

Poly(propylene-*co*-1-pentene-*co*-1-heptene) terpolymers: mechanical and rheological behavior

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Abstract

This work describes the important effects of microstructural features on crystalline structure, mechanical behavior and molten state response for poly(propylene-*co*-1-pentene-*co*-1-heptene) terpolymers. The study was carried out in a wide range of compositions, varying the 1-pentene/1-heptene ratio and the thermal history applied. Molecular features, as propylene sequences and compositional triads, allow predicting the material behavior. Moreover, rheological response has demonstrated the influence of molecular weight, comonomer content and short-chain branches on the properties. The flow activation energy can justify the importance of the material density over the whole spectrum of properties.

Keywords: Terpolymers; crystalline polymorphs; microstructure; rheological activation energy

Introduction

A new polymorph was described in 2005 for metallocene copolymers based on isotactic polypropylene, iPP, with amounts in 1-hexene as comonomer¹ higher than about 10 mol %. Up to that moment and depending on the polymerization procedure, thermal history and use of different nucleants, the polymorphs known for iPP were²⁻⁹: the monoclinic α , the metastable hexagonal β , and the orthorhombic γ crystalline modification, all sharing a three-fold conformation, together with a phase of an intermediate or mesomorphic order. In those copolymers, an increase in crystal density was found as the driving force inducing crystallization at those contents, due to the inclusion of 1-hexene units within the crystal¹⁰. A trigonal cell^{10,11,12}, also named as δ , similar to that exhibited by the form I of isotactic polybutene, was shown by that polymorph. Crystallization rate turned on an important variable for its competition with the monoclinic α or the mesomorphic polymorphs^{1,10,12,13}. An analogous trigonal δ lattice was also reported by substituting 1-hexene by 1-pentene^{14,15} in these propylene-based copolymers. Later on, this lattice was also observed for propylene terpolymers incorporating both 1-pentene and 1-hexene as comonomeric units^{16,17} and in propylene-*co*-1-pentene-*co*-1-heptene terpolymers¹⁸. This type of crystallites was not, however, developed in the corresponding propylene-*co*-1-heptene copolymers¹⁹ independent of the crystallization conditions²⁰.

Interest has been mostly focused, up to now, on the assessment of crystalline and structural aspects in these copolymers/terpolymers able to generate the trigonal δ form. Specifically, propylene terpolymers have found a niche market in the manufacturing of films, exhibiting good heat seal properties and broad sealing windows. Presence of the trigonal δ modification might alter, complete or partially, the spectrum of properties and, consequently, the range of applications. Nevertheless, very few investigations in these materials have dealt with a detailed estimation of properties, which becomes mandatory because of their feasible importance at the industrial level. Tensile stress-strain experiments were carried out for propylene-1-hexene copolymers^{1,21,22,23}, propylene-1-pentene-1-hexene terpolymers¹⁶ and propylene-1-pentene-1-heptene terpolymers¹⁸.

Mechanical tests were also carried out in propylene-1-pentene-1-hexene terpolymers¹⁶ at a global content around 25 mol %. Very low values of strength were

observed but the mechanical parameters were not quantified. On the other hand, two distinct dependences of the modulus and the yield stress upon total composition and comonomers ratio were described¹⁸ for rapidly crystallized propylene-1-pentene-1-heptene terpolymers.

The aim of this work is to perform a complementary evaluation of the mechanical behavior by depth sensing indentation (DSI) experiments in these poly(propylene-*co*-1-pentene-*co*-1-heptene) terpolymers. Crystallization has been now carried out using two rather different cooling rates to get a better comprehension. The DSI measurements have been chosen because they provide information of plastic parameters and creep-related processes, additionally to that from elastic magnitudes ascribed to rigidity. In addition, and in order to get a better knowledge on the processability, a rheological study will be also performed on some of the specimens and it will be compared with the response shown by the corresponding copolymers.

Experimental Part

Synthesis of poly(propylene-co-1-pentene-co-1-heptene) terpolymers

The preparation of poly(propylene-*co*-1-pentene-*co*-1-heptene) terpolymers was performed in a 500 mL Büchi glass ecoclave at -5 °C in 250 mL of toluene by using *rac*-dimethylsilylbis(1-indenyl) zirconium dichloride/MAO ([Al]/[Zr] = 3650). The synthetic procedure for obtainment of terpolymers and polypropylene homopolymer was reported extensively elsewhere¹⁸. Several terpolymers with varying total content in comonomers and also with three different ratios between 1-pentene (Pe) and 1-heptene (Hp) counits (approximately 75/25, 50/50 and 25/75, as deduced from Table 1) were synthesized. The terpolymers attained are named as **T** followed by the total mol % content in comonomers (*x*) and the ratio between counits: 75Pe-25Hp, 50Pe-50Hp and 25Pe-75Hp. The sets of terpolymers in relation to the three comonomers ratios are, accordingly: T_{*x*}-75Pe-25Hp, T_{*x*}-50Pe-50Hp and T_{*x*}-25Pe-75Hp, respectively. Polypropylene homopolymer has been labeled either as iPP or T0. Moreover, poly(propylene-*co*-1-pentene) copolymers and poly(propylene-*co*-1-heptene) copolymers have been also used for comparative reasons and they have been named as cPPe and cPHp followed by the closest integer value of the 1-pentene and 1-heptene mol % content, respectively.

Preparation of films

Films of the different terpolymers were carried out by compression molding in a Collin press between hot plates, using a pressure of 2.5 MPa for 3 min and at a temperature 30 °C above their corresponding melting point. They were subsequently cooled down to room temperature at two different rates: the so-called Q (quick) treatment consisted of a fast cooling (at approximately 80 °C/min) between plates cooled with water after melting in the press, and the labeled as S (slow) specimens, which were crystallized from the melt at a rate around 1.5 °C/min, by allowing the press to cool down after switching off the power. The thickness of the different films ranged from 100 to 120 µm.

Size exclusion chromatography

The molecular weight (M_w) and polydispersity (PDI) were estimated by size exclusion chromatography in a Waters GPC/V 2000 composed by a refractive index detector and a viscometer. Three columns of the PL Gel type were used with 1,2,4-trichlorobenzene as a solvent. The measurements were carried out at 145 °C and a flow rate of 1 mL/min. Narrow molecular mass distribution standards of polystyrene were used for calibration.

Nuclear Magnetic Resonance Characterization

The total comonomer composition, the ratio between counits and the tacticity were determined by carbon nuclear magnetic resonance (^{13}C NMR) at 80 °C in an Innova 400 spectrometer (100 MHz). The solvent used was 1,1,2,2-tetrachloroethane-*d*₄ (70 mg/mL).

A minimum of 8000 scans were performed with broad band proton decoupling and using an acquisition time of 1 s, a relaxation delay of 4 s and a pulse angle of 45°. The homopolymer was characterized in a Bruker Avance DPX-300 (75 MHz) spectrometer, from solutions in 1,2,4-trichlorobenzene at 100 °C, using deuterated *o*-dichlorobenzene as an internal reference.

X-Ray Diffraction

Conventional wide-angle X-ray diffraction patterns were acquired in the reflection mode by using a Bruker D8 Advance diffractometer provided with a Goebel

mirror and a PSD Vantec detector (from Bruker, Madison, WI). Cu K α radiation ($\lambda = 0.1542$ nm) was used. The equipment was calibrated with different standards: Al₂O₃ (Corundum) and Cr₂O₃.

Calorimetric Analysis

The calorimetric analysis was carried out in a PerkinElmer DSC-7 calorimeter with a cooling system. The apparatus was calibrated with diverse standards as indium, zinc and *n*-dodecane. The specimen weights ranged from 2 to 5 mg. A scanning rate of 10 °C/min was applied for the different runs.

