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Synthesis and Characterization of Ethylene/Propylene Copolymers in the Whole Composition Range

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Summary: The incorporation of comonomer molecules in the backbone of a homopolymer can influence the final properties of the material, decreasing its crystallinity and the melting and glass transition temperatures, and increasing its impact resistance and transparency. In the present work, ten ethylene/propylene copolymers have been synthesized using a supported metallocene catalytic system covering the whole composition range. Any desired composition was obtained by controlling the feed composition during the reaction. These synthesized copolymers have been characterized by different techniques in order to study the effect of the comonomer incorporation onto their final properties. When the comonomer content is low, the behaviour of the copolymer is similar to that of the corresponding homopolymer. Nevertheless, if the comonomer content increases, the copolymer becomes more amorphous (low crystallization temperature and soft XRD signals) and easily deformable, reaching a behaviour close to that corresponding to an elastomeric material. In order to corroborate these results the samples have been characterized by TREF and GPC-MALS. TREF analysis showed that copolymers containing less than 10% and more than 80% of ethylene are semicrystalline, with elution temperatures typical of this kind of polymers. Molecular weights are higher for homopolymers and they decrease as the comonomer concentration increases, whereas the polydispersity index keeps almost constant at the expected value for this kind of samples.

Keywords: ethylene/propylene copolymers; gel permeation chromatography (GPC); metallocene supported catalysts; multiangle light scattering (MALS); temperature rising elution fractionation (TREF)

Introduction

The thermoplastic polymer production with elastomeric properties has been the focus of scientists and manufacturers in the last decade.[1] Polypropylene (PP) is a semicrystalline polymer widely used in packaging, textile, and automobile industries because of its good processability and properties. Nevertheless, its applications are limited because PP toughness is low, especially at room and low temperatures.[2] This is the reason why the copolymerization products of propylene with small amounts of ethylene are of practical importance since they allow to control the crystallization processes.[3]

The development of metallocene catalyst technology has provided a rich set of new copolymers materials with well-defined microstructures.

In order to synthesize these products, the combination of single site catalysts with methylaluminoxane (MAO) as cocatalyst for olefin polymerization throughout the last two decades has been the subject of intensive research, as a result of high

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catalytic activity and versatile control of polymer structure and properties via manipulation of the ligand sphere surrounding the metal atom[4] allowing the preparation of homogeneous products covering a wide range of copolymer microstructures and properties.[5]

It is of great importance[6] to immobilize the homogeneous metallocene catalysts on inorganic carriers[4] for applying them to gas or slurry phase[7] polymerization processes because supported catalysts can avoid reactor fouling, allow the reduction of the amount of cocatalyst during the reaction,[8] and control the morphology of the produced polymer more easily.[9] The anchorage of the catalytic system can be carried out by several well-known techniques.[10,11]

In addition to the catalytic system used, the properties of ethylene-propylene copolymers also depend on comonomer content (composition) and its distribution, which, in turn, essentially depend on polymerization conditions.[12] Such conditions have to be kept constant over the entire polymerization period,[3] with a good control of the feed monomer ratio to obtain a copolymer with a defined composition in a semi-batch reactor.

The influence of these properties can be studied by analyzing the samples through different techniques. The use of gel permeation chromatography (GPC) with light scattering detector (MALS) provides quantitative information on molecular weight distribution and conformation of the chains; this technique has been studied intensively in recent years,[13–15] but there are not publications for ethylene/propylene copolymers. The behaviour of semicrystalline copolymers can be studied using different techniques. Differential scanning calorimetry (DSC) allows the measurement of transition temperatures and crystallinity percentage. Such crystallinity is related with the signals obtained by X-ray diffraction (XRD). Temperature rising elution fractionation (TREF) yields the qualitative estimation of chemical composition distribution (CCD) which is also related to crystallinity.

In this work, the catalytic system MAO/ rac-$Me_2Si[2Me\text{-}Ind]_2ZrCl_2$ was impregnated on a thermally-treated silica support. This catalyst was used in ethylene-propylene copolymerization reactions. The polymerization processes was carried out with a variable and controlled feed of the monomers which allowed the synthesis process to take place in a wide range of relative concentration of the different monomers in the solution.

In order to check the effect of the copolymers composition on their properties, the copolymers were analyzed by X-ray diffraction (XRD), differential scanning calorimetry (DSC), ^{13}C nuclear magnetic resonance (^{13}C-NMR), scanning electron microscopy (SEM), temperature rising elution fractionation (TREF), and gel permeation chromatography coupled to multi-angle light scattering (GPC-MALS).

