Polymer chain conformation of copolymers with different monomer size: ^{13}C NMR spectroscopy and MALS study

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ABSTRACT

Copolymer composition, distribution and molecular size of the comonomer influence the final properties of polymer materials. Such influence can be followed from the effect on the chain conformation in solution determined from the scaling law between radius of gyration and molecular weight.

In this work, several copolymers, with similar comonomer content (mol%) and distribution but with different comonomer size, have been studied. Ethylene/propylene (EP), ethylene/1-hexene (EH), ethylene/4-methyl-1-pentene (EMP) and propylene/1-butene (PB) with a comonomer content up to 20 mol% have been analyzed.

Characterization was carried out by nuclear magnetic resonance (^{13}C NMR spectroscopy) and by gel permeation chromatography with a multi-angle light scattering (GPC-MALS). Obtained copolymers present a relatively homogeneous comonomer sequence distribution along the chain, but ^{13}C NMR spectroscopy results revealed a more homogeneous comonomer chain distribution for EP copolymers, probably due to the monomer size.

MALS data were adequately treated with algorithm for self data reduction. No significant effect of overall composition was found and the MALS results were averaged for each kind of copolymers. Linear dependence of $\log(R_g)$ vs. $\log(n)$ according to regular scaling law was adequate for EP and PB samples along the whole analyzed range. However, a marked non-linearity was found for EH and EMP samples and, consequently, a unique linear regression of $\log(R_g)$ vs. $\log(n)$ was not recommended. A new method of regression including two different contributions was developed in this work and different values for the shape parameter (q) was obtained in function of molecular weight range.

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1. Introduction

Polyethylene (PE) and polypropylene (PP) constitute the two most highly consumed thermoplastics in the world [1]. Their growth can even be increased because copolymerization processes allow creating new materials with novel and enhanced properties [2].

In this sense, the production of this thermoplastic polymer with some elastomeric properties has been the focus of scientists and manufacturers in the last decade [3]. Thus, ethylene/propylene (EP) copolymers and ter-polymers with 1-hexene or 1-butene have become elastomers with important commercial applications.

Ethene/4-methyl-1-pentene (EMP) copolymers have been considered an interesting family of materials since the early 1970s because the properties of the polymers can be significantly influenced by incorporation of small amount of sterically hindered olefins. Indeed, the bulky branched substituent is expected to reduce polyethene density more effectively than linear α-olefins (e.g., 1-butene, 1-hexene, and 1-octene) at a similar level of incorporation [4].

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The properties of copolymers depend on many factors, such as molecular structure (composition, monomer distribution, molecular weight, molecular weight distribution, etc.) and supramolecular structure (morphology, crystallinity, entanglements, etc.) [5].

Gel permeation chromatography (GPC) with refraction index and viscosity detectors, is the most common way to determine the molecular weight (M_w) and molecular weight distribution (MWD), usually by means of the universal calibration that requires a set of standard mono disperse polymers. Because the interest of determining absolute and calibrant-independent values for the molecular weight averages and distributions, the use of multiple detection, mainly light scattering (LS) detector, methods in GPC has increased. When GPC separation is combined with a light scattering (LS) detector it offers additional advantages because the simultaneous determination of the molecular weight and the molecular dimension in solution in terms of the mean square radius of gyration (R_g) [6] and both magnitudes are measured in an absolute way [7–9].

In a previous work [10], a data analysis procedure was presented for the GPC-MALS (GPC-multi-angle light scattering) technique that allows the determination of both R_g and M_w magnitudes with their confident ranges. The method is based on statistical analysis and avoids the effect of the user experience.

Combination of R_g and M_w values allows the study of the molecular configuration of polymers in solution described by the scaling law relating R_g and M_w:

$$R_g = Q \cdot M_w^q \tag{1}$$

The q parameter is known as shape parameter, it reaches values of 0.33 for globular polymers and 0.5 for random coil polymers at theta conditions, but random coil polymers in good solvents can present values of q up to 0.6 [11]. Nevertheless, more complex systems were described where Eq. (1) is not valid over all the molecular weight range, thus requiring a nonconstant q parameter or several fits for different ranges in order to study the solution conformation of chains [12]. This behavior was also previously observed for ethylene–propylene copolymers obtained from different catalytic system. Heterogeneous comonomer distribution increases the probability to get a random coil conformation, but also the q values increase with molecular weight, and both variables have to be considered [13].

When copolymers are studied, the different monomer weight introduces a big effect on Eq. (1) for copolymers with the same polymerization degree that lead to very different Q values. In order to avoid such influence, the above scaling law can be modified to describe R_g against the number of monomer units in the chain (n). Thus, the new scaling law is [13]:

$$R_g = Q' \cdot n^q \tag{2}$$

where values of Q' are expected very similar and independent of the monomer structure, while q parameters should be very similar to those in Eq. (1).