Nanoindentation Measurements

Depth Sensing Indentation (DSI) experiments were performed at 20 °C with a Shimadzu tester (model DUH211S) equipped with a Berkovich-type diamond indenter. At least 10 distinct indentations were carried out at different regions on the square surface for all specimens: isotactic polypropylene homopolymer and the several terpolymers, at the two thermal treatments.

The applied experimental protocol involved in several stages¹⁹: a) application of a load of 10 mN at a loading speed of 1.46 mN/s; b) maintenance of this constant load for 5 s; and c) release of the load at an unloading speed equal than the one used along the loading stage. Finally, indentation depth was registered for 5 additional seconds after reaching the minimum load (0.1 mN).

Rheological Studies

The rheological characterization was performed in a strain controlled ARES rheometer (TA Instrument) using parallel plate configuration with a diameter of 25 mm, under nitrogen atmosphere. The viscoelastic properties of the molten polymeric materials (storage modulus G' and loss modulus G'') were determined in small-amplitude oscillatory shear flow as a function of frequency and temperature. Furthermore, diverse temperature ranges were used according to the melting point of the materials (see Table 1). The dynamic tests were performed at small strains ($\gamma_0 < 0.03$) to ensure the linear viscoelastic regime. Finally, some series of frequency sweeps were repeated with the same sample at different temperatures. Small torque values were observed for the samples with low molecular weights. Consequently, the samples were

tested at the lowest temperature allowed, and a reference temperature of 140 °C was selected for the master curves. The crystallization temperature of a given polymeric material was the limit for the lowest temperature used. In all cases, the diverse specimens were heated up to 20 °C higher than their melting temperature (given in the last column of Table 1) for 5 min. Then, samples were cooled down to 10 °C over their melting temperature. As indicative that crystallization processes did not take place during the rheological measurements, differences between modulus for each material were not found.

Results and Discussion

The synthesis of these terpolymers was extensively described in a preceding work¹⁸. Table 1 lists the global composition in comonomers, which ranges from 0 to 16 mol % at the three distinct 1-pentene/1-heptene ratios. It is observed that molecular weight of terpolymers decreases, as expected, on increasing overall composition in comonomers. Isotacticity also undergoes a drop in the *mmmm* sequences with the comonomers content, whereas polydispersity exhibits a rather constant value close to 2, related typically to the metallocene catalytic system used for synthesizing these tailored polypropylene derivatives.

Figure 1 shows the X-ray profiles at room temperature for the different terpolymers at the two thermal treatments used from the molten state. A remarkable polymorphic behavior is observed in these samples. The variation of the crystalline lattices with the overall content in comonomers and thermal treatment is clearly noticeable.

Thus, the slowly crystallized iPP homopolymer exhibits the diffractions corresponding to both the monoclinic α lattice and the orthorhombic γ modification, with a majority in the first one, judging from the relative intensities of the (130) reflection from the monoclinic α polymorph²³ and of the characteristic (117) reflection stemming from the orthorhombic γ cell²⁴. Presence of comonomers in the S specimens of T4-75Pe-25Hp, T4-50Pe-50Hp, and T4-25Pe-75Hp significantly favors the formation of γ crystallites^{25,26,27}. Monoclinic α crystals are, however, the unique polymorph in the Q samples for this overall composition (and for the homopolymer).

Table 1. Molecular features of poly(propylene-*co*-1-pentene-*co*-1-heptene) terpolymers and T_m values obtained from the second melting run.

Sample	Comonomer content (mol %)			Overall weight comonomer content (wt.%)	M_w (kg/mol)	PDI	[<i>mmmm</i>]	T_m (°C)
	Global	Pe	Hp					
	iPP	-	-					
T4-75Pe-25Hp	3.8	3.0	0.8	6.7	122	2.0	92.4	130.0
T4-50Pe-50Hp	4.0	2.2	1.8	7.6	128	2.0	91.1	128.0
T4-25Pe-75Hp	3.2	0.9	2.3	6.6	103	2.0	93.4	129.0
T6-75Pe-25Hp	6.4	5.1	1.3	11.0	111	2.0	92.0	115.5
T6-50Pe-50Hp	6.0	3.2	2.8	11.2	104	2.0	92.0	116.0
T6-25Pe-75Hp	6.7	1.9	4.8	13.3	116	2.0	91.1	115.0
T10-75Pe-25Hp	11.3	8.5	2.8	18.9	90	2.0	86.4	95.5
T10-50Pe-50Hp	10.1	5.4	4.7	18.2	80	2.0	88.1	96.0
T10-25Pe-75Hp	10.5	2.5	8.0	20.3	83	2.0	86.7	90.0
T13-75Pe-25Hp	12.8	10.0	2.8	21.0	72	2.2	84.7	92.5
T13-50Pe-50Hp	13.1	6.9	6.2	23.0	74	2.0	85.1	90.5
T13-25Pe-75Hp	12.9	3.5	9.4	24.2	73	2.0	84.9	88.0
T16-75Pe-25Hp	16.0	12.2	3.8	25.8	72	2.0	80.8	64.5
T16-50Pe-50Hp	15.4	8.2	7.2	26.5	71	2.0	82.1	54.0
T16-25Pe-75Hp	16.0	4.7	11.3	28.9	73	2.0	82.5	48.0

Slowly crystallized T6-75Pe-25Hp, T6-50Pe-50Hp, and T6-25Pe-75Hp samples display analogous characteristics than those just commented for the T4 series, i.e., major content in orthorhombic γ crystals. On the contrary, mesomorphic entities^{28,29,30,31} compete now with the monoclinic α polymorph in the rapidly cooled T6 samples.

