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Low-Temperature Crystallization of Ethylene-*ran*-propylene Copolymers: Conformational Rearrangement of Sequences during the Formation of the Aggregates

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ABSTRACT: Low-temperature (220−290 K) ethylene-*ran*-propylene copolymer crystallization was followed by DSC and solid-state NMR spectroscopy that can detect the formation of even small and short-living crystalline aggregates (minimum lifetime of 3 ms). NMR at 282 K reveals a sharp and reversible melting−crystallization transition in the copolymer with 74% ethylene units. The trans conformation fraction identifying the aggregates is detected at all temperatures independent of the thermal history, as at each temperature a quick gauche/trans equilibration is realized with no evidence of hysteresis. Transition occurs in both ethylene homosequences and heterosequences, indicating the inclusion of propylene units in the aggregates. The heterosequences do not aggregate in a separate phase, proved by the fast equilibration of the hydrogen magnetization to the same relaxation times as for the homosequences ($T_{1\rho}(^1H)$ value of ≈4 ms). Both chain mobility and fast carbon spin−lattice relaxation times ($T_1(^{13}C) \approx 1$ s) are promoted by the random distribution along the chain of the propylene units that push the vicinal chains apart. The copolymer chain segment behavior in the aggregates is dynamic, similar to that of polyethylene, as arranged in the hexagonal packing obtained at high temperature and pressure and to that of polyethylene mesophases confined to crystalline nanochannels.

Introduction

Polyethylene (PE), like *n*-alkanes, can exhibit unusual states of aggregation in the crystal phase.[1−3] Some allomorphs contain more dynamic disorder than conventional phases stable at room temperature, and such allomorphs have been called rotator phases, conformationally disordered crystals (condis crystals) or columnar mesophases.[4]

The easy accessibility of conformations that deviate greatly from trans-planar arrangements, and the relatively low energy required for trans/gauche conversion, promotes chain flexibility. In the extended form, motion coexisting with limited loss in order is the result of fast conformational averaging along each chain. Thus, the chains statistically occupy cylindrical spaces,[5,6] finding a favorable arrangement in the hexagonal packing, and because of the entropy gained in the solid state, the crystal phase is stable up to high temperatures. At 230 °C and under ultrahigh pressures, high molecular weight polyethylene is arranged in the hexagonal phase, which reverts to the usual orthorhombic phase during cooling and after pressure removal.[1,7]

The hexagonal phase, due to its intrinsic mobility, is also an important intermediate phase in the formation of the extended-chain conformation. The annealing process produces lamella thickening, to the limits of thermodynamically stable extended-chain crystals.[8] On the basis of blurred reflections in X-ray diffraction data and of IR and Raman spectroscopies, conformationally disordered chains in hexagonal packing have been proposed.[9]

Several efforts have been made to obtain the hexagonal phase under mild conditions, exploiting the existence of a metastable "pseudohexagonal" form at accessible temperatures and pressures.[10] Extended-chain polyethylene in the hexagonal phase can also be induced by drawing the specimen just below fusion: this phenomenon produces high modulus material.[11,12]

The presence of motion in the hexagonal phase was recently proved by ^{2}H NMR, performed on PE at 3000 bar.[13] The mechanism of motion appears to be similar to that of PE extended chains restricted to ideal cylinders in inclusion compounds (ICs), as demonstrated by ^{13}C and ^{2}H NMR.[14,15] Squeezing the single chains into a nanochannel of the host crystal can result in chain arrangements similar to the hexagonal phase. The space provided by the crystal environment of ICs tends to promote the thermal motion of polyethylene chains, preventing the collapse of the chains to the amorphous phase. The gauche defects are mostly concentrated at the chain ends, but they can also propagate throughout the inner methylene units.[16] In fact, NMR has revealed fast defect propagation along the polymethylene chain, and the mechanisms of motion have been modeled by RIS calculations[5] and molecular simulations.[17]

To establish the conformations and properties of polyethylene crystallites formed in ethylene−propylene (EP) copolymers, we have made a comparison of the DSC and NMR data. Methyls inserted randomly along the chain reduce intermolecular specific interactions without preventing (although reducing) crystallization. It can be seen from recent literature that there is a great deal of interest with regard to the influence of comonomer distribution on ethylene sequence crystallization in copolymers with α-olefins.[18,19] EP copolymers containing a substantial fraction of propylene can crystallize when cooled below room temperature,[20] and ori-

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ented samples of such copolymers, obtained by stretching at room temperature, have been described to form a hexagonal phase.[21] This prompted us to investigate the formation of crystallites at low temperatures without applying mechanical stress.