In this work, the general data analysis procedure previously developed has been applied to several ethylene and propylene copolymers with 1-hexene, 4-methyl-1-pentene or 1-butene in order to analyze the influence of the comonomer size. Copolymers have been synthesized with similar comonomer content by using different catalytic system. Ethylene/1-hexene (EH) and ethylene/4-methyl-1-pentene (EMP) copolymers were prepared with the so called "constrained geometry" half-sandwich complex (CGC) while EP copolymers were prepared with a highly regio- and stereospecific metallocene catalyst. It is well known that both systems allow a homogeneous distribution of comonomer [14], but the open structure of CGCs permits an even easier incorporation of bulky α-olefins and ethylene macromonomers. For comparison purposes, a commercial propylene/1-butene (PB) was also included in the study.

Taking into account that the comparison is carried out in a similar range of total comonomer incorporation the only difference between them is the size in the comonomer molecule.

2. Experimental and data analysis

2.1. Copolymers samples

Ethylene/propylene copolymers were synthesized following a procedure developed in our laboratories and previously reported [15]. The supported metallocene catalyst used was rac-dimethyl-silylbis(2-methylindenyl)zirconium dichloride (Boulder Scientific Company) and the cocatalyst was triisobutylaluminium (TIBA, 1 M in toluene, supplied by Witco). Copolymerization reactions were carried out during 30 min in a 1-L Büchi® stirred glass reactor at 70 °C, 5 bar with an Al/Zr molar ratio of 400, n-heptane was used as solvent that was saturated with an ethylene/propylene gas mixture previously to the copolymerization reaction. Monomers were fed continuously during reaction through calibrated gas flow-meters.

Ethylene/1-hexene and ethylene/4-methyl-1-pentene were synthesized by Losio et al. according to Ref. [14]. In a typical polymerization reaction, a 0.25-L Büchi® autoclave equipped with a mechanical stirrer was charged under nitrogen with a solution of the proper amount of comonomer (4-methyl-1-pentene or 1-hexene), 7.5 mmol of dry methylaluminoxane (MAO) in anhydrous toluene (total volume = 90 mL). A 25-mL injector was charged with 10 mL of a solution of 10 μmol of [Me$_2$Si(η_5-Me$_4$Cp)-(η_1-N-^{t}Bu)TiCl$_2$], CGC catalyst, (Boulder Scientific Company) and 2.5 mmol of MAO in toluene (total MAO/Mt ratio = 1000). After thermal equilibration of the reactor system at 70 °C, ethylene was continuously added until saturation. When the equilibrium pressure (3.8 bar) was reached, the injector with the metallocene solution was pressurized with nitrogen, and the solution was injected into the reactor.

For comparison purposes, a third kind of copolymers were included. Propylene/1-butene copolymers (PB) were commercial polymers supplied by Aldrich. Copolymers with three different compositions were chosen PB6, PB9 and PB11 (reference numbers: 43,108-7; 43,109-5; and 43,110-9, respectively).

Table 1 lists the samples included in this study whose name was formed by the principal component (E: ethylene; P: propylene) followed by a comonomer acronym (H: 1-hexene; MP: 4-methyl-1-pentene; B: 1-butene), and a number according to the molar comonomer percentage.

Average molecular weights, M_w, and polydispersity indexes are also presented in Table 1. They were determined by gel permeation chromatography (GPC) by means of a Waters Alliance 2000 equipped with refractive index and viscometer detectors. The GPC separation was carried out by using two columns PLgel 10 μm Mixed-B, 300 × 7.5 mm and one PLgel 10 μm 10E6 Å, 300 × 7.5 mm, the temperature was set at 145 °C and the flow rate was 1 mL/min. The solvent was 1,2,4-trichlorobenzene (TCB) with 400 mg/L Irganox 1010 added in order to stabilize the polymer against oxidative degradation. The software used to these calculations was Empower Login 2002, from Waters.

Copolymer composition was determined by ^{13}C NMR spectroscopy as described in the next section.

2.2. ^{13}C NMR spectroscopy

Ethylene/1-hexene (EH) and ethylene/4-methyl-1-pentene (EMP) ^{13}C NMR spectra were acquired on a Bruker AVANCE 400 spectrometer, equipped with a SEX 10 mm probe with automatic matching and tuning, operating at 100.58 MHz, 103 °C, 14.30 μs as 90° pulse; 32 K data points, acquisition time 2.14 s, relaxation delay 18 s, 3 K transients. Proton broad band decoupling was achieved using bi_walz16_32 power-gated decoupling. Samples were dissolved in TCE (1,1,2,2-tetrachloroethane-d$_2$), and referenced to the internal HMDS (hexamethyldisiloxane) signal.