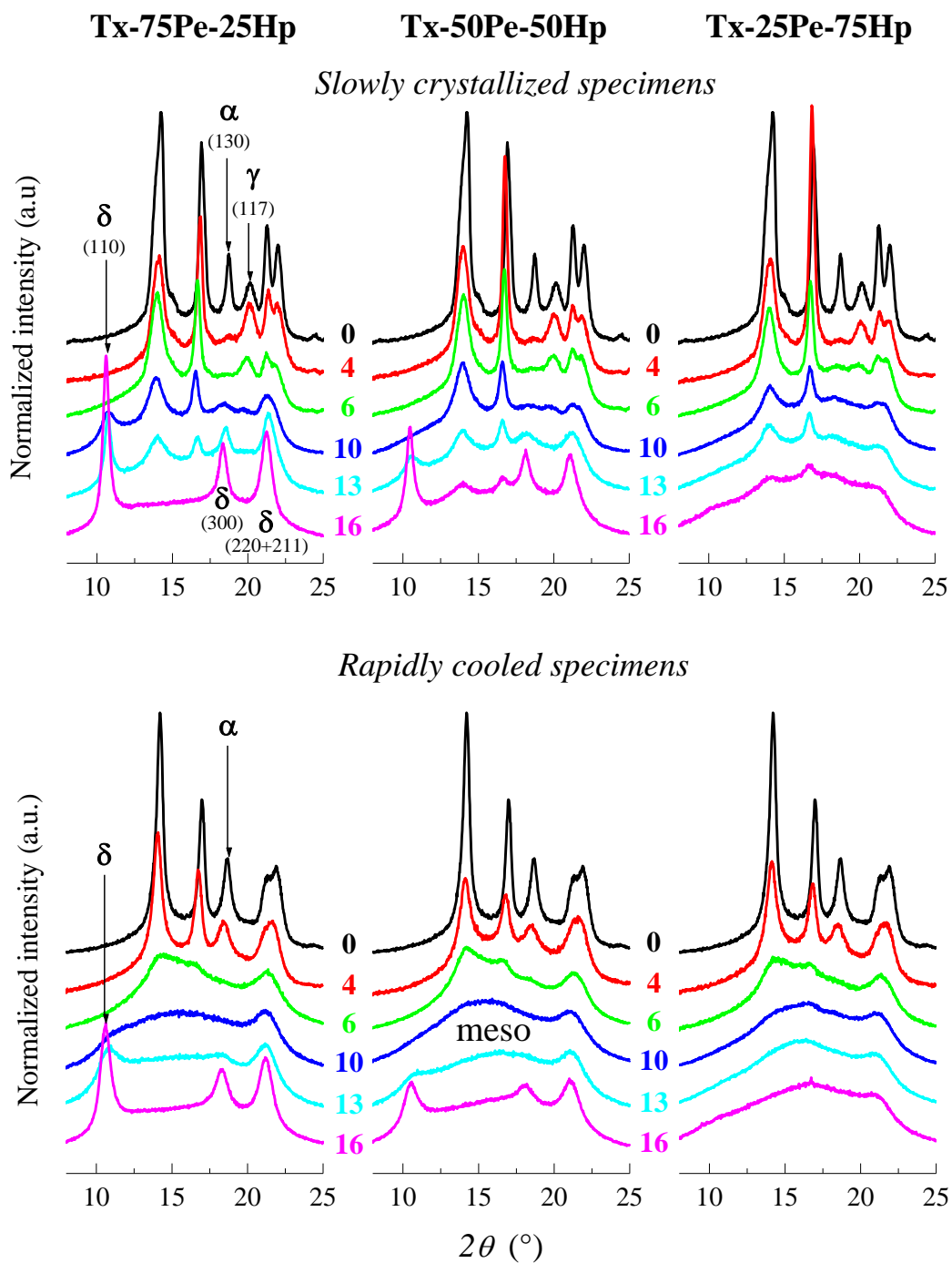


Figure 1. Wide angle X ray scattering (WAXS) at room temperature for the iPP homopolymer and the different Tx terpolymers at the distinct overall composition (x) and the three 1-pentene/1-heptene ratios for both thermal treatments: slow and rapidly crystallized specimens from the melt, S, and Q, respectively.

The situation changes also significantly at an overall content around 10 mol % in comonomers. Trigonal δ lattice is developed in the slowly crystallized T10-75Pe-25Hp terpolymer, as deduced from the presence at approximately 10.5° of its (110) reflection. This polymorph cocrystallizes with, probably, orthorhombic γ crystals, since these were mostly generated in the T4 and T6 series, although monoclinic α crystallites could also develop in a small amount. This assumption cannot be fully assured because the (130) characteristic diffraction from monoclinic α polymorph is observed in the same 2θ angular interval as the (300) reflection from the trigonal δ lattice.

At the other two ratios, T10-50Pe-50Hp and T10-25Pe-55Hp terpolymers, the trigonal δ modification is absent and the orthorhombic γ and monoclinic α lattices seem to coexist. Crystallites become defective as 1-heptene raises and global crystallinity is reduced, as deduced from the reflections intensity. The rapidly cooled T10 samples are, however, mostly ordered into mesomorphic entities. It should be commented that the δ (110) diffraction, at around 10.5° , appears to be noticeable in the Q T10-75Pe-25Hp terpolymer.

The T13 family exhibits a behavior rather similar to that just commented of the T10 terpolymers but a significantly higher proportion of trigonal δ lattice is developed. This modification is now observed in T13-75Pe-25Hp and T13-50Pe-50Hp at both, slow or fast, cooling rates. Moreover, T13-25Pe-75Hp behaves identically than the T10-75Pe-25Hp sample: coexistence of rather defective monoclinic α and orthorhombic γ crystals in the S specimens and mesomorphic entities in the Q samples.

More perfect trigonal δ crystals are formed in the T16-75Pe-25Hp and T16-50Pe-50Hp terpolymers for both thermal treatments. In fact, this is the unique polymorph observed at both crystallization rates in the former while trigonal δ form coexists with orthorhombic/monoclinic crystallites in the slowly cooled T16-50Pe-50Hp and with mesomorphic entities in the rapidly crystallized specimen. Finally, the highest 1-heptene ratio at this global composition leads to a significant reduction of the total crystallinity and of the perfection of the ordered entities (monoclinic / orthorhombic / mesomorphic / trigonal), as evidently noticed from Figure 1. A careful control of the 1-pentene/1-heptene proportion allows modulating total crystallinity and the amount of trigonal δ crystallites at the highest comonomers compositions. These results also show that overall crystallinity is less dependent on the comonomers ratio than on the thermal

treatment, since differences of only around 5 % are deduced between S and Q treatments while values can change up to around 25 % with 1-pentene/1-heptene ratio (as seen in Figure 2).

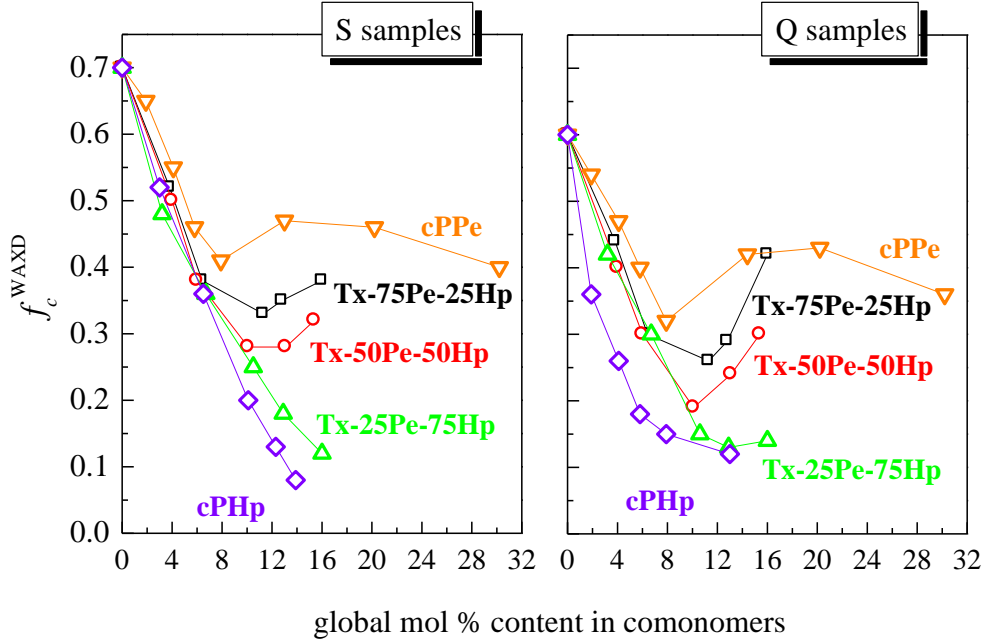


Figure 2. Variation of the WAXD degree of crystallinity (f_c^{WAXD}) with global content in comonomers for the two thermal treatments, S (on the left) and Q (on the right). Data from cPPE and cPHp have been taken from literature^{19,35,32}.

The overall degree of crystallinity, f_c^{WAXD} , has been estimated from the diffractograms represented in Figure 1. An accurate determination requires the knowledge of the corresponding amorphous component at a particular composition. Variable-temperature X-ray diffraction experiments have been carried out for these specimens (results under analysis) and their amorphous molten patterns are available. Thus, the total crystallinity has been obtained for these terpolymers following the procedure described before for poly(propylene-*co*-1-pentene)³³ and poly(propylene-*co*-1-heptene)¹⁹ copolymers. Once the different amorphous halos at room temperature are determined, their subtraction from the actual profile at a specific content in comonomers allows estimating the degree of crystallinity^{19,32,34}. The deconvolution into the distinct characteristic reflections permits estimation of the amount of each polymorph.