Here, we describe for the first time the conformational arrangement of polyethylene segments and copolymer sequences during low-temperature crystallization. The low-temperature crystallization of EP copolymers such as EPDM rubbers was described many years ago,[22] but there has never been a detailed in-situ characterization. This was our aim, and it was achieved by high-resolution solid-state NMR which has proved successful for characterizing mesophases, interphases, and the motional behavior of polyolefins.[23−28]

Experimental Section

Materials. Ethylene−propylene (EP) copolymers are prepared using homogeneous metallocene-based Ziegler−Natta catalysts (*rac*-EBTHIZrCl$_2$). Such copolymers are characterized by a varying ethylene content (EP-54 sample, 54 mol % of ethylene; EP-62 sample, 62 mol % of ethylene; EP-74 sample, 74 mol % of ethylene), show a narrow chemical composition distribution, and have a good degree of regioregularity.[29]

DSC Analysis. We performed the calorimetric analysis (DSC) with a Mettler Toledo Star^{e} thermal analysis system equipped with a liquid N$_2$ low-temperature apparatus, running the experiments under N$_2$ atmosphere from 173 to 353 K with heating and cooling rates of 10 K/min. The sample weights for the DSC measurements were about 6.5 mg and were measured to an accuracy of 0.05 mg.

Solid-State NMR. ^{13}C magic angle spinning (MAS) NMR spectra were run at 75.5 MHz, on a Bruker MSL300 instrument operating at a static field of 7.05 T. A MAS Bruker probe head was used with 7 mm ZrO$_2$ rotors spinning at a standard speed of 4 kHz. In all the experiments there was a high-power decoupling (DD) field: 90° pulse for proton was 4.7 μs (≈55 kHz). Single pulse excitation (SPE) experiments were run using a recycle delay of 100 and 10 s. Cross-polarization (CP) MAS experiments were performed by applying a recycle delay of 10 s and a contact time of 2 ms.

Carbon resolution was checked on glycine (the width at half-height of C═O group is 23 Hz). Crystalline polyethylene was taken as an external reference at 32.85 ppm from tetramethylsilane (TMS).[30] (The literature often reports chemical shift values as referred to PE at 33.63 ppm from TMS.)

Spectral profiles were fit by Lorentzian line shapes. The trans fractions of ethylene sequences in the EP-74 sample at varying temperatures were evaluated considering the peak areas at 33.6 and 30.8 ppm. The heterosequence peak area was subtracted from the peak area at 33.6 ppm at each temperature.

The ^{13}C spin−lattice relaxation time (T_1) values were obtained using the method developed by Torchia.[31] Spectra were acquired with 15 different τ values. Proton relaxation times in the rotating frame, $T_{1\rho}(^{1}\mathrm{H})$, were measured indirectly, varying the duration of a ^{1}H spin-lock period before a fixed $^{1}\mathrm{H} \rightarrow {}^{13}\mathrm{C}$ cross-polarization contact time (2 ms).

Results and Discussion

Thermal Behavior. Figure 1 shows the heating traces from 193 to 333 K of copolymers containing varying amounts of ethylene. The samples had been kept at room temperature for a long time (a few months) and then quickly cooled to 173 K before the heating process. The EP-54 sample, being substantially amorphous, reveals the presence of a sharp glass transition temperature at 215 K. The glass transition temperature of the copolymer of higher ethylene content is slightly higher and has a smoother DSC trace. The trend is consistent with the presence of increasing amounts of crystalline material, which reduces the mobility of the amorphous phase. A large endotherm ranging from 230 to 303 K is observed in EP-74; this is due to the melting of crystal species ($\Delta H = 35$ J g^{-1}) and is consistent with literature results.[20] Similar transitions, though at lower temperatures and absorbing less heat, are detected when the ethylene content of the samples is lower ($\Delta H = 14$ J g^{-1} for EP-62 and $\Delta H = 4$ J g^{-1} for EP-54). Unlike in the other samples, there is, in the EP-74 copolymer, a small amount of crystalline material that melts above room temperature, as shown by the transition at 318 K.

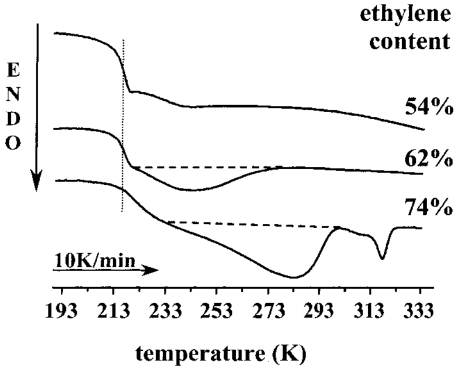

Figure 1. DSC traces of the EP-74, EP-62, and EP-54 samples recorded from 193 to 333 K with a heating rate of 10 K/min.