Ethylene/propylene (EP) and propylene/1-butene (PB) ^{13}C NMR experiments were acquired on a Bruker AVANCE III 500 spectrometer, equipped with a SEX 10 mm probe with automatic matching and tuning, operating at 125 MHz, 103 °C, 14.50 μs as 90° pulse; 32 K data points,

acquisition time 1.29 s, relaxation delay 3 s, 2 K transients. Proton broad band decoupling was achieved using walz 16 power-gated decoupling. Samples were dissolved in TCB (1,2,4-trichlorobenzene), with 1,2-dichlorobenzene-d$_4$ as deuterated reference.

Copolymer microstructure was determined at the triad level through ^{13}C NMR analysis. All the copolymers were analyzed according to the assignment of chemical shift previously reported: ethylene/propylene and ethylene/1-hexene according to Randall [16] and Kakugo [17], propylene/1-butene according to Zhang [18–20] and ethylene/4-methyl-1-pentene according to Losio et al. [14].

2.3. GPC-MALS

GPC Waters Alliance 2000 is combined with a multi-angle light scattering detector (MALS) DAWN EOS of Wyatt Technology. MALS technique is equipped with a laser at 690 nm and 17 multi-angle detectors. Temperature was also set at 145 °C. The DAWN EOS photometer was calibrated with toluene, and the detectors were normalized with a standard monodisperse polystyrene, PS, (M_w = 30 kg/mol), which was also used to determine inter-detector volume [15]. The standard software, ASTRA V 5.1.9.1, from Wyatt Technology, allowed on-line data acquisition of molecular weight and radius of gyration.

Differential refractive index increments, dn/dc, for the several copolymers were determined following a procedure previously described [21] by combining bibliographical values at several λ and values for the several copolymers with different compositions measured by the GPC refractive index detector. A constant dn/dc value of -0.101 mL/g was found for EP, EH and EMP samples while PB copolymers presented a slightly composition dependent dn/dc values, thus -0.094, -0.096 and -0.096 mL/g were used for PB6, PB9 and PB11, respectively.

Direct analysis of experimental R_g and M_w data is very difficult because those obtained by MALS technique are usual very disperse data. Such point was critical in this work because results obtained for EH and EMP samples were even more disperse than previous typical values. Fig. 1 displays analysis of EH10 as an example. In order to avoid such difficulty, the numerical method previously developed [10] was used in this work. Both, M_w and R_g, experimental values obtained from MALS were analyzed against elution time. An iterative procedure is carried out in four steps that automatically increases/decreases the number of involved data points according to a well established statistical procedure. As can be seen in Fig. 1, along the fitting procedure both parameters for the polynomial fitting function and the range where experimental data appears to be confident were obtained and final results are fully independent on the user.

3. Results

3.1. ^{13}C NMR spectroscopy

All copolymers were carefully examined through ^{13}C NMR analysis. For all the series of copolymers, the eight tri-
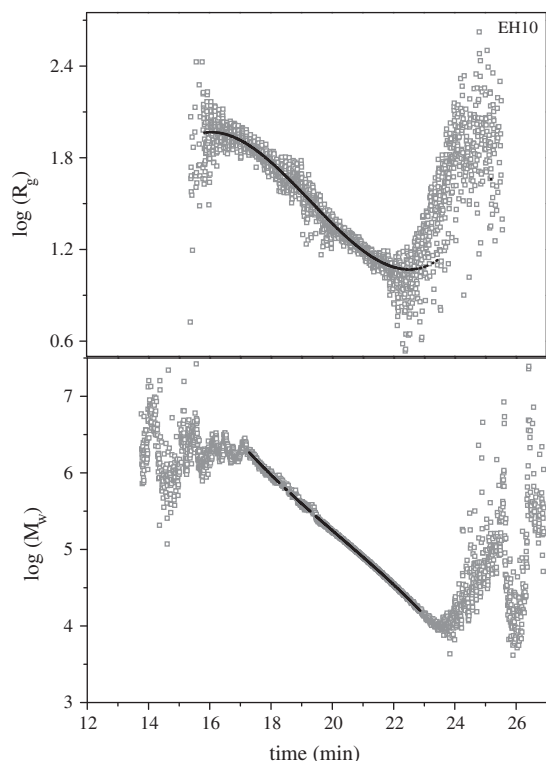
Table 1
Studied copolymers and values for their average molecular weight and polydispersity index determined by GPC.