The results for the total WAXD crystallinity as function of the global comonomer content are shown in Figure 2 for the analyzed terpolymers under the two thermal treatments and compared with those attained in the two pristine copolymers: the propylene-*co*-1-pentene^{33,35} (cPPe) and propylene-*co*-1-heptene¹⁹ (cPHp) ones. The cPPe copolymers show an unusual dependence of total crystallinity on 1-pentene content. The existence of a minimum value at intermediate compositions is clearly deduced from Figure 2 for the two thermal treatments.

This tendency was not found in other cPPe copolymers reported in the literature¹⁵. A fast decrease of crystallinity was described up to nearly 10 mol % of pentene for those copolymers that crystallized in the α form and a slower diminishment was seen for copolymers that crystallized in the trigonal δ form¹⁵ at higher pentene concentrations. A decreasing trend was also found for the melting enthalpy³⁶ in other 1-pentene copolymers. This dependence of crystallinity on the composition was also not found in the propylene-hexene copolymers^{1,12,21}, which are also able to develop the trigonal δ form. These differences could be attributed to the variations existing in microstructural details (tacticity, molecular weight, polydispersity, among others) because of the different metallocene catalyst used for the synthesis and to differences in the thermal treatment applied to the specimens^{1,12,15,21,36}.

The presence of a crystallinity minimum is also observed in the Tx-75Pe-25Hp and Tx-50Pe-50Hp terpolymers, although its location has been moved up to slightly higher total content in comonomers. This feature is in agreement with the behavior previously described for propylene-*co*-1-pentene-*co*-1-hexene terpolymers³⁷. The reason behind this dependence can be ascribed to the capability of developing the trigonal δ lattice at compositions around and higher than 10 mol %. In these terpolymers at those molar contents, the trigonal δ formation involves the inclusion of either 1-pentene or 1-heptene comonomers within the crystalline cell. The latest is incorporated as a defect since this trigonal δ modification is not developed under any crystallization rate in the cPHp copolymers^{19,20}, as aforementioned. It is for this reason that development of trigonal δ lattice becomes more hindered as 1-heptene is increased in the comonomers ratio. Thus, an almost constant value is reached at the highest global content in comonomers for the Tx-25Pe-75Hp series (Q samples) and a decreasing tendency is seen in the S specimens, although the trend at low total composition is rather independent of the ratio in comonomers. Nevertheless, crystallinity at those small

contents in counts is significantly higher than that exhibited by cPHp copolymers at similar compositions, mainly for the rapidly crystallized samples, because of the presence of 1-pentene in these terpolymers.

Summarizing these WAXD results, two well differentiated intervals of comonomer content are observed in these terpolymers: the former at global comonomer content up to around 8 mol%, where the crystallinity decreases as the content increases, as expected, and the ratio between comonomers does not play a significant role. The second range at global contents above around 10 mol%, where ratio between 1-pentene and 1-heptene is of capital importance at a given overall composition. In this range, 1-pentene favors the development of this trigonal δ form while 1-heptene constitutes an obstacle for its formation and is included as a defect in the terpolymers if its content in the comonomers ratio is not the highest. The key factor in this second interval is ascribed to the amount of trigonal δ modification obtained.

In a next step, several parameters obtained from depth sensing indentation experiments are correlated to structural changes and molecular features. These measurements, which consist of successive loading–maintenance-unloading processes, are suitable for determining different relevant mechanical magnitudes and require a relatively small amount of material. As aforementioned in the introduction, Young's modulus (E) and yield stress, attained from stress-strain measurements, were observed to be significantly dependent on 1-pentene/1-heptene ratios at high overall comonomer contents in rapidly crystallized specimens¹⁸. A minimum value was observed for those two bulk mechanical magnitudes at around 10 mol% in the 75Pe-25Hp series. That minimum was seen at about 13 mol% in the 50Pe-50Hp set while a continuous decrease was exhibited in the 25Pe-75Hp family. The argument in favor of these trends was the unusual features in crystallinity degrees found at those overall comonomer contents, just mentioned above.

Figure 3 shows the loading-maintenance-unloading processes observed in all the terpolymers at both crystallization rates. It should be commented that the magnitudes attained from DSI experiments are associated with the mechanical characteristics at the surface and not in the bulk of these materials, taking into account the average thickness of the films. The expected effect in copolymers is the decrease of parameters related to

stiffness as count content increases. This trend is due to the regular diminishment of crystallinity upon comonomer composition^{19,38}.

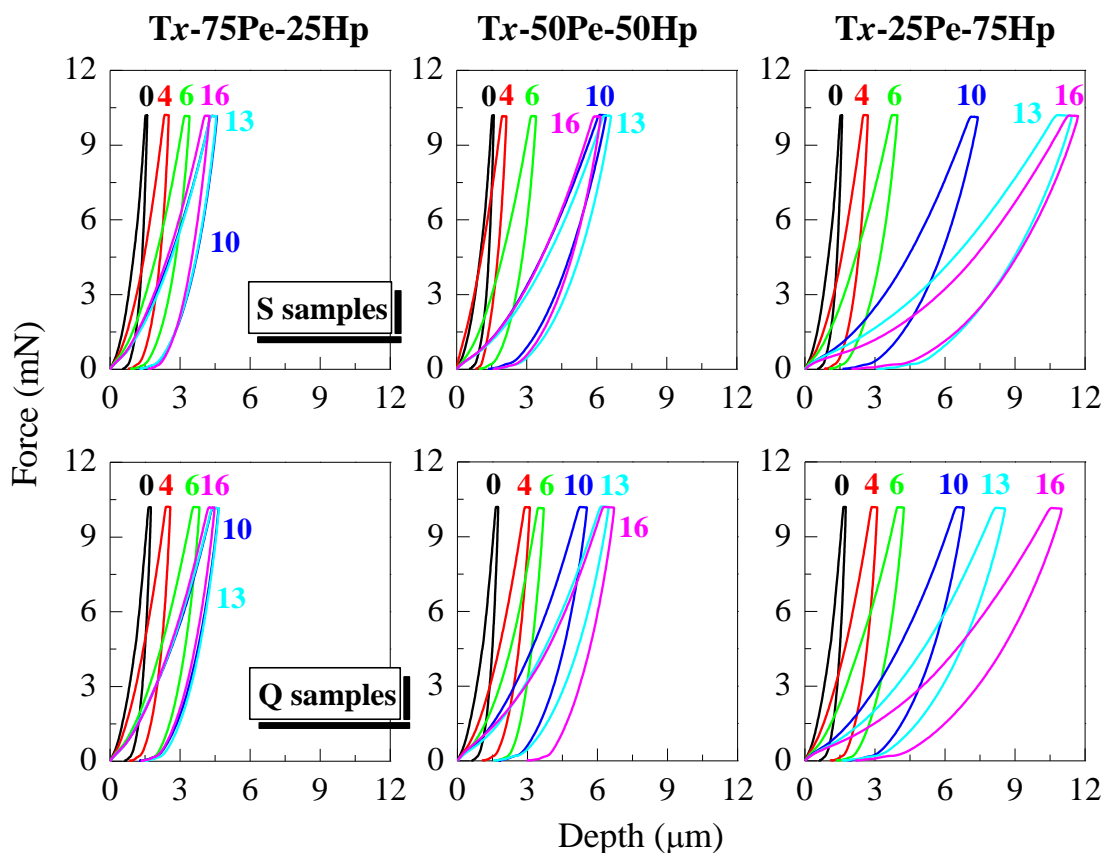


Figure 3. Variation of force on indentation depth found along loading–maintenance–unloading processes for the slowly and rapidly cooled, S and Q, samples.