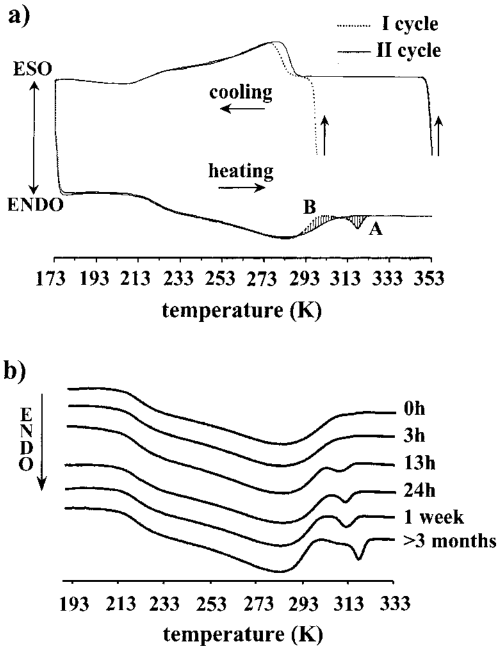

Figure 2. DSC traces of the EP-74 sample, recorded at 10 K/min: (a) Thermal cycles: in the first cycle the sample is cooled from room temperature to 173 K and successively heated to 353 K (dashed line). In the second cycle the sample is cooled from 353 to 173 K followed by a heating process to 353 K (full line). The shaded area A refers to crystallite melting at 318 K during the first cycle. The shaded area B represents the crystallites melting above 293 K in the second cycle. (b) Heating traces of the EP-74 sample after different times of annealing at room temperature. The memory of the thermal history was previously reset by a thermal treatment at 353 K. The heating and cooling processes are performed with a rate of 10 K/min.

Two thermal cycles of the EP-74 copolymer are presented in Figure 2a. The first cycle (dashed line) starts with the cooling from room temperature and shows a crystallization exotherm at about 278 K; the

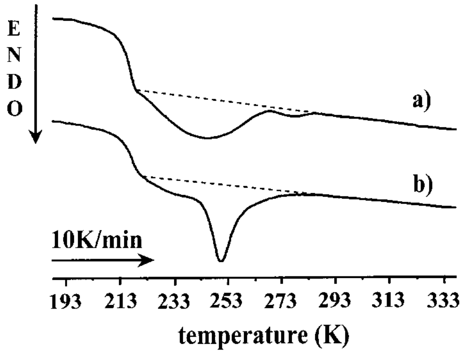

Figure 3. DSC traces of the EP-62 sample recorded from 193 to 333 K with a heating rate of 10 K/min. The sample was previously subjected to the following annealing treatments: (a) at 263 K and (b) at 243 K, for 3 h.

heating trace exhibits the pattern shown in Figure 1. The second cycle (full line) follows the thermal memory resetting by melting at 353 K: crystallization occurs at 283 K; upon heating a single broad endotherm is observed. The melting peak at 318 K (area A) is present only in the first cycle, there appearing in the second cycle a corresponding area (B) at lower temperature but no melting peak. In fact, it was only after a long residence time (>3 months) at room temperature that the melting peak at 318 K was observed. After 13 h the DSC scan exhibits an endotherm peak at 308 K, as shown in Figure 2b. This melting peak (above room temperature) increases with the residence time (ΔH = 3 J g^{-1}) and in the course of a week reaches 311 K. Therefore, the peak at 318 K is due to a process of annealing at room temperature. In the EP-62 sample, 3 h annealing at 263 K (Figure 3a) and at 243 K (Figure 3b) generates melting peaks at 275 and 250 K, respectively.

In conclusion, DSC experimental observations confirm that long residence times at given temperatures improve crystal quality, and there is no delay in crystallization for short residence times.

Solid-State NMR Characterization. Figure 4a shows the ^{13}C MAS NMR spectrum of the EP-74 sample obtained at 323 K without cross-polarization and applying delay times of 10 s. The spectrum is interpreted following the well-established assignment of solution NMR spectra of ethylene–propylene copolymers, according to Randall et al.,[32] Tritto et al.,[29] and references therein. The most probable ethylene (E)–propylene (P) sequences are indicated at the triad level.

At 323 K sharp resonances with half-height line width of 15 Hz become evident, the copolymer consisting entirely of a highly mobile amorphous phase, as 323 K is about 100 K above the glass transition and far above the crystallite melting point. In fact, the amorphous phase is so mobile that resolution can be achieved at the triad level. The peak emerging at 20.5 ppm (EPE sequence) indicates the presence of a quite substantial amount of isolated propylene units. The propylene monomer units (already observed by solution NMR) are distributed randomly along the polymer chain, and adjacent propylene units have low probability, being detected as minor signals at 21.3 and 22.0 ppm.