Sample	M_w (kg/mol)	P.I.
EH0.5	364	5.29
EH2	237	4.04
EH10	152	1.81
EH13	148	2.12
EH19	125	1.99
EMP6	118	1.81
EMP8	90	1.76
EMP10	113	2.49
EMP11	109	2.71
EMP12	172	1.94
EP1	261	3.63
EP6	268	2.78
EP13	164	3.01
EP19	55	2.54
PB6	254	4.87
PB9	220	5.21
PB11	204	4.91

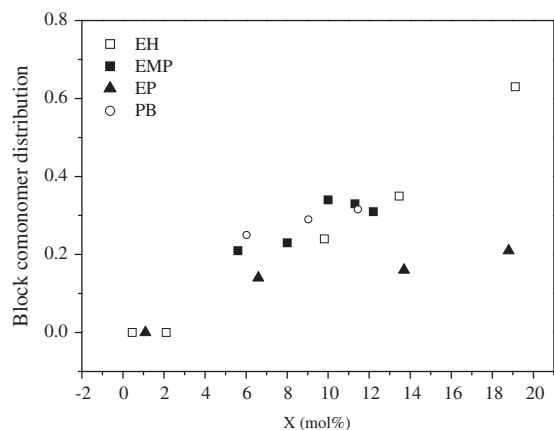Fig. 1. GPC-MALS experimental data and results for log (R_g) and log (M_w) vs. elution time obtained for EH10.

Fig. 2. Plot of block comonomer distribution determined by ^{13}C NMR spectroscopy vs. total comonomer content for the studied copolymers.

Table 3
Covered log (n) range and σ_s deviations for each copolymer sample.

Sample	log (n) range	σ_s
EH0.5	3.6–4.9	0.005
EH2	3.3–4.9	0.006
EH10	2.8–4.7	0.033
EH13	2.9–4.9	0.032
EH19	2.7–4.2	0.013
EMP6	3–4.5	0.025
EMP7	3–4.6	0.010
EMP8	2.7–4.7	0.034
EMP11	3–4.1	0.039
EMP12	3–4.6	0.017
EP1	3.3–4.9	0.006
EP6	3.4–4.9	0.002
EP13	3.2–4.9	0.008
EP19	3.2–4.3	0.007
PB6	3.4–4.6	0.011
PB9	3.4–4.5	0.006
PB11	3.4–4.5	0.019

ads MMM, MXM, XMX, MMX + XMM, XXM + MXX and XXX (where M is the principal component and X is the comonomer) have been accurately determined by ^{13}C NMR spectroscopy. The total comonomer content, X(mol%), is determined as the sum of the comonomer centred triads MXM + (XXM + MXX) + XXX as shown in

Table 2
^{13}C NMR characterization of copolymers analyzed at triad level.

Sample	X[a]	XXX	XXM + MXX	MXM	XMX	MMX + XMM	MMM
^{13}C NMR (mol%)							
EH0.5	0.45	0.00	0.00	0.45	0.00	0.49	99.06
EH2	2.110	0.00	0.00	2.11	0.00	3.76	94.13
EH10	9.80	0.00	2.37	7.43	1.03	14.78	74.39
EH13	13.45	1.02	3.69	8.74	2.08	17.94	66.52
EH19	19.12	7.61	4.46	7.05	2.24	15.01	63.64
EMP6	5.70	0.00	1.18	4.52	1.18	8.22	84.90
EMP8	7.37	0.00	1.69	5.68	1.44	9.84	81.35
EMP10	10.07	0.00	3.47	6.60	3.05	11.33	75.54
EMP11	11.29	0.34	3.34	7.61	2.98	12.35	73.33
EMP12	12.94	0.11	3.90	8.93	3.72	15.26	68.08
EP1	1.05	0.00	0.00	1.05	0.00	1.94	97.00
EP6	6.56	0.29	0.61	5.66	0.75	10.50	82.20
EP13	13.73	0.61	1.62	11.50	2.85	20.20	63.30
EP19	18.79	0.70	3.29	14.80	4.77	25.00	51.40
PB6	6.01	0.00	1.50	4.51	0.00	11.28	82.71
PB9	9.03	0.00	2.58	6.45	0.00	16.77	74.19
PB11	11.44	0.00	3.61	7.83	0.00	17.47	71.08