The dependence of indentation modulus on f_c^{WAXD} crystalline content is represented in Figure S1 of Supporting Information. Simultaneously to the reduction in rigidity, an increase in the indentation depth at the end of loading process is found since material becomes softer and indenter can go deeper inside at the same load. This is, for instance, the behavior observed in the Tx-25Pe-75Hp series, as depicted in Figure 4 from results represented either in the left or right Y axes.

The response is rather different for the sets of Tx-75Pe-25Hp and Tx-50Pe-50Hp. Their degree of crystallinity undergoes a noticeable and unusual increase upon counts content at composition higher than 10 mol %. Then, indentation modulus and hardness values rise whereas the depth of indentation diminishes for those terpolymers with superior crystallinity. These samples are those ones where trigonal δ polymorph is

developed in a sufficient amount and perfection. The only presence of either mesophase entities or orthorhombic/monoclinic crystallites would not be able of improving those indentation magnitudes at those high compositions, probably because they would be already very defective, as described previously for propylene-1-heptene copolymers¹⁹. Figure S1 shows the importance of presence of the trigonal δ lattice in the value of indentation modulus. It also reveals the significant effect that the type of existing polymorphs has on the final rigidity. Thus, those specimens containing trigonal δ crystallites are softer than some other samples belonging to the identical series with similar crystallinity where monoclinic / orthorhombic / mesomorphic crystals are present.

The trend found on the surface agrees rather well with the one observed in the Q specimens from bulk measurements by stress-strain experiments. Figure 4 shows that, similar to the WAXD results, the indentation modulus decreases as overall comonomer content increases in the region of low global contents, but there is no dependence on counts ratio. On the contrary, a significant variation is seen at those comonomer contents where the trigonal δ phase is able to be favorably generated, i.e., when 1-pentene ratio increases at a given composition for both thermal treatments.

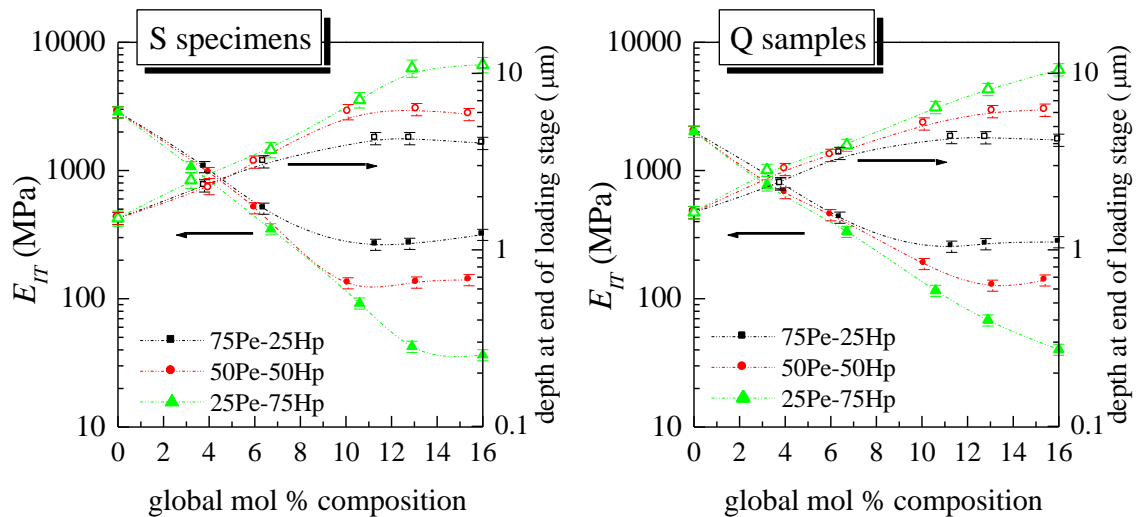


Figure 4. Dependence of indentation modulus (E_{IT}) (solid symbols, left Y axis) and depth reached at the end of the loading process (open symbols, right Y axis) upon overall composition for the homopolymer and the Tx-75Pe-25Hp (black squares), Tx-50Pe-50Hp (red circles) and Tx-25Pe-75Hp (green up triangles) terpolymers at both thermal treatments.

Comparison of left and right plots in Figure 4 allows analyzing the effect of the thermal history applied. At low comonomer content, the modulus is maintained practically independent of comonomer ratio, as mentioned above, and the E_{IT} values in the slowly crystallized S samples are higher than those attained from the fast cooled Q specimens at a given terpolymer. At an overall content above 10 mol% different dependences are found: for the Tx-75Pe-25Hp set, the values in the S samples are greater than in the Q ones; in the Tx-50Pe-50Hp terpolymers, similar magnitudes are found for both thermal treatments; and for the Tx-25Pe-75Hp series, a reduction of modulus is seen, at identical composition, in S specimens compared with the Q ones. This last feature was already described in propylene-1-heptene copolymers¹⁹ and was ascribed to the inferior reinforcement influence of very defective monoclinic α crystals compared with that triggered by the mesomorphic entities (right bottom plot in Figure 1). The polymorphic details of these 1-heptene-enriched terpolymers are more complex but the feasible presence of orthorhombic γ (exclusively or together with monoclinic α ones) crystals in the S samples (right upper plot in Figure 1) seems to contribute to a decrease in the stiffness parameters. The existence of more perfect trigonal δ crystallites in the S specimens (left upper plot in Figure 1) than in the Q ones (left bottom plot in Figure 1) for the Tx-75Pe-25He series is underlying their higher stiffness. A balance between perfection and type of polymorphs generated seems to dominate in the Tx-50Pe-50Hp set (middle plots in Figure 1).

Regarding the molecular features, the most important microstructural characteristics were discussed in a previous work, where the tacticity, compositional triads, and propylene sequences were investigated¹⁸. The analysis of their influence in mechanical properties turns out interesting although is usually not performed. Table S1 of Supporting Information details the different values of the relative content of triads and average propylene length (n_p) for the different terpolymers and Figure 5 represents the dependence of indentation hardness upon n_p in these terpolymers for both thermal treatments. Reduction of n_p , ranging between 32 to 6 units from the lowest to the highest overall content in comonomers, has an important influence on the hardness because of its relationship with the total crystallinity degree, crystal thickness, and crystalline polymorphs.

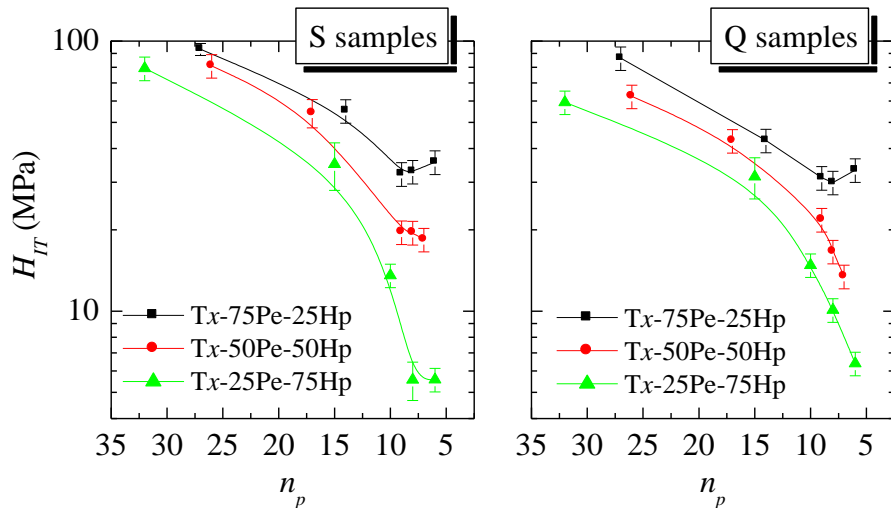


Figure 5. Dependence of indentation hardness (H_{IT}) on average propylene length (n_p) for the terpolymers at both thermal treatments, S and Q, on the left and right, respectively.

