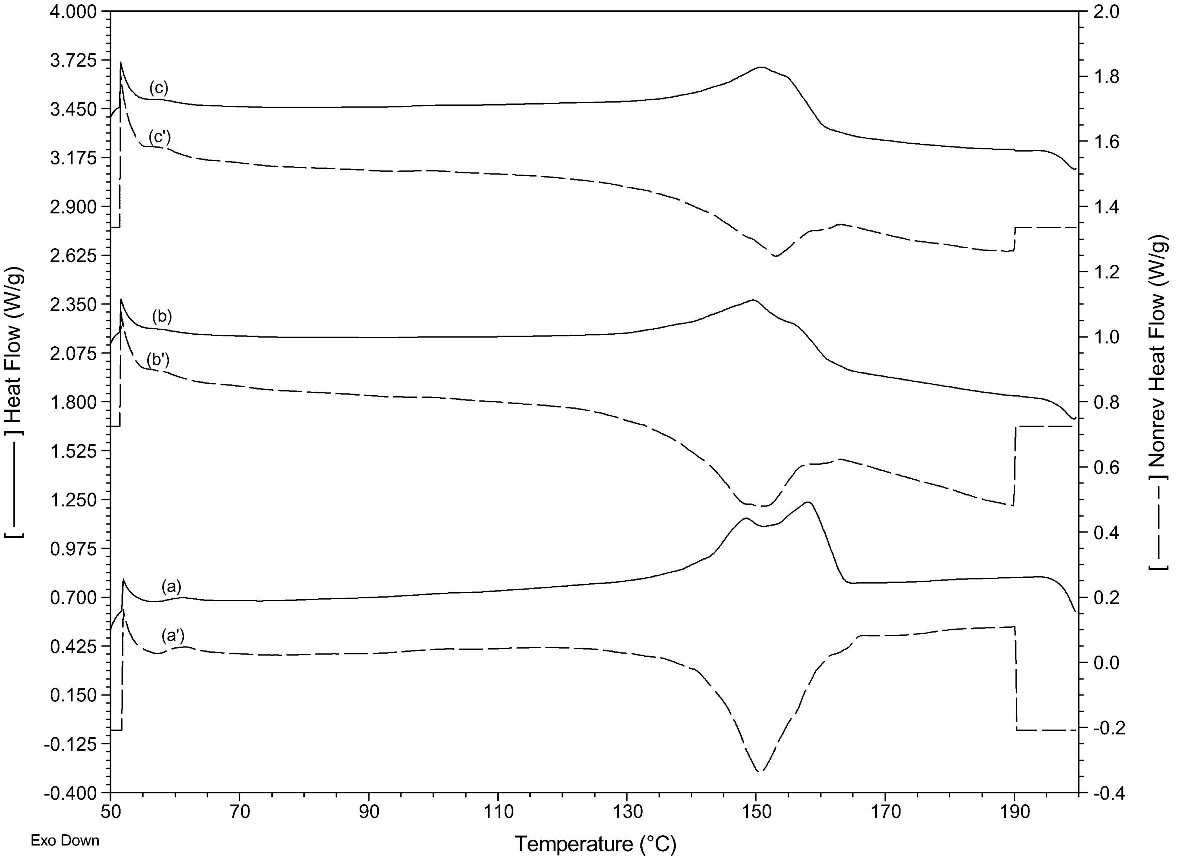

Figure 7. Second heating scans of as-received (a), precipitated (b), and coalesced (c) i-PP1. (a′), (b′), and (c′) represent the nonreverse heat flows of the above corresponding total signals.

After holding the coalesced i-PP1 in the melt at 210 °C for an extended period of time, the characteristics described above were retained. To confirm that this significant increase in the recrystallization rates of coalesced i-PP is not a result of small traces of remaining γ-CD acting as a nucleating agent, blends of i-PP with 1% γ-CD in the cage or channel structures were prepared. The nucleating efficiency of the γ-CD was determined to be very low.

Second heating thermograms in Figure 7 reveal double melting endotherms for all three i-PP samples. According to the literature, the double meting peaks are related to recrystallization and reorganization of imperfect monoclinic crystals. The peak at the lower temperature represents the melting of the imperfect crystals formed during the cooling process, whereas the higher temperature peak is due to the melting of more stable lamellae derived from recrystallization or reorganization of the imperfect crystals.[43] Zhu et al. noticed that a decrease in the cooling rate leads to a larger fraction of the sample that crystallized perfectly with a diminishing fraction obtained upon recrystallization.[43] This results in a decrease of the endotherm area at the higher temperature and an increase of the endotherm area at lower temperature because of the decreased reorganization and recrystallization. Finally, only one endotherm appears at 5 °C/min.