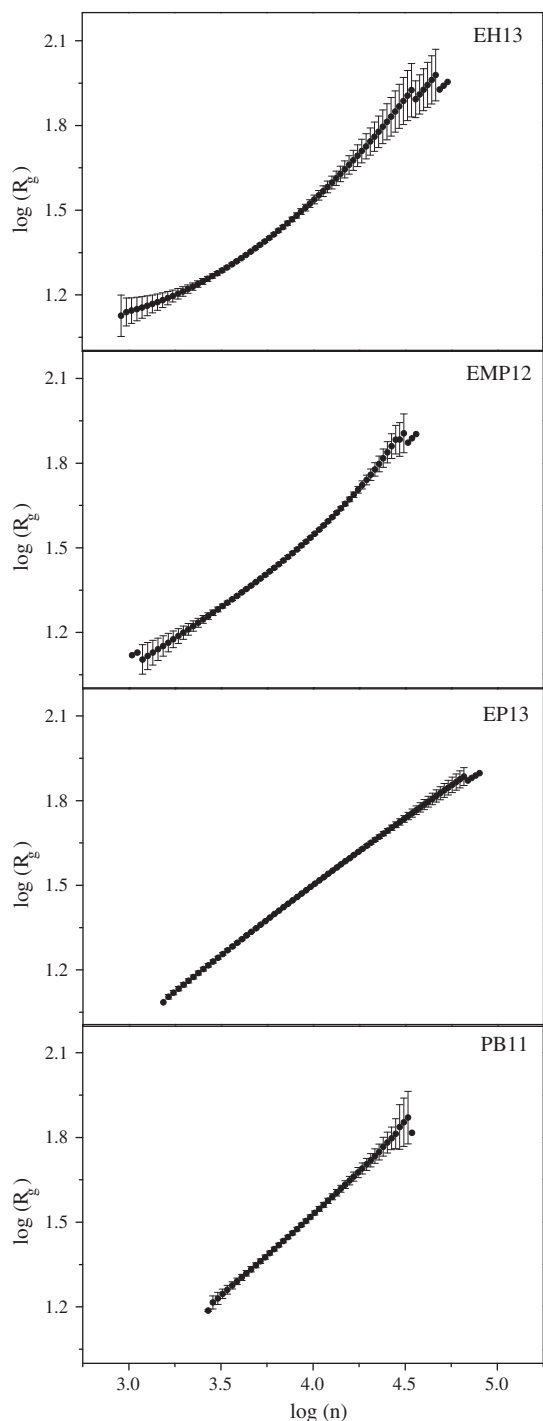[a] From triad distribution as X = (XXX + MXX + XXM + MXM).

Fig. 3. Radius of gyration for copolymers EH13, EMP12, EP13 and PB11 with similar comonomer content against number of monomer units.

Table 2. In addition, a measure of heterogeneous distribution of comonomer, named as block (B), in the copolymer has been calculated from triads as:

$$B = \frac{XXX + (XXM + MXX)}{XXX + (XXM + MXX) + MXM} \quad (3)$$

Table 4
Covered log (*n*) range and $\sigma_{s,av}$ average deviations for each copolymer sample.

Sample	log (*n*) range	$\sigma_{s,av}$
EH	2.7–4.9	0.038
EMP	2.7–4.7	0.034
EP	3.2–4.9	0.017
PB	3.4–4.6	0.015

Fig. 2 plots block comonomer distribution for each copolymer against comonomer content (mol%). As can be seen, for similar composition more heterogeneous comonomer distribution is obtained in EH, EMP and PB copolymers.

3.2. GPC-MALS

As a first point, the influence of total comonomer percentage on polymer chain conformation has been studied. In order to establish a clear effect, a detailed statistical analysis has to be carried out. Each sample has been analyzed several times, and next average values and standard deviations can be calculated:

$$[\log R_g]_m^i = \frac{1}{n_s} \sum_s [\log R_g]_s^i \quad (4)$$

$$\sigma^i = \left(\frac{\sum_s ([\log R_g]_s^i - [\log R_g]_m^i)^2}{n_s - 1} \right)^{0.5} \quad (5)$$

$$\sigma_s = \frac{1}{n_d} \sum_i \sigma^i \quad (6)$$

where $[\log R_g]_s^i$ is the log (*R_g*) value of a i-slice in a single analysis, n_s is the number of involved analysis, $[\log R_g]_m^i$ is the average value, and σ^i is the corresponding standard deviation. Subscript *i* refer to i-slide of the analysis that, in this work, means the same value of *n* (according to Eq. (2)) and subscript s refer to the involved system. Consequently, σ_s, is the average standard deviation for a given system and calculated according to Eq. (6), with the sum is extended over all the data and n_d being the number of data.

Table 3 lists values for the *n* range covered and the obtained deviations, σ_s, for each sample. As example of typical results, Fig. 3 plots the results obtained for samples with similar comonomer content. Studied ranges are quite similar for all the copolymers, but deviations differ, being the smallest for EP copolymers and the highest for the EH and EMP copolymers.