This factor is associated with composition defects of the polymeric chains for the different samples, in such a way that more interruptions exist in the macrochains as the amount of comonomers increases and, consequently, the n_p sequences become shorter. This length in isotactic propylene sequence directly affects the crystallization capability, since it is an indication of the chain regularity, which must reach a minimum value for developing ordered morphologies. Moreover, hardness is strongly changed by crystalline details and its decreasing trend is disrupted in the S samples as n_p values diminish because trigonal δ lattice is developed. Its crystallization is favored as 1-pentene is raised in the Pe/Hp ratio and, consequently, the dependence observed is more noticeable. This evidence is even observed for the Q samples in the Tx-75Pe-25Hp series. It should be reminded that formation of trigonal δ polymorph involves both propylenic sequences and comonomeric units together, these being included in the trigonal δ lattice, in contrast to the other ordered structures, where the comonomers act as defects, excluded from the lattice.

Anyway, comonomers are considered as microstructural defects by the macrochains in copolymers and terpolymers. Figure 6 shows the variation of indentation modulus with the content in different triads, XPS, PPX and PPP (X = 1-pentene or 1-heptene, P = propylene) for the slowly crystallized specimens. In general, comonomer units are isolated, as shown in Table S1 of Supporting Information. Compositional

triads are growing from around 4 to 16 mol % in the global comonomer content. The T16 specimens reach a value of 21 % of the XX sequence. Two trends are observed in these compositional triads: at the lower overall composition, up to 10 mol%, the PPP change is slightly lower than the variation found for the PPX and XPX triads. The XPX sequence exhibits the highest slope because it involves segments enriched in comonomers, which contribute to accelerate the loss of mechanical properties since they act as defects into the crystalline structure. Another trend, well different, is found at total comonomers composition above 10 mol % because of the capability of developing trigonal δ lattice in an amount and perfection good enough, fact that contributes to enlarge the mechanical performance. There are no significant differences between these slopes because the partial incorporation of the comonomer into the trigonal δ polymorph could not distinguish between the compositional sequences. This fact could suggest that 1-pentene comonomer or 1-pentene-enriched ratio is easily incorporated, independently of the distribution of the triad into the trigonal δ lattice because the comonomer participates in the crystalline structure and it does not act as a defect.

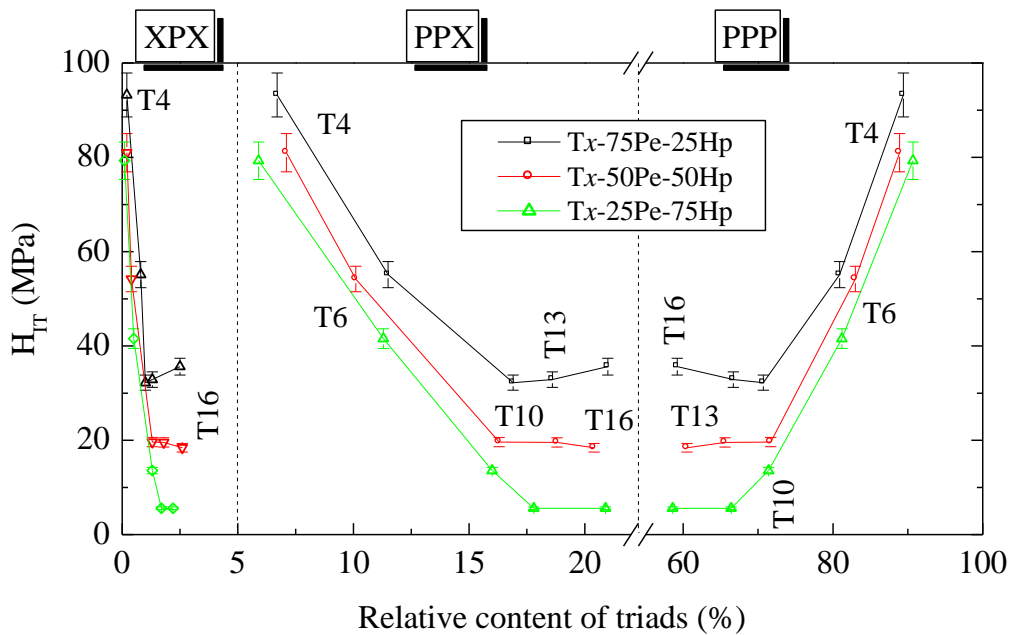


Figure 6. Dependence of indentation hardness upon the content of indicated compositional sequences (X = 1-pentene or 1-heptene, P = propylene) for the distinct terpolymers crystallized slowly from the melt.

Another important feature deduced from Figure 6 is the opposite trend between curves from PPP sequences and those exhibited by the PPX and XPX triads. This is related to the favorable contribution of PPP triads to improve crystalline details, since the higher they are, the larger chain regularity exists, and, consequently, the better mechanical response is attained. Therefore, the knowledge of molecular features can be very useful to predict the mechanical behavior of this kind of materials.

The rheological response is another important aspect to attain a more complete knowledge of the global viscoelastic performance in polymeric materials, in this case obviously in the molten state. Figure 7 shows master curves for the storage (G') and loss (G'') moduli for the Tx-50Pe-50Hp series, taken as representative of these terpolymers since the rheological behavior found in the other two sets with different ratios here analyzed is quite analogous. The reference temperature has been 140 °C, used to validate the time-temperature superposition principle (TTS) at different temperatures. Its accomplishment indicates that thermo-rheological simplicity is found for all these specimens.

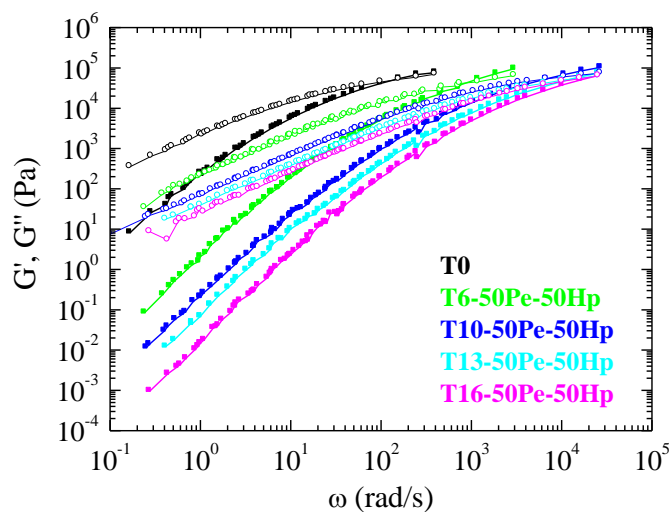


Figure 7. Variation of storage (solid symbols) and loss moduli (open symbols) with frequency for the homopolymer and the Tx-50Pe-50Hp specimens at 140 °C as a reference temperature.

Moreover, it can be also easily deduced from Figure 7 that incorporation of comonomers reduces both storage and loss moduli compared with those exhibited by

the polypropylene homopolymer. This fact was associated with the effect of adding short-chain branching on the viscoelastic behavior of the propylene³⁹. These differences could be also ascribed to changes in molecular weights because incorporation of comonomers leads to transfer processes during polymerization (see values in Table 1) and might also trigger changes in topology^{19,35}.

Table 2 reports values of the moduli and frequencies found in the crossover point ($G' = G''$)⁴⁰. The vertical shifts of modulus crossover point apparently reflect differences existing between distinct compositions, like entanglement molecular weight. These values can be useful for explaining the effects of long chain branches and PDI on the polymeric rheological properties but here length of side chains is always the same and PDI is almost unchanged because a metallocene catalytic system has been used during the synthetic procedure and all the values of PDI are around 2 (see Table 1)..