All i-PP samples in our study were cooled to 50 °C, at 5 °C/min, from the melt. Two endothermic peaks with almost the same area (54/46 relative ratio area) were revealed for the as-received i-PP1 in the second heating scan. However, the precipitated and coalesced i-PP1 present a larger fraction of perfect crystals that melt at lower temperature against a smaller fraction of the recrystallized, further perfected ones. The relative areas calculated after deconvolution of the double endothermic peak are 95/5 and 96/4 for precipitated and coalesced i-PP1, respectively. The total signal of the MDSC heat flow may be separated into reversing and nonreversing heat flow components as a result of the temperature modulation employed. Thermal transitions in the reversing signal arise from thermodynamic phenomena such as T_g and melting, while the nonreversing signal reflects kinetic phenomena, including evaporation and recrystallization. For the first time the recrystallization of imperfect lamellae is supported by our MDSC study, which shows in the nonreversing heat flow an exothermic recrystallization occurring at a temperature between the two endothermic peaks in the total heat flow signal. As presented in Figure 7, the areas of these exothermic peaks are in good correlation with the relative areas observed in the second heating scan mentioned above. More detailed MDSC studies of both coalesced i-PP samples, as well as isothermal experiments, are still in progress and will be published in a future paper.

2. Coalesced i-PB Samples. X-ray diffractograms of as-received, precipitated, and coalesced i-PB2 are presented in Figure 8. The diffractograms of both as-received and precipitated i-PB2 show clearly form I polymorph with the (110) reflection at 9.9°, the (300) at 17.3°, and the (220) at $2\theta = 20.2°$. In contrast, the coalesced i-PB2 predominantly adopts form II, along with some form III, which are normally obtained from melt or solution casting, respectively. The characteristic diffraction peaks of form II appear at $2\theta = 11.8°$ (200), 16.8° (220), and 18.1° (213). Form III has a strong reflection (110) at $2\theta = 11.8°$ and three weak (200),

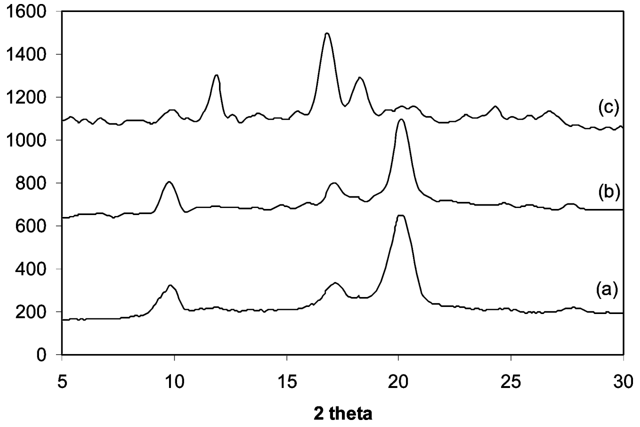

Figure 8. WAXD patterns of the as-received (a), precipitated (b), and coalesced (c) i-PB2.

(111), and (120) reflections at $2\theta = 13.8°$, 16.8°, and 20.7°, respectively. Although very noisy, the peak at 13.8° indicates the presence of form III. The diffraction peak of form III at $2\theta = 20.7°$ overlaps with a diffraction peak belonging to form I′. However, the weak peak at $2\theta = 10.0°$ reveals a (110) reflection from form I or form I′. Form I and form I′ cannot be distinguished by X-rays but exhibit different T_ms in the DSC.[20]

Interestingly, after quiescent storage for 6 months at room temperature, i-PB2, with a high molecular weight of 380 000, shows exactly the same diffraction pattern. It is very well-known in the literature that form II (tetragonal) is metastable and transforms to form I (hexagonal) at atmospheric pressure and room temperature with a half-life in the range 250−1600 min.[20] The same crystalline stability has not been observed for low molecular weight i-PB1. As previously mentioned, CD IC formation forces the included polymer chains to adopt a more extended conformation in the host narrow channels, which in the case of i-PB favors the formation of form I, with a more extended conformation, from among its polymorphs. However, an investigation of the phase transformations in i-PB upon drawing has demonstrated the formation of form II upon tensile drawing and a strong dependence of the deformation process on the crystal form of the initial starting sample.[23] These observations require further study, and a detailed study of the polymorphic transformations of i-PB coalesced samples is in progress.

To discern among different crystalline forms observed in the X-ray patterns, DSC scans were run for the as-received, precipitated, and coalesced i-PB2 (see Figure 9). The endotherm peak at 125 °C in the first scan of as-received i-PB2 corresponds to form I (see Figure 9a). In the second heating scan, after holding the sample in the melt for 5 min, a melting peak at 110 °C is evident for the tetragonal form II, which is always obtained by recrystallization from the melt. The multiple endothermic peaks in the first DSC run of coalesced i-PB2 (see Figure 9c) indicate an interesting polymorphism for this sample. The first endothermic peak at around 90 °C and a second endotherm with a maximum at 99 °C may be assigned to form III and form I′, which have been reported to have T_m between 90 and 100 °C.[12] The third peak at 115 °C corresponds to the melting of form II. The DSC results are in very good correlation with X-ray data of i-PB2. Consequently, we may conclude that the coalesced i-PB2 mainly adopts form II, together with small fractions of forms III and I′. After melting, the coalesced i-PB2 behaves the same as the as-received i-PB2 and entirely recrystallized into form II (endothermic peak at 110 °C in the second scan). As shown in Figure 9b, the precipitated i-PB2 control sample presents a main endothermic peak at 124 °C (form I melting) and a significant smaller endotherm which may correspond to the melting of form III. Since no diffraction peaks belonging to form III were identified in the X-ray pattern of precipitated i-PB2, one can assume that this sample is dominated by crystalline form I. Like the as-received i-PB2, this sample completely transforms to form II upon recrystallization from the melt (see second DSC scan). It is also noteworthy