In a previous work [22], obtained values for the *q* shape parameter range from 0.53 to 0.47 for EP1 and EP19, respectively, using the standard MALS method of calculation. Such slightly dependence with composition was even lower for the rest of studied copolymers. According to such negligible composition effect for the sets of studied copolymers, all the compositions were considered simultaneously and, averaged for each kind of copolymers following equations similar to Eqs. (4)–(6), by extending the
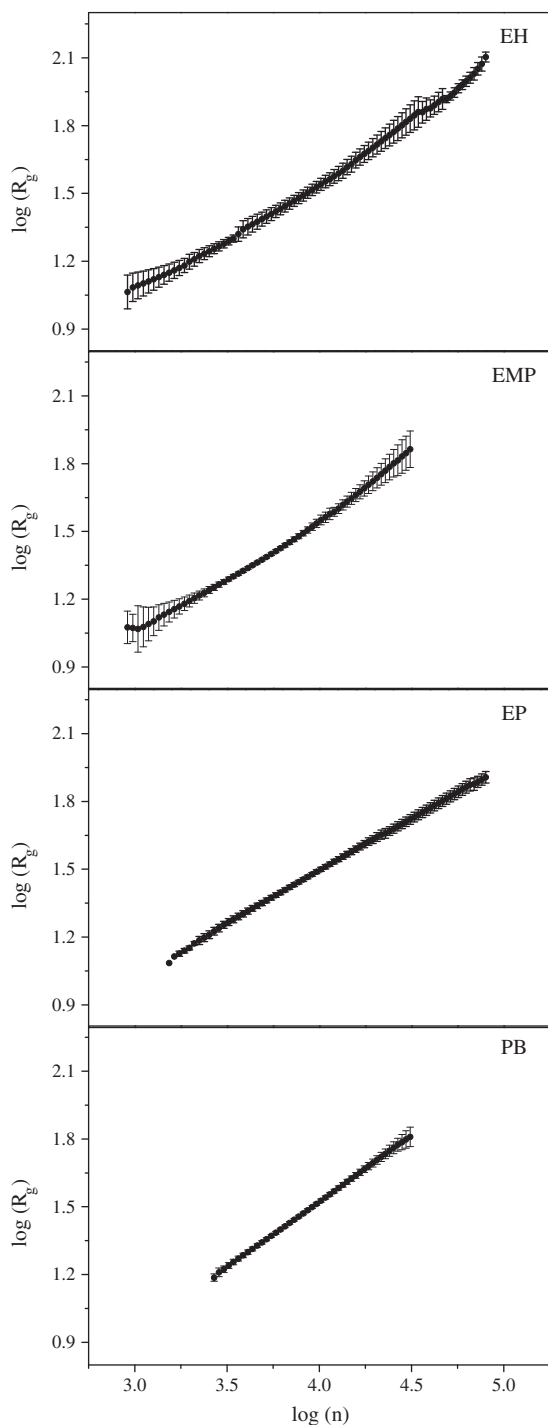
Fig. 4. Average radius of gyration for copolymers EH, EMP, EP and PB against number of monomer units.

Table 5
Results for the several fits of log (R_g) vs. log (n) for each kind of copolymers.

Sample	Number data	Polynomial fit deviation, σ_{fit} (%)		
		Order 1	Order 2	Order 3
EH	85	0.56	0.09	0.10
EMP	62	0.30	0.01	0.01
EP	72	0.03	0.01	0.01
PB	48	0.04	0.03	0.03

Table 6
Values of q parameter obtained for copolymers samples in function of two linear fit.

Sample	σ_{fit} (%)	q_1	
EP	0.03	0.47	
PB	0.04	0.57	
Sample	σ_{fit} (%)	q_1	q_2
EH	0.12	0.46	0.59
EMP	0.02	0.47	0.64

deviations in Table 4 are similar or only slightly higher than those listed in Table 3 thus showing that composition effect can be averaged without introducing any systematic effect. Fig. 4 plots average values obtained for radius of gyration for copolymers EH, EMP, EP and PB against number of monomer units, and, as can be checked, is quite similar to Fig. 3 for a given composition. Consequently, conformation study can be carried out independent of the comonomer final content.

Despite averaging procedure carried out, according to the power law given by Eq. (2), the dependence of log (R_g) vs. log (n) should be linear. This can be qualitatively checked and verified for EP and PB samples along the whole analyzed range both in Fig. 3, for a typical sample, and in Fig. 4, for average values. However, the same figures display a marked nonlinearity for EH and EMP samples and, consequently, a unique linear regression of log (R_g) vs. log (n) over the whole data range cannot be recommended. In order to quantitatively point out such different behavior, fits to different polynomial order functions have been checked.