Figure 4b–d shows the quantitative ^{13}C MAS NMR spectra of the EP-74, EP-62, and EP-54 samples, recorded at room temperature applying a recycle delay of 100 s. The fraction of triads containing two or three propylene units (PPE and PPP) increases with increasing of propylene content, and in the methyl region the signals at 21.3 and 22.0 ppm ($P_{\beta\delta}$ and $P_{\beta\beta}$) increase accordingly. A further feature to be noted is the increase in methylene peak intensity ($S_{\alpha\alpha}$ and $S_{\beta\beta}$), in line with the propylene content. Considering the integral of the methyl signals in relation to the full spectrum and the number of carbon atoms of the monomer units, the quantitative spectra confirm the molar percentages indicated by the acronyms (Figure 4b–d). The estimate of the ethylene fraction is in agreement with the molar composition obtained by solution spectra.

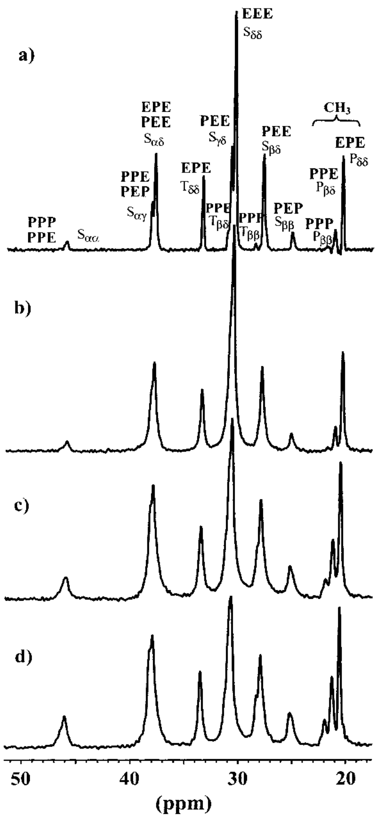

Figure 4. (a) ^{13}C MAS NMR spectrum of EP-74 copolymer recorded at 75.5 MHz; spectrum recorded with 10 s recycle delay at 323 K; assignments are given according to the methyl substitution along the main chain (position α, β, γ, etc., with respect to the observed carbon atom: P = methyls; S = methylenes; T = methynes); the most probable ethylene (E)–propylene (P) sequences are given at the triad level. Fully relaxed ^{13}C MAS spectra recorded with 100 s recycle delay at room temperature of (b) EP-74 sample, (c) EP-62 sample, and (d) EP-54 sample.

Figure 5 shows the ^{13}C cross-polarization (CP) MAS NMR spectrum of EP-74 at room temperature. The most probable chain segments of EP-74 and the observed carbon atoms (black dots) are indicated according to refs 29 and 32. Sample response and signal intensity, recorded with a mixing time of 2 ms, match the fully relaxed spectrum except for the underestimation of the methyls (Figure 4b). The chemical shift of the ethylene homosequences at 30.8 ppm coincides with amorphous phase signals of polyethylene.[23] The line width in conventional polyethylene at room temperature is much greater due to the restricted amorphous phase motion in the presence of a large amount of crystallized material.

CP MAS experiments performed at varying temperatures on EP-74, from 287 down to 273 K, are presented in Figure 6. In addition to the line broadening with

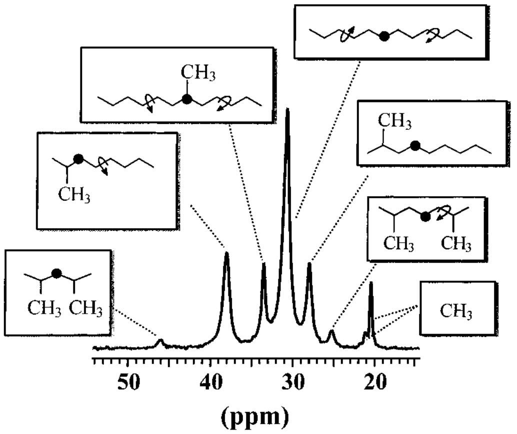

Figure 5. ^{13}C CP MAS NMR spectrum of the EP-74 sample recorded at 298 K with a contact time of 2 ms. The assignments of the resonances to carbon atoms (black dots) in the most probable chain sequences are reported.