The results show how the behaviour of the copolymers is typical of an elastomeric material when the percentage of both monomers is similar, while they are very close to the homopolymer behaviour when the content of one of the monomers is much higher than the other.

Experimental Part

Synthesis

The chemicals used were ethylene (Air Liquide S.A., polymerization grade 99.99%), propylene (Air Liquide S.A., polymerization grade 99.99%) and n-heptane (Scharlab S. A., 99%) as solvent. The metallocene cata lyst used was rac-dimethyl-silylbis (2-methylindenyl) zirconium dichloride (Boulder Scientific Company) supported on silica (Grace Davidson) modified with methylaluminoxane, MAO (Witco, 30 wt% in toluene) and the cocatalyst added to the reactor was triisobuthylaluminium, TIBA (Witco, 1 M in toluene).

All the air-sensitive compounds were handled in a dry nitrogen atmosphere inside a glove box and by using Schlenk techniques.

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The conditions of the support pretreatment, the determination of the hydroxyl content and the physical properties of the silica in these conditions were reported previously.[16]

The immobilization method was carried out in two steps: 1) reaction between 1 g of silica material and MAO (30 wt % in toluene) solution to a volume ratio of three, at room temperature and 30 rpm in a stirred vessel; 2) anchorage of the metallocene on 2 g of the silica/MAO sample previously synthetized. The catalyst (rac-$Me_2Si[2MeInd]_2ZrCl_2$) was dissolved in 75 mL of toluene and this mixture was kept at room temperature under stirring (900 rpm) for three hours.

Copolymerization reactions were carried out in a 1 liter Büchi stirred glass reactor which allows the control of the temperature during the reactions at 70 °C. The solvent (400 cm^3 of n-heptane) was saturated with an ethylene/propylene gas mixture previously to the copolymerization reaction. The Al/Zr molar ratio used in all the reactions was 400.

Ethylene and propylene were deoxygenated and dried through columns containing R-3/15 BASF catalyst, alumina and 3 Å molecular sieves before entering the polymerization reactor. The monomers were fed in order to keep the reactor pressure at 5 bar during the entire copolymerization.

The ethylene/propylene ratio in the gas phase (C_2/C_3) was kept constant. Real-time monitoring of the gas phase composition was performed by means of a Micro-GC (MGC supplied by Varian). The reactions were carried out during 30 minutes, and finally, the copolymers were precipitated by acidic methanol, washed and dried in vacuum.

Characterization

Copolymers synthetized were observed by SEM (XL30 ESEM) in order to study the replication phenomenon and the external morphology. Crystallinity was analyzed by powder X-ray diffraction (Philips X'PERT MPD diffractometer using Cu K_α). Melting points and glass transition temperatures were measured by differential scanning calorimetry (DSC, 822^e METTLER TOLEDO).

^{13}CNMR spectra were recorded in deuterated 1,1,2,2-tetrachloroethane and 1,2,4-trichlorobenzene at 100 °C using a BRUKER AC300 spectrometer and the final composition of the copolymers was calculated by ^{13}C-NMR triad distribution using known methods.[17,18]

GPC-MALS is a combined method of gel permeation chromatography (Waters ALLIANCE GPCV 2000) with multi-angle light scattering (DAWN EOS 18 angle light scattering photometer, Wyatt Technology). Polymer conformation can be obtained by GPC-MALS by direct application of the Zimm-Stockmayer approach.[19] Solvent was 1,2,4-trichlorobenzene (TCB) at a flow rate 1 mL/min and the temperature was 145 °C. At each chromatographic slice, both the absolute molecular weight (M_w) and radius of gyration (R_g) can be obtained.[20] The refractive index increment d*n*/d*c* value for these copolymers in TCB and 145 °C is 0.101 mL/g.[21]

Chemical composition distributions were measured by TREF 200 (Polymer Char) using o-dichlorobenzene (oDCB) as a solvent. In the elution step oDCB flowed through the column at a constant flow rate of 0.5 mL/min with a temperature profile from 35 °C to 140 °C at a constant rate (1 °C/min). The concentration of polymer was measured by a two-channel infrared detector.