Next standard deviation for each fit has been defined:

$$\sigma_{fit}(\%) = \left(\frac{\sum_i ([\log R_g]^i - [\log R_g]^i_{calc})^2}{n_d - 1} \right)^{0.5}$$
$$\times \frac{100}{([\log R_g]_{max} - [\log R_g]_{min})} \quad (7)$$

where $[\log R_g]^i$ is the averaged log (R_g) for each kind of copolymer, $[\log R_g]^i_{calc}$ is the log (R_g) calculated from log (n) using a polynomial function, n_d is the number of involved data, $[\log R_g]_{max}$ and $[\log R_g]_{min}$ are the maximum and minimum log (R_g) values included in order to present the σ_{fit} as a percent related to such log (R_g) covered range, σ_{fit}(%).

Table 5 summarizes, for each kind of copolymers, the involved number of data considered, and the obtained
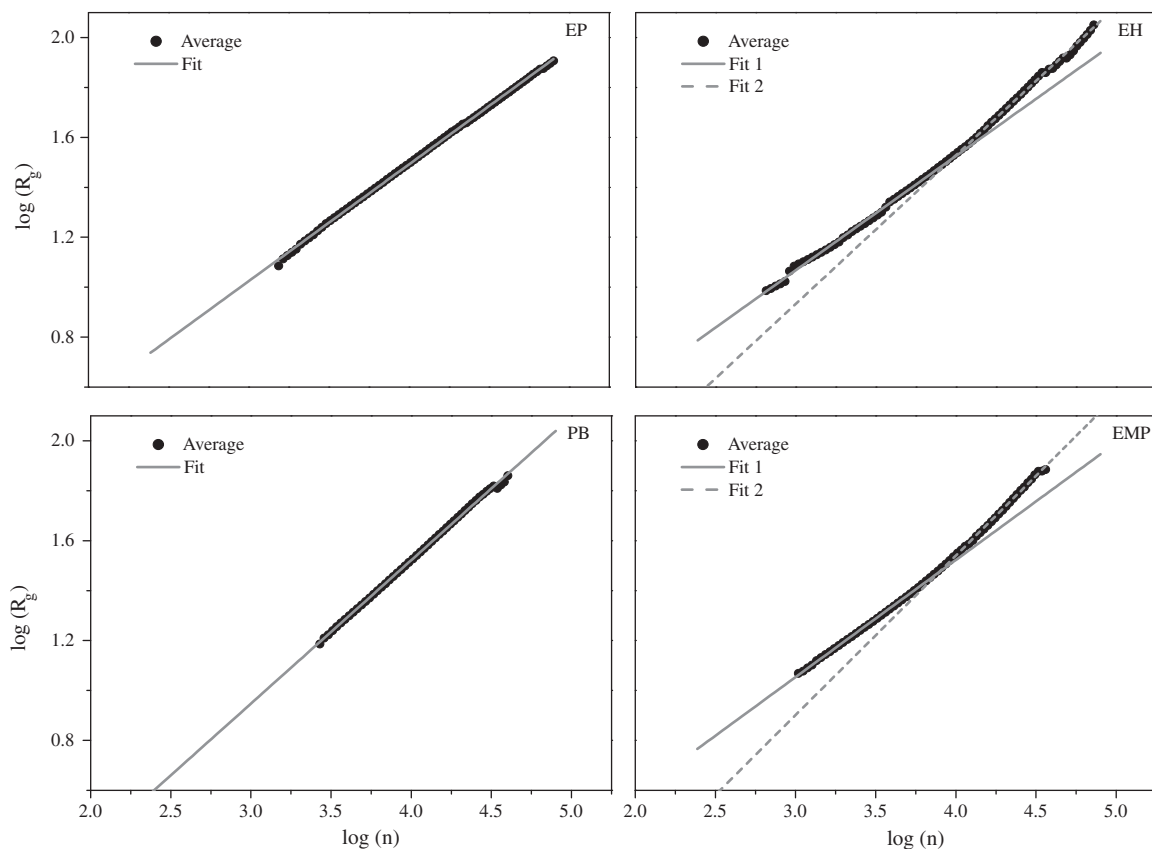
sums to all the systems despite their composition. Final average standard deviation was named $\sigma_{s,av}$, and represents the average deviation of the several analyses for different compositions of the same kind of copolymers.

Table 4 shows the log (n) range and the obtained average deviations for each kind of copolymer system. Average

Fig. 5. Double linear fit carried out on log (R_g) vs. log (n) experimental data for EP, PB, EH and EMP samples.

deviations, $\sigma_{fit}(\%)$, when a 1st, 2nd, and 3rd polynomial order function is used to describe the dependence of log (R_g) vs. log (n). As expected, higher deviations are obtained for linear fit (order 1) because flexibility attained with the inclusion of additional parameters in 2nd and 3rd order. However, very different behavior can be observed.