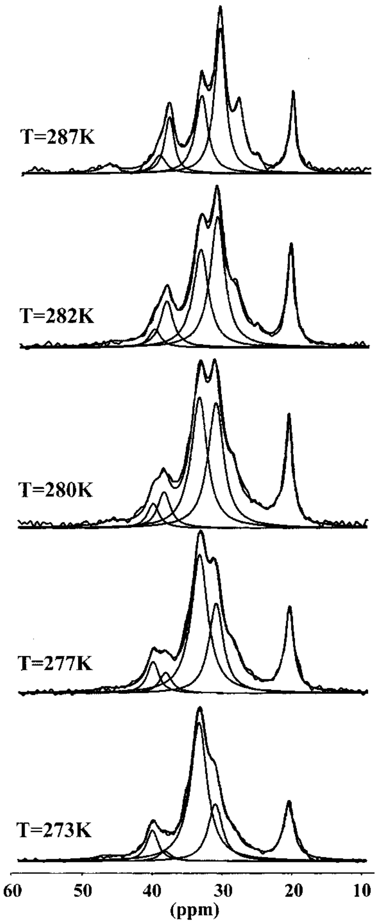

Figure 6. ^{13}C CP MAS NMR spectra of the EP-74 sample recorded with a contact time of 2 ms at temperatures from 287 to 273 K. Spectra were fully deconvoluted by Lorentzian line shapes, and the single lines are reported for trans EEE sequence at 33.6 ppm, gauche-rich EEE sequence at 30.8 ppm, trans PEE sequences at 40.0 ppm, and gauche-rich PEE sequence at 38.2 ppm.

lowering temperature, some change in profile is apparent: the signal at 33.6 ppm increases and the signal at 30.8 ppm decreases.

The signal change from upfield (30.8 ppm) to downfield (33.6 ppm) below 282 K is due to the change from gauche-rich to all-trans conformations in the ethylene homosequences (EEE). The ^{13}C chemical shift dependence on polyethylene segment conformation has already been described in the literature for both high molecular weight polyethylene and *n*-alkanes.[30,33,34] In fact, at 4.7 T or higher, high molecular weight polyethylene crystallized in the orthorhombic form shows a signal at 32.80 ppm, which corresponds to the crystalline phase.[30,33] Crystallization in other forms is observed through a further downfield shift of the chemical shift. For example, the monoclinic phase shows the signal of the crystalline phase at 34.27 ppm,[33] and *n*-alkanes in the rotator phase show signals at values of 33.38 ppm[30] in the high field limit. These values for the crystalline phases are due to bonds arranged mainly in trans conformations along the main chain, and this, for EP-74, supports the 33.6 ppm peak assignment to ethylene homosequences crystallized in trans conformations. The effect of packing on the chemical shift will be described in detail later.

On the other hand, the assignment of the upfield signal at 30.8 ppm to gauche-rich conformations of EEE sequences is in agreement with the γ-gauche effect quantified as a -5 ppm shift for alkanes.[34] The chemical shift of the amorphous phases of polyethylene and *n*-alkanes is about 31 ppm, consistent with a 0.4 fraction of gauche bonds.

In Figure 6 there appears, lowering the temperature, a downfield peak at 40.0 ppm, with a corresponding reduction in signal intensity at 38.2 ppm. The peaks of this region are assigned to sequences containing a methyl in the α position with respect to the observed methylene (see also Figure 5). This downfield shift is similar to that just discussed for pure ethylene sequences. The transition from gauche-rich to trans sequences occurs even in the chain segment close to the methyls (i.e. in heterosequences) where a methyl interrupts the polymethylene sequences. This is an indication of the presence of methyls either close to the crystallized microphases of polyethylene or included in its crystal structure. The intensity of the signal at 28.0 ppm, again due to sequences containing a single methyl in the β position with respect to the observed methylene, is also reduced, although the signal partly overlaps the main signals. Thus, NMR allows the observation of the crystallization of both pure ethylene homosequences (EEE triads) and ethylene sequences close to methyls.

The quantitative determination of the trans fraction of the ethylene triads EEE, obtained by the deconvolution of the spectra of Figure 6, is reported in Figure 7a as a function of temperature. The sigmoidal curve shows a flex at 282 K. In the transition range the distribution of the EEE triad conformations varies significantly with temperature (during the cooling a 0.3 fraction of trans conformations is formed within 5 K). No further increase in trans content (a fraction of 0.8) is observed below 270 K. The same phenomenon occurs in heterosequences observed at about 40 ppm at slightly lower temperature (Figure 7b). The temperature range of the heterosequence transition is even narrower than that of homosequences, as shown by the derivative curves in Figure 7. If the persistence time of the conformations is longer than about 3 ms (a difference of 5 ppm, equal to 375 Hz at 75.5 MHz, corresponds to about 3 ms), nuclear magnetic resonance of the ^{13}C nucleus can detect two distinct resonances, not a single exchange peak, for trans and gauche conformations. Since the trans conformation is associated with the presence of crystalline aggregates (or at least coherence regions among the