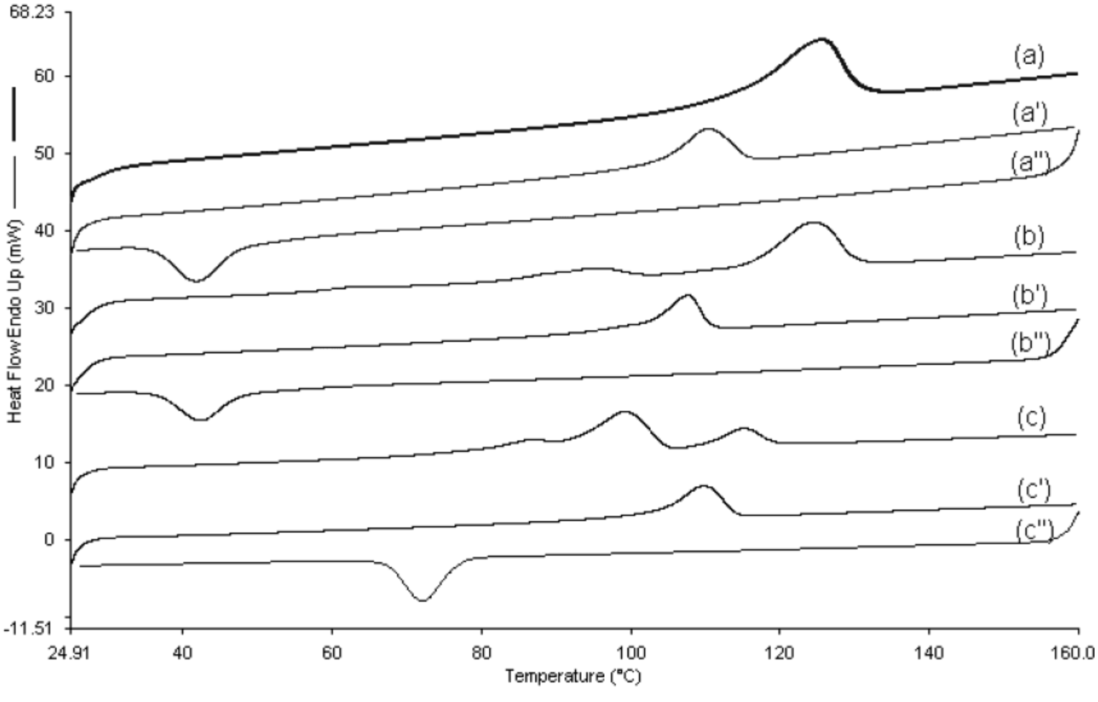

Figure 9. DSC scans of as-received (a), precipitated (b), and coalesced (c) i-PB2. a, b, c are the first heating scans; a′, b′, c′ are the second heating scans; and a″, b″, c″ are the intervening cooling scans.

to mention the observation of a similar, yet even more significant, increase in the recrystallization kinetics from the melt of coalesced i-PB2 (crystallizes at 71 °C upon cooling) compared with the as-received or precipitated i-PB2 (both crystallize at 42 °C upon cooling).

Conclusions

Crystalline inclusion compounds formed between host γ-CD molecules and two different high molecular weight isotactic polyolefin guests (i-PP and i-PB) were obtained for the first time and fully characterized. A combination of analytical methods demonstrated that i-PP− and i-PB−γ-CD IC powders possess a channel type crystalline structure with isolated guest polyolefin chains included in an extended conformation. Coalescence of the included polymers was performed by removing the host lattice with a very good solvent that is exclusive for the host γ-CD molecules. At least locally, it is likely that coalescence takes place rapidly, which does not allow the polymer chains time sufficient to disorganize and assume their randomly coiling conformations, but instead they maintain a certain degree of their extended and unentangled, included natures. Consequently, a significant increase in the crystallinity for the coalesced i-PPs has been detected by MDSC. Another interesting property of coalesced i-PPs is related to their faster crystallization rates, which were demonstrated not to be a result of any trace γ-CD acting as a nucleating agent. Because of their modified conformations, a larger fraction of more perfect crystals results after crystallization of coalesced i-PPs from their melts. Interesting thermal properties have also been observed for coalesced i-PBs, which, in addition, seem to exhibit a completely different polymorphic behavior compared with as-received and precipitated samples. The coalesced i-PB2 predominantly adopts a surprisingly stable form II polymorph, along with small portions of forms III and I′.

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