Table 2. Values of modulus and frequency in the crossover point $G' = G''$ (ω) for the homopolymer and the different Tx-50Pe-50Hp.

Sample	Total content in comonomers (mol %)	$G' = G''$ (Pa)	Angular frequency (rad/s)	M_w (kg/mol)
T0	0.0	49000	130	223
T6-50Pe-50Hp	6.0	42400	870	104
T10-50Pe-50Hp	10.1	53400	6840	80
T13-50Pe-50Hp	13.1	52600	12640	74
T16-50Pe-50Hp	15.4	59900	22000	71

The horizontal shifts of the crossover point describe, otherwise, a significant increment of the angular frequency, associated with the reduction in the molecular weight and with the increase in the comonomers content. Then, isotactic polypropylene exhibits a value of 130 rad/s and T16-50Pe-50Hp reaches 22000 rad/s. A crossover point that appears at low angular frequency is associated with high values in molar mass⁴⁰. The increase of counits into the polymeric architecture increases the polymer elasticity, thus leading to higher angular frequencies. These results are in agreement to those previously reported for 1-hexene copolymers where the angular frequency of

crossover point increased sensitively with an increase in the polymer density in long chain branches owing to the greater enhancement of polymer elasticity⁴¹.

The effect of presence of comonomers may be associated with changes in the absolute value of the complex viscosity, $|\eta^*|$, as displayed on the left plot of Figure 8. Incorporation of counits leads to a reduction of viscosity within the frequency region analyzed. Again, diverse factors, as variation of molecular weight or alteration of topology, could explain these important dynamic viscosity changes measured at low frequencies. An important change is also exhibited in the right plot of Figure 8, where dependence of the dynamic viscosity on molecular weight for the Tx-50Pe-50Hp terpolymers is compared with that estimated in copolymers synthesized with the same catalyst and based on propylene and 1-pentene, cPPE, and those incorporating 1-heptene, cPHp, as comonomer. It is clearly noticeable that the behavior of the terpolymers is rather similar to that shown by the cPHp copolymers. At a given molecular weight, the complex viscosity values vary significantly depending on the length of comonomer unit. This conclusion can be attained since the catalyst is the same for all of the different samples, terpolymers and copolymers in Figure 8b.

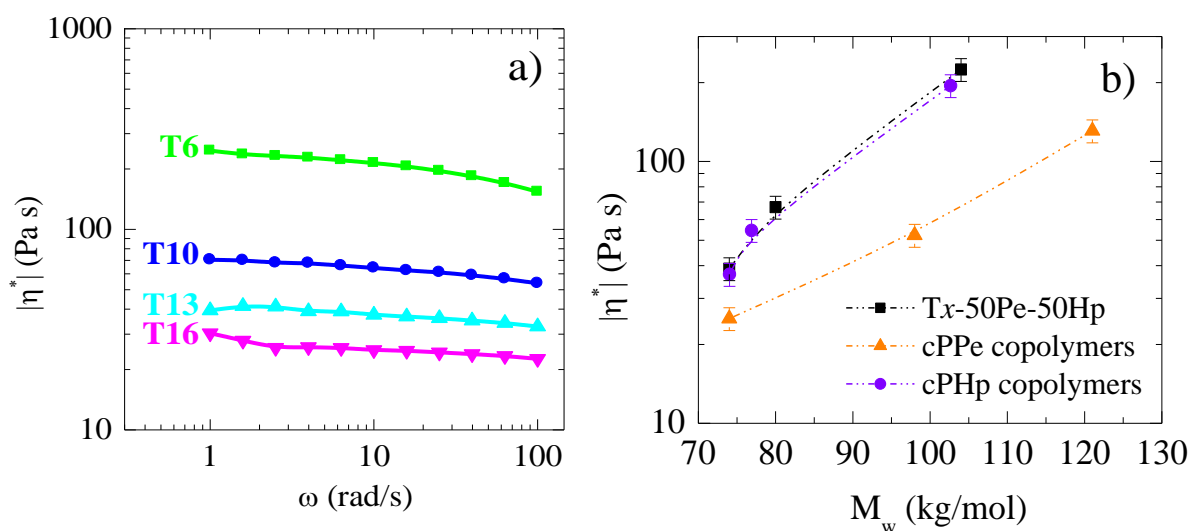


Figure 8. (a) Frequency dependence of dynamic viscosity at 140 °C for the terpolymers with distinct global content in comonomers at the Pe50-Hp50 ratio. (b) Dependence of absolute value of the complex viscosity at 5 rad/s on weight average molecular weight for Tx-50Pe-50Hp terpolymers and their parent cPPE and cPHp copolymers.

Moreover, the zero shear-rate viscosity has been estimated according to literature^{42,43} and represented versus M_w in Figure S2 of Supporting Information. As expected, the zero shear-rate viscosity increases as molecular weight is raised. A linear function was reported⁴³ from the plot of $\log \eta_0$ versus $\log M_w$ in linear polyethylenes with different molar mass distributions in a very broad molecular weight interval above the critical molar weight value. That result pointed out that the η_0 - M_w correlation was independent of the molar mass distributions. Figure S2 shows also a linear relationship between η_0 and M_w , but a unique trend is not observed. Lines of similar slopes are attained although the one for the cPpE copolymers is slightly shifted. Molar mass distributions cannot be considered as a variable in these polypropylenic derivatives, as deduced from Table 1 for the Tx-50Pe-50Hp terpolymers and from literature^{19,35} in the cPpE and cPHp copolymers. Thus, branching length seems to be a significant parameter.

Figure 9 represents the corresponding Van Gorp-Palmen plots, which are a valuable tool to analyze changes caused within polymeric chains independently of molecular weight. Their results show effects of polydispersity and differences in topology, *i.e.*, if the short chain branching affects the rheological behavior^{44,45}. In this sense Figure 9 displays that the behavior found in the Tx-50Pe-50Hp terpolymers is rather similar to that exhibited by the iPP homopolymer in the whole interval of $|G^*|$ studied. Consequently, these short chain branches do not seem to induce changes. These results agree with those observed in other copolymers^{39,44,45}.

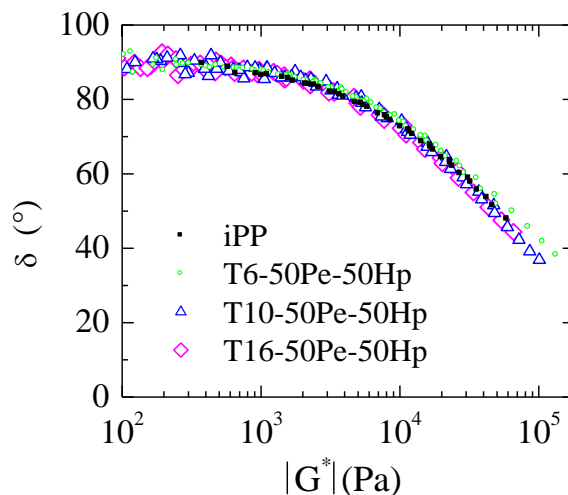


Figure 9. Phase angle δ as a function of the complex shear modulus $|G^*(\omega)|$ at 140 °C for the homopolymer and the terpolymers with distinct global content in comonomers at the 50Pe-50Hp ratio.