Results and Discussion

Table 1 lists the copolymers obtained. They were named EP followed by an integer number related to the molar percentage value of ethylene. As can be seen, in the synthesis procedure the gas phase composition C_2/C_3 was controlled in the range 0.010 to up to 100 and that lead to copolymers in the whole composition range.

The external morphology of the samples was observed by SEM. Three SEM micrographs for different copolymers are shown in Figure 1. When supported catalytic

Table 1.
Obtained copolymers.

Copolymer	C_2/C_3 (mol/mol) gas phase composition	% E molar[a)]
EP3	0.010	3.4
EP6	0.013	5.8
EP13	0.029	12.7
EP21	0.126	20.5
EP31	0.390	30.4
EP59	0.970	59.0
EP81	5.046	80.7
EP87	6.740	86.7
EP94	19.000	93.8
EP99	107.69	99.0

[a)] Copolymer composition obtained from triad distribution as $E = EEE + EEP + PEP$.

systems are used, it is expected that the polymer particles replicates the shape of the support.[22] This behaviour can be seen in Figure 1.a and 1.b, with independent particles distribution, for copolymers where one of the monomers is the main component in the backbone of the chain. However, when the percentage of both monomers in the copolymer chain is similar, the final product does not present a defined morphology, as can be seen in the SEM image corresponding to the EP59 sample (Figure 1.c). This characteristic is typical of polymers synthesized with a dissolved catalytic system.[23] Such different behaviour could be related to the amorphous character of the material: EP59 is elastomeric and the support particle can not be broken when the polymerization takes place.

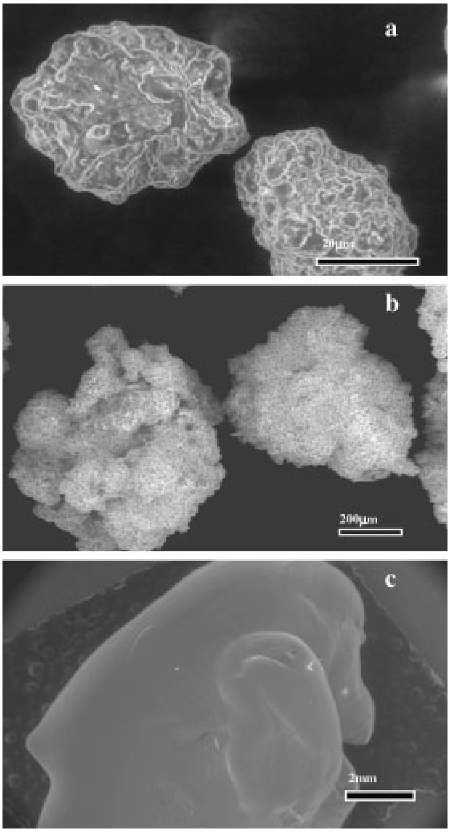

Figure 1.
SEM micrographs for three different copolymers (a: EP99, b: EP3, c: EP59).

The crystallinity of the synthesized samples has been studied qualitatively by XRD. The results are shown in Figure 2 for all the copolymers. It is possible to check how for copolymers EP99 and EP3 the typical peaks for polyethylene and polypropylene, respectively, are obtained. When the propylene is the monomer with higher percentage (Figure 2, EP3), it is possible to distinguish four fundamental signals in the spectra for 2θ values of 14.1, 16.9, 18.6, and 21.7, associated to the α or monoclinic modification of iPP.[24]

The peaks are wider when the ethylene content increases because the second monomer inclusion introduces higher disorder into the lattice. The maximum disorder is found for the EP59 copolymer, where it is impossible to distinguish any characteristic peak of the homopolymers.[12] On the other composition limit, when the ethylene content is larger, two signals can be observed which could be related with the orthorhombic[25] phase for 2θ values of 21.5° and 23.9°, respectively.

Figure 3 shows the results obtained by DSC for the glass transition temperature (T_g) and the melting temperature (T_{m2}) in function of the ethylene content. It is clear that values for these temperatures are lower for copolymers close to 50/50 ethylene/propylene ratio. This is related to the considerable decrease of crystallinity, since the crystal domains which are being formed