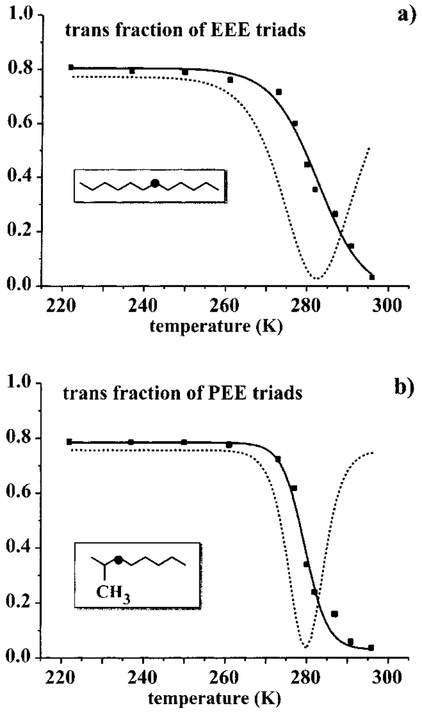

Figure 7. (a) Diagram of the trans fraction of the EEE homosequences of the EP-74 sample as a function of temperature. The trans fraction of EEE triads was determined from an analysis of the peak areas at 33.6 and 30.8 ppm. (b) Diagram of the trans fraction of the PEE heterosequences of the EP-74 sample as a function of temperature. These heterosequences contain a methyl in the α position with respect to the observed methylene; the trans fraction of the triads was determined from an analysis of the peak areas at 40.0 and 38.2 ppm. The areas of the peaks were obtained from the deconvolution of the CP MAS NMR spectra performed at varying temperatures, from 298 to 222 K. Some of the deconvoluted spectra are reported in Figure 6. Experimental values are fitted by sigmoidal curves (full lines), and the first derivatives are also reported (dotted lines).

chains), aggregates are detected if they have a minimum lifetime of 3 ms at each temperature. Thus, short-living and small aggregates can be detected by NMR already in the early stages of their existence.

Varying temperature experiments were performed, not only by decreasing the temperature from room to lower temperatures as shown above (following the crystallization process) but also by heating the samples from these low temperatures in order to observe crystallite melting. The spectra collected on returning to a given temperature after the cooling or heating process are identical, as shown for the example at 280 K in Figure 8 (below). This equilibrium is reached quickly, within the time needed to set the temperature of the sample. This indicates that, by NMR, we can define the conformational arrangement distribution at the different temperatures of EEE segments in copolymer aggregates at equilibrium with the amorphous phase (Figure 8, above), and no hysteresis is observed for the aggregation and melting cycles.

Low-Temperature Spectra and Conformations about Propylene Units. Below 273 K the spectral pattern of the EP-74 sample (Figure 9) remains substantially unaltered, except for general line broadening and methyl transition in the 261−250 K range. The transition appears as a splitting of the methyl resonances, most likely determined by the main-chain conformations close to the methyls. A splitting of about 3 ppm has already been observed in the methyl spectra of atactic polypropylene[35] and in amorphous syndiotactic polypropylene[27,36] in the proximity of the glass transition. The glass transition of atactic polypropylene was observed by DSC at 239 K, i.e., 20 K lower than the NMR determination, due to the different observation frequencies. In our case, splitting occurs at 250 K and glass transition was observed by DSC at about 220 K, confirming the glass transition temperature shift detected by the two techniques. The downfield (22 ppm) and upfield (18 ppm) peaks, according to the above-reported γ-gauche effect, are assigned to resonances associated with trans and gauche conformations with respect to the methyl carbon. Thus, at low temperature the conformations of the EPE sequences can be detected singly.

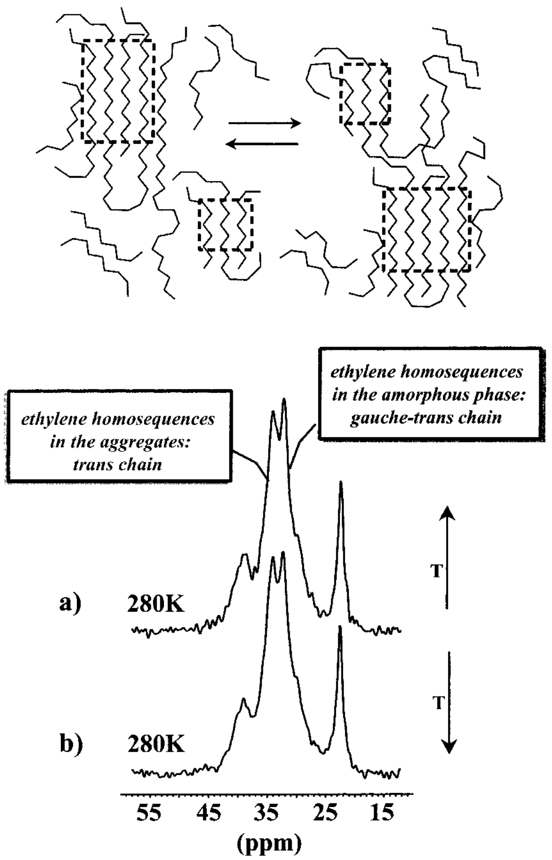

Figure 8. ^{13}C CP MAS NMR spectra recorded at 280 K of EP-74 sample: (a) after heating the sample from low temperature to 280 K; (b) after cooling the sample from room temperature to 280 K. A simple model of the ethylene homosequence exchange between the aggregates and the amorphous phase is reported above.