A thorough analysis about the influence of the contribution of propylene units was carried out because changes in the molar mass were not able to explain the important variations in viscosity. Evaluation of the ratio between the experimental viscosity (η_{polymer}) and the zero-shear-rate viscosities for equivalent polypropylenes with the same molar mass than the corresponding copolymer ($\eta_{\text{linear-equivalent}}$) exhibits a drop with the presence of comonomer content, as seen in Figure 10a. The determination of $\eta_{\text{linear-equivalent}}$ was carried out according to Palza *et al.*³⁹ and previous propylene rheological studies⁴⁶. That behavior is similar to the one observed in Figure 10a for the cPPE and cPHp copolymers based on propylene with 1-pentene or 1-heptene. Thus, importance of the type of the comonomer can be inferred. These differences could be associated with the incorporation of the comonomer along the propylene backbone, where the flexibility of polymer chain is modified.

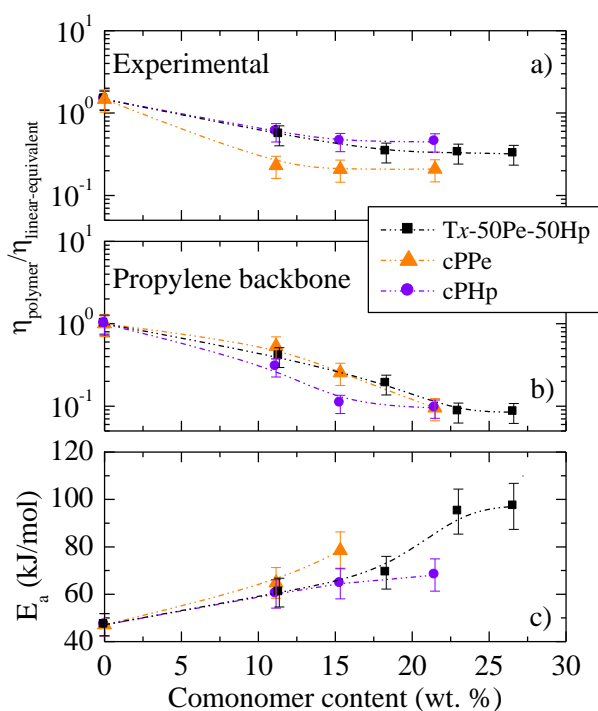


Figure 10. Variation with the content in comonomers of: a) experimental ratio between the viscosity of the terpolymers (or corresponding copolymers); b) the viscosity of the equal molar mass homopolymer, and c) activation energy of flow (E_a) for the Tx-50Pe-50Hp materials and some cPPE and cPHp copolymers.

Furthermore, the $\eta_{\text{linear-equivalent}}$, calculated according to the relation between the viscosity and the propylene backbone, is displayed in Figure 10b. The behavior is rather similar to the experimental one, so that the propylene backbone length can explain the decrease in viscosity because of the comonomer transfer reactions that occur during the polymerization. The differences between comonomers cannot be detected since the viscosity values exclusively consider the propylene units and they do not distinguish between types of comonomer.

Estimation of activation energy of the flow (E_a) is a valuable approach to analyze also the effect of the comonomer content. This can be deduced from Arrhenius equation if the TTS principle is validated^{47,48,49,50}. The fits to the Arrhenius behavior attained for the different materials analyzed are represented in Figure S3 of Supporting Information. The activation energy of flow is related to the restrictive force exerted by the polymer chains that need to be overcome for the melt to flow. Figure 10c shows E_a values for the different compositions in comonomers in the Tx-50Pe-50Hp terpolymers, cPPE and cPHp copolymers as well as for the isotactic polypropylene. It can be observed that E_a increases with the comonomer content for the different materials. This fact can be ascribed to changes in the mobility of the polymeric macrochains where the presence of comonomers hinders the overall chain mobility.

Studies of the flow activation energies are not found in open literature for these terpolymers and are rather scarce in copolymers based on propylene, since results are essentially related to ethylene based copolymers. Vega et al.⁵¹ observed in poly(ethylene/1-hexene) copolymers with narrow molecular weight distribution activation energies higher than those for linear polyethylenes. Later, Stadler et al.⁵⁰ detected an increment of the activation energy with the side-chain content for ethene- α -olefin copolymers and PP. This was ascribed to a hindrance in mobility within the chains because of the comonomer incorporation. Consequently, the increase in activation energy was due to the concentration of side chains and the side chain length itself. There was not observed a dependence on the comonomer length probably because of the limited range of materials analyzed⁵⁰. Kessner et al.⁵² described an increase of activation energy with the length of the side branches for poly(ethylene-butene), poly(ethylene-hexene) and poly(ethylene-octene) copolymers. They commented that the type of comonomer and the length of the chain defined the resistance to flow.

A linear correlation of E_a with the 1-heptene weight (wt.%) composition is obtained for the 1-heptene copolymers (such good correlation is not achieved by exchanging the global wt.% composition for the mol % content). Similar linear dependence of E_a as a function of the wt. % content has been described for diverse ethylene copolymers⁵⁰ in a wide range of compositions, as aforementioned. On the contrary, cPPE copolymers and the Tx-50Pe-50Hp terpolymers do not exhibit this linear trend at high contents in comonomers, as observed in Figure 10c. These results could be associated with the fact that rheological characterization is able to distinguish between the length of the distinct counts, as Kessner et al.⁵² showed in copolymers of ethylene. Consequently, material density might have a great importance¹⁵. These density changes can be responsible for a better thermal stability in cPPE copolymers and terpolymers at high compositions. The opposite trend associated with the length of the chain reported for copolymers with ethylene⁵² could support the hypothesis of density changes according to the differences between the main comonomers: ethylene and propylene. Anyway, the results on the influence of the size in the lateral branches are not conclusive due to the error associated with these estimations (Figure 10c).

Conclusions

The complex polymorphic behavior exhibited by poly(propylene-*co*-1-pentene-*co*-1-heptene) terpolymers is dependent on crystallization rate and molecular details. Two important molecular characteristics are the overall content in comonomers and the ratio between the 1-pentene and 1-heptene comonomers.

Compositional sequences (and other microstructural features) are of great importance in the final properties of these terpolymers where longer PPP triads clearly implies the enhancement of the crystalline details and, consequently, of the mechanical response. The presence of PPX and XPX triads leads to a loss of mechanical properties because these units act as compositional defects into the crystalline structure. Development of the trigonal δ lattice changes this trend if 1-pentene is the major comonomer since its role is completely different: from being an excluded defect to become a constituent of the crystalline trigonal δ lattice, where that comonomer is included. The 1-heptene units, however, behave always as a defect, leading to a reduction in crystallinity and in the mechanical performance.

At high enough comonomer content, and especially for the ratio 75Pe/25Hp, the different mechanical parameters analyzed in the terpolymers show a clear change of tendency, these mechanical magnitudes improving rather significantly as the trigonal δ lattice is developed.

Rheological characterization has allowed studying the influence of the molecular weight, propylene backbone length, comonomer content and the kind of counit on the molten state characteristics. Microstructural features affect the dynamic viscosity results and variation of molecular weight, comonomer content and topology of samples explain the decrease of their values.

The activation energy of the flow, E_a , increases with the comonomer content due to the changes of mobility in the polymeric macrochains because counits hinder the overall capability of motions. This parameter shows a linear dependence for cPHp copolymers, but the linear correlation is not fulfilled in the case of cPPE copolymers and Tx-50Pe-50Hp terpolymers at high comonomer contents. This experimental finding is ascribed to the ability of that parameter of distinguishing between distinct counits. The density changes could play an important role according to the stability obtained for cPPE copolymers and terpolymers at high compositions regarding to cPHp.

A new perspective for the copolymers and terpolymers able to develop the trigonal δ lattice in the solid state is now opened since they exhibited good rheological properties and thermal stability at high comonomer contents as well as an appropriate $\eta_{\text{polymer}} / \eta_{\text{linear-equivalent}}$ relationship.

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