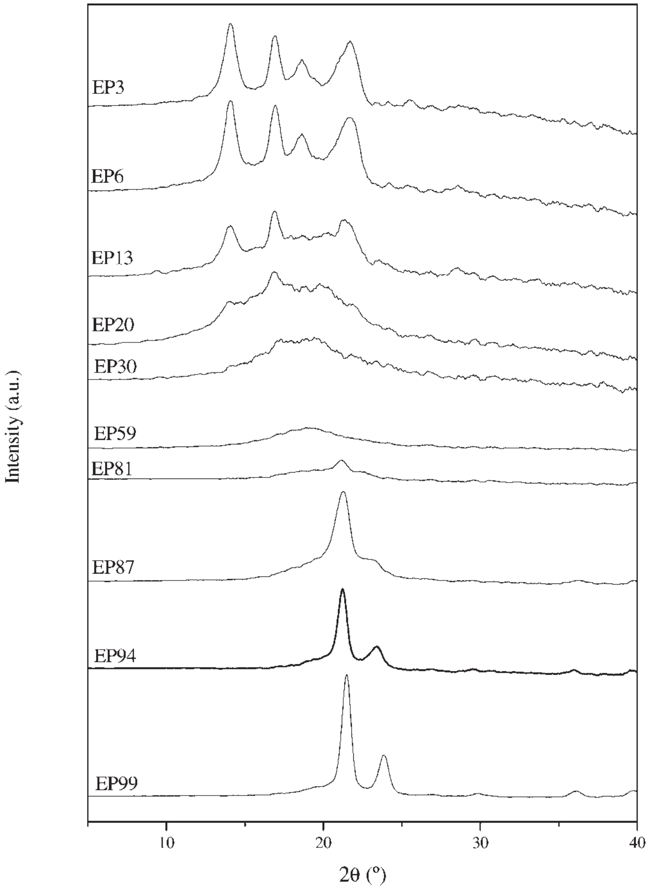

Figure 2.
Qualitative comparison of the crystallinity determined by XRD for copolymers with different percentages of ethylene.

are smaller because the increase of irregularities in the macromolecular chains.

From DSC results, values for the enthalpy of this second melting of the copolymers are obtained. It is possible to determine the percentages of crystallinity by relating such values to those for the corresponding homopolymers (291.6 J/g for polyethylene[26] and 207.1 J/g for polypropylene[27]). The calculated values are listed in Table 2 and corroborate how the copolymers with close to 50/50 ethylene/propylene ratio are amorphous materials, in agreement with the characterization by XRD.

From the experimental triad values for the copolymers determined by ^{13}C-NMR, it is possible to calculate the parameters $\overline{n}_E$ and $\overline{n}_P$, which represent the relative average number of ethylene and propylene units in the copolymer chain, respectively, and they give information about the distribution of comonomers along the copolymer chain. The values calculated for $\overline{n}_E$ and $\overline{n}_P$ are also listed in Table 2 and they can be related directly to the crystallinity obtained by DSC analysis. It can be concluded that, in the heterogeneous copolymers in the conditions of the reactions, when a chain contains 5 units of the same consecutive monomer, it crystallizes.

Another set of experimental properties related to crystallinity is the elution temperature (T_e) and the percentage of soluble fraction (SF %) determined by TREF.

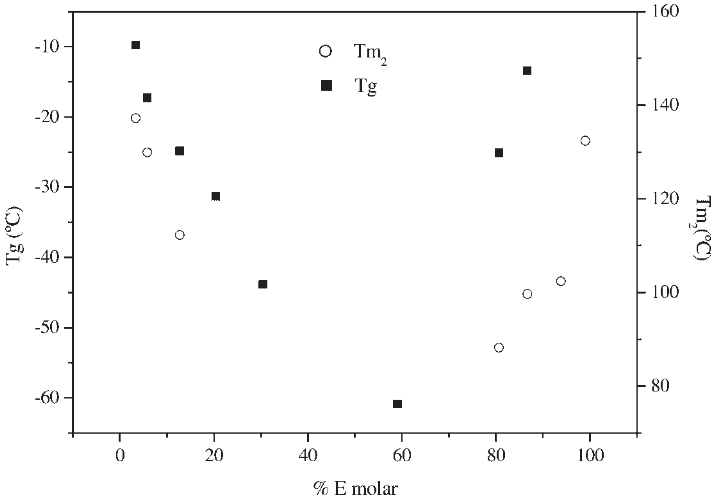

Figure 3.
Glass transition and second melting temperatures for the copolymers in function of the ethylene content (% E molar).

Figure 4 shows the results obtained by TREF as a function of the ethylene comonomer content and Figure 5 shows the TREF profiles for these copolymers.