The accuracy of the fitting was improved only slightly for EP and PB samples when polynomial order is increased. $\sigma_{fit}(\%)$ value is reduced from 0.03% to 0.01% for EP samples when polynomial order is changed from 1 to 2 or 3. Similar values are found for PB samples, where $\sigma_{fit}(\%)$ changes from 0.04% to 0.03%. On the opposite, linear fit for the EH and EMP samples was less accurate ($\sigma_{fit}(\%)$ values of 0.6% and 0.3%, respectively), and clearly was improved when polynomial order is increased ($\sigma_{fit}(\%)$ values are reduced to 0.09% and 0.01%, respectively, for 2nd order fit, and similar values for 3rd order fit).

According to the linear dependence of scaling law and the meaning of the q shape parameter, directly related with the conformation chain of copolymer in solution, a polynomial dependence should represent a q parameter strongly dependent of the polymerization degree or the molecular weight.

In order to find out an alternative interpretation with q values approximately constants, an alternative method of fit has been developed. In that approach, $[\log R_g]_{calc}^i$ is obtained from log (n) by using a set of two 1st order polynomial functions, i.e. a double linear fit that separates

higher and lower log (n) ranges. The limiting value was determined by minimizing deviation given by Eq. (7). Similar results can be obtained without such minimizing procedure by defining an arbitrary number of data points in each fit. Results of such double fit are presented in Table 6. Values of $\sigma_{fit}(\%)$ for EP and PB samples were 0.03% and 0.04%, respectively, i.e. the same values previously obtained for single 1st order fit thus showing that no improvement can be obtained by including a second function. However, values of $\sigma_{fit}(\%)$ for EH and EMP were 0.12% and 0.02%, respectively, that compares favourably with those obtained for 2nd order fit. When all the samples are compared, this method lead to similar deviation values for all samples.

Fig. 5 plots this double linear fit carried out on log (R_g) vs. log (n) for EP, PB, EH and EMP samples. Results for EP and PB samples can be fitted with only one linear equation leading to a unique value for the q slope. However, EH and EMP samples requires n range decomposition in two different linear contributions and, consequently, two different q slope values are obtained. Values for the q shape parameters are listed in Table 6 next to σ_{fit} (%) for each fit.

According to theory, q values for typical configurations are 1/3 (spherical particles), 0.5 (polymer coil in theta conditions), 0.6 (polymers coil in very good solvents), and 1.0 (rigid rod polymers) [7]. An increase in q represents a more extended conformation in solution. Therefore values of random coil polymers at theta conditions are obtained

for EP copolymers ($q = 0.47$). These copolymers present very low composition heterogeneity values and similar comonomer size. PB represent a random coil polymers in good solvent ($q = 0.57$) with more heterogeneous distribution and in this case the difference of comonomer size imply that lateral chains increase to overall coil radius. However, EH and EMP present both behavior depending on the molecular weight range. The n separation value can be approximately set in 10^4 units. For polymers with less than 10^4 units, both kind of copolymers appears to be at theta conditions ($q_{EH} = 0.46$, $q_{EMP} = 0.47$), but for longer chains the coil expand ($q_{EH} = 0.59$, $q_{EMP} = 0.64$).

4. Conclusions

The GPC-MALS technique next to ^{13}C NMR spectroscopy is a powerful characterization tool that allows simultaneous determination of MWD, comonomer distribution and conformation properties in solution.

Effect of comonomer size has been evaluated on four different sets of copolymers in a similar composition range. Heterogeneity of comonomer distribution has been related with block comonomer distribution calculated at triads level and higher values were found for the samples EMP, EH and PB.

Previously developed numerical method was successfully applied for data reduction of MALS technique despite the dispersion of experimental data.

Conformation of polymer chains in solution was analyzed according to the scaling law between radius of gyration and the number of repeating units. Obtained results appear to be independent on overall composition and were averaged without introducing any systematic error.

Expected linear trend for log (R_g) vs. log (n) was adequate to analyze EP and PB samples. However nonlinearity was found for EMP and EH copolymers. A new method of decomposition in terms of different n ranges was developed corresponding to a double linear fit. That method leads to accurate linear fits whose deviations compare favourably with fits to higher order polynomial functions.

The obtained results show the influence of comonomer size on polymer conformation. Values of random coil polymers at theta conditions are obtained for EP and low molecular weight range of EH and EMP copolymers, while PB and high molecular weight range of EH and EMP show a more expanded coil corresponding to a random coil in good solvents.

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