The low-temperature spectra of the EP-74, EP-62, and EP-54 samples can be compared in Figure 10. From the deconvolution of the methyl region the conformation distributions of the EPE sequence at 222 K can be measured. The EP-54 sample consists essentially of an amorphous phase, as previously shown by DSC, and a 0.20 fraction of EPE sequence methyls in gauche arrangement to the chain (Figure 10c). Thus, for the first time, single conformational arrangements about an isolated propylene unit in the copolymers below the glass transition have been identified. In the EP-62 and EP-74 samples, containing a nonnegligible amount of crystalline phase, the fractions of the EPE sequence in the gauche arrangement (with respect to the total area of methyl signals) at 222 K are increased to 0.24 and

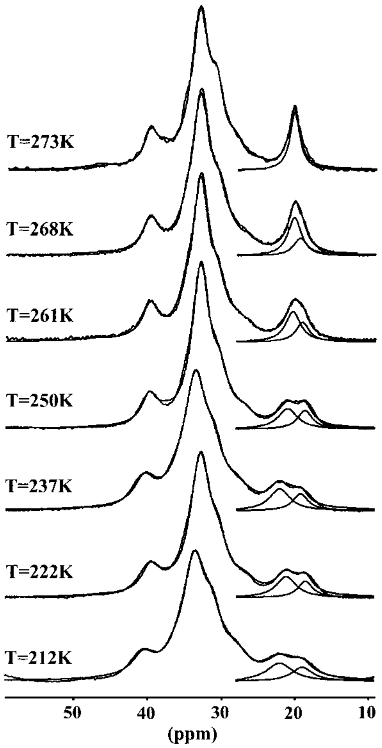

Figure 9. ^{13}C CP MAS NMR spectra of the EP-74 sample recorded with a contact time of 2 ms at temperatures from 273 to 212 K. Spectra were fully deconvoluted by Lorentzian line shapes, and the single lines are reported for the methyl region.

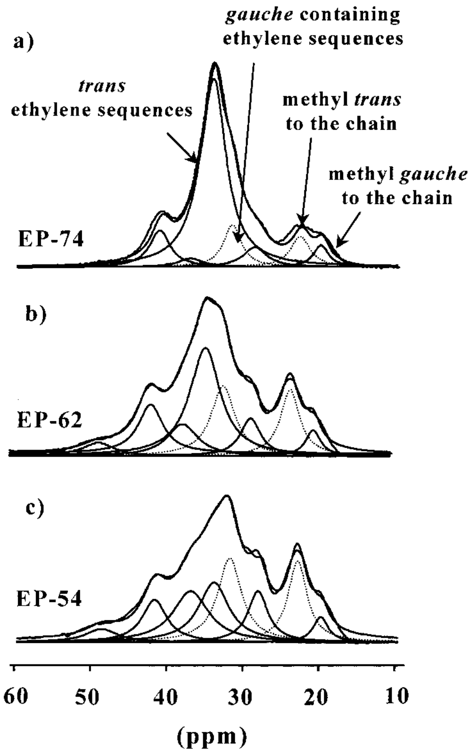

Figure 10. ^{13}C CP MAS NMR spectra recorded with a contact time of 2 ms at 222 K of (a) the EP-74 sample, (b) the EP-62 sample, and (c) the EP-54 sample. The deconvolutions were performed by Lorentzian line shapes.

0.36, respectively. Considering that for methyls gauche conformations would be generated by a sequence of trans conformations along the main chain, we can conclude that, in EP-62 and EP-74, the conformations of the main chain close to propylene units are in the trans arrangement. This is a demonstration that the crystalline phase induces extended chain conformation about the propylene units. On the other hand, a comparison of the EEE triad signals at 30.8 and 33.6 ppm (Figure 10) confirms that with increase in ethylene content there occurs a progressive increase in the trans conformations of the ethylene homosequences, consistent with the increase in low-temperature crystallinity.

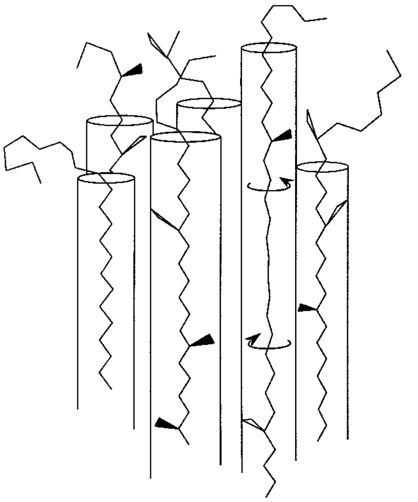

Figure 11. Schematic representation of the aggregates in the ethylene-*ran*-propylene samples. The polymer chains are represented as included in ideal cylinders. Isolated propylene units are distributed randomly along the trans chains. Large librations can reorient the copolymer chains within the ideal cylinders, inducing low-density packing.