This technique was limited to copolymers with very different comonomer contents, since in the middle range of comonomer content an amorphous copolymer was reached. In this case, the limit is lower than 10% molar of ethylene and higher than 80% molar of ethylene. For copolymers with low ethylene content (EP3 to EP13), values for T_e decreases faster with % E molar than in the high ethylene content (EP81 to EP99). This should be due to the fact that the crystallinity of copolymers with high propylene content is influenced by the composition and sequence distribution, besides tacticity. This make the study of the chemical composition distribution of polypropylene copolymers more complicated. The study of both tacticity and composition distribution should be completed with other techniques like FTIR. For low and high comonomer contents, the *SF* is low too, while for intermediate comonomer contents the *SF* is very high, as expected.

Table 2.
Crystallinity and $\overline{n}_E$ and $\overline{n}_P$ values for the copolymers.

Copolymer	Crystallinity (%)[a]	$\overline{n}_E$	$\overline{n}_P$
EP3	38.9	1.05	30.06
EP6	35.3	1.20	20.42
EP13	19.0	1.15	7.88
EP21	–	1.14	4.51
EP31	–	1.25	2.85
EP59	–	2.07	1.41
EP81	18.1	4.64	1.14
EP87	28.2	6.67	1.12
EP94	37.5	15.00	1.10
EP99	51.1	81.84	1.00

[a] Calculated from the second melting point.

In Table 3 the weight average molecular weight ($\overline{M}_w$) and the polydispersity index ($\overline{M}_w/\overline{M}_n$) of the copolymers by GPC and GPC-MALS are shown.

$\overline{M}_w$ and $\overline{M}_w/\overline{M}_n$ values obtained by GPC are higher than the ones obtained by GPC-MALS. The $\overline{M}_w$ values are dependent on comonomer content, showing the lowest values from 20 to 60%E molar. The polydispersity index is approximately constant, as expected for this single-site catalyst.[28]

The use of a multiangle light scattering detector allows the evaluation of both the molecular weight and the mean radius of gyration (R_g), for each slice of the size exclusion chromatogram. The dependence

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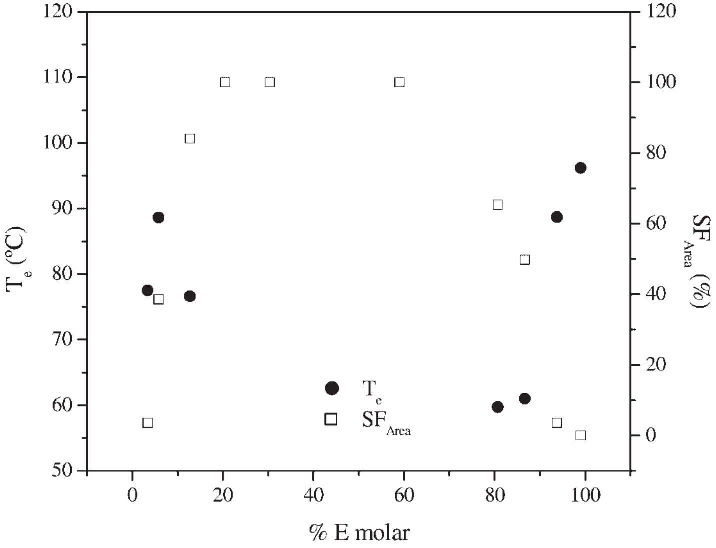

Figure 4.
Influence of comonomer content on TREF elution temperature and percentage soluble fraction.

of R_g on molecular weight is established by the scaling law $R_g = Q \cdot M_w^q$.[29] Figure 6 shows the plot of R_g *versus* M_w obtained for the copolymers that were shown in Figure 1, together with values for polyethylene (NBS 1475) and polypropylene (PP isotactic), taken as reference.

The slope of the plot provides the q coefficient which is related with the shape of the chain. The results obtained for the parameter q for all the samples studied are shown in Table 4. Values of q in the range 0.5 to 0.6 are typical for linear random-coil chains.[30]

A value of $q = 0.54$ was obtained for both homopolymers, thus showing a typical random coil in 1,2,4-TCB. However, the presence of comonomer decreases the value

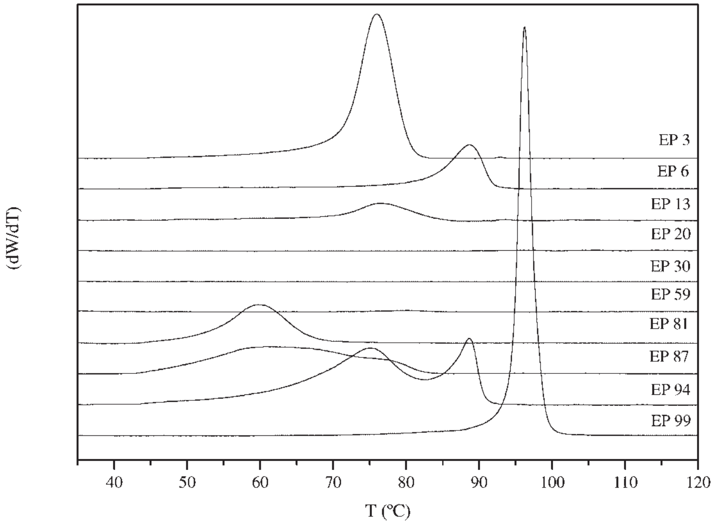

Figure 5.
Influence of comonomer content on TREF profiles.

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Table 3.
Molecular weight and polydispersity index obtained by GPC and GPC-MALS.

Samples	GPC		GPC-MALS	
	$\overline{M}_w$ (g/mol)	$\overline{M}_w/\overline{M}_n$	$\overline{M}_w$ (g/mol)	$\overline{M}_w/\overline{M}_n$
EP3	112387	2.049	95 900	1.664
EP6	115940	2.215	98 270	1.780
EP13	86273	2.092	73 490	1.658
EP21	71163	2.005	57 450	1.687
EP31	61636	2.084	49 360	1.691
EP59	68752	2.289	54 470	2.001
EP81	128611	2.760	98 910	2.266
EP87	151595	2.647	11 8500	2.213
EP94	268488	2.780	20 1500	2.361
EP99	303465	3.382	22 7000	2.530

Table 4.
Values of *q* for ethylene/propylene copolymers.

Samples	q
PP[a)]	0.54
EP3	0.51
EP6	0.50
EP13	0.47
EP21	0.47
EP31	0.42
EP59	0.47
EP81	0.47
EP87	0.50
EP94	0.50
EP99	0.53
NBS 1475[b)]	0.54

[a)] polypropylene isotactic (Sigma-Aldrich);
[b)] polyethylene linear reference (NBS).

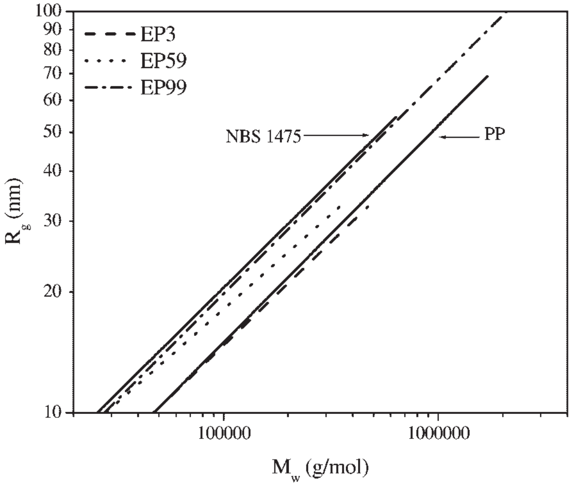

Figure 6.
Relationship between radius of gyration and molecular weight for some copolymers.

for the parameter *q*, reaching a value of 0.42 for copolymers with an ethylene molar percentage of 31%. This result shows how the presence of comonomers modifies the random coil structure of a homopolymer in the same way as the presence of long chain branching.

Conclusions

Good control system for the gas phase C_2/C_3 ratio in the polymerization process allows obtaining copolymers in the whole composition range. Different studies in function of composition have been carried out. SEM clearly shows the lack of morphology in copolymers close to 50/50 ethylene/propylene ratio, which could be related to the absence of crystallinity of those samples. DSC and XRD analyses show, for copolymers with low comonomer content, similar behaviour to that of the corresponding homopolymer, but when the comonomer content increases, the melting temperature and glass transition temperature decrease and the copolymer becomes amorphous. TREF analysis indicates that copolymers containing between 10% and 80% of ethylene comonomer are essentially amorphous,

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while copolymers with ethylene comonomer content out of this range are semicrystalline in the tested conditions.

GPC-MALS technique shows the dependence of M_w with comonomer content, showing a minimum in the intermediate position. The incorporation of comonomer also affects the shape (random coil) of the polymer in solution.

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