Structure of the Aggregates of Polyethylene Sequence. The chemical shift of 33.6 ppm for the EEE sequence resonates about 1 ppm downfield with respect to the orthorhombic phase of PE.[30] This is in agreement with the change in magnetic susceptibility due to low-density packing.[37] A downfield shift (~0.5 ppm) has also been described in *n*-alkanes in the high-temperature hexagonal modification (called rotator phase) which presents low-density packing.[37] No gauche defects in the crystalline phase can be present as these would determine, according to the γ-gauche effect, an opposite and upfield shift.[34] The low-density packing in the aggregates suggests the presence of methyls distributed randomly along the polymethylene chains: the methyls generate a steric hindrance that prevents close packing with the vicinal segments of polyethylene, setting the chains at a greater distance. The fact that the extended trans chains in the crystallites bear methyls of the propylene units is also in agreement with the gauche/trans transition of heterosequences. Figure 11 introduces the model of extended ethylene-rich copolymer chains fitting cylindrical spaces in hexagonal-packed aggregates.

Short ^{13}C spin−lattice relaxation times of 1 and 2 s, measured at 275 K on the signals of trans-rich conformations at 33.6 and 40.0 ppm, are consistent with loosely packed chains endowed with great mobility. Closely packed crystal structures of orthorhombic polyethylene show relaxation times from 50 s to hundreds of seconds. On the other hand, single polyethylene chains confined to nanochannels of perhydrotriphenylene inclusion compounds[15] present a ^{13}C(T_1) of 6 s and when confined to slightly narrower nanochannels of tris(*o*-phenylenedioxy)spirocyclotriphosphazene a ^{13}C-

(T_1) of 12 s.[16] In such cases efficient relaxation pathways were demonstrated, these being due to the marked diffusional motion of the chains about their axes within the cylindrical cavities of the inclusion compounds. ^{2}H NMR[14] and molecular dynamic simulations support this description.[17] The hexagonal modification of the polyethylene, obtained at high temperature and pressure, also shows a high degree of mobility of the extended chain conformation.[38] We can deduce that this common behavior occurs whenever there is enough space for the chains to move within the cylinders. The librations along the many bonds allow a flexible chain to undergo complete reorientation about its axis.[17] In our case, the efficient relaxations and the low-density packing are compatible with the above-described behavior, supporting the proposed model in Figure 11. It is also very likely that there is a rapid small-crystal aggregate to amorphous phase interchange, as has been described in even large crystallites of polyethylene at high temperature.[39,40]

Further evidence of high mobility in the aggregates, and intimacy among the phases, can be seen in the short proton relaxation times in the rotating frame $T_{1\rho}(^1\text{H})$ of 1.5−2.5 ms at 277 K and of 3.9−5.3 ms at 260 K for all the signals of the EP-74 copolymer. The propylene carbon values are virtually the same as those for ethylene carbons; this supports the conclusion that the amorphous and crystalline phases are closely mixed to the nanometer scale and that the heterosequences, identified by methyls, do not segregate into a separate phase (Figure 11).[41] In the rubbery phase at room temperature the methyl $T_{1\rho}(^1\text{H})$'s of propylene units ($\cong$10 ms) have different values from the rest of the system ($\cong$4 ms); this is due to the high mobility of the amorphous material that quenches spin diffusion.

Conclusion

The first NMR observation of low-temperature crystallization in random copolymers has been reported here. The follow-up phase transformation was achieved in-situ by lowering the temperature and observing the formation of trans conformations. The method is particularly accurate for recording the onset of the aggregation phenomenon at the level of small clusters of chains, a quick equilibration with no evidence of hysteresis being realized for all temperatures.

The triad conformations of ethylene-*ran*-propylene in aggregates could, as the temperature decreased, be detected selectively: ethylene homosequences first form trans conformations, and then the chain segments next to the methyls undergo a transition. Isolated propylene units show residual motion down to the glass transition; however, in EPE triads, the chain bonds next to the methyls are mostly stretched.

The proposed model is that methyl-created bulges are the origin of wide librations in the ethylene segments, and it is these bulges that keep the surrounding chains apart, just as the rigid walls of crystalline inclusion compounds allow enough space for macromolecules to move.

Disorder starting from methyls substituted randomly along the polymethylene chains generates an unusual crystal packing containing a substantial amount of diffusional motion. This diffusional motion provides a better filling of space and compensates unfavorable low-density packing when hexagonal structures are realized. Thus, it can be seen that such behavior in ethylene−propylene copolymers resembles the behavior realized in mesophases of linear alkyl chains like rotator phases and in the hexagonal phase of pure polyethylene obtained under high pressure and under stretching.

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