Polymer Testing 52 (2016) 265–271

Contents lists available at ScienceDirect

Polymer Testing

journal homepage: www.elsevier.com/locate/polytest

Analysis Method

GPC-VIS-MALS study of EVA copolymers: Quantification and interactions of SCB and LCB

Inmaculada Suárez, Baudilio Coto*

Chemical and Energy Technology, Chemical and Environmental Technology, Mechanical Technology and Analytical Chemistry Department, ESCET, Universidad Rey Juan Carlos, c/ Tulipán s/n, 28933, Móstoles, Madrid, Spain

ARTICLE INFO

Article history:
Received 29 November 2015
Received in revised form
12 April 2016
Accepted 20 April 2016
Available online 25 April 2016

Keywords:
EVA copolymers
Multi angle light scattering (MALS)
Intrinsic viscosity
Long chain branching (LCB)
Branching index
Data analysis

ABSTRACT

Long-chain branching (LCB) is a structural phenomenon that affects important properties in polyethylene (PE) and some copolymers. Quantification of LCB frequency (λ) can be carried out by gel permeation chromatography dotted with detector for viscosity (GPC-VIS) or light scattering (GPC-MALS) by calculating branching indexes against a linear reference. In copolymers, interactions between LCB and SCB (short chain branching) have been described and lead to errors in quantification.

In this work, ethyl vinyl acetate (EVA) copolymers of composition ranging 3–20 wt% VA have been studied. A numerical method, developed for the reduction of GPC-VIS and GPC-MALS data of PE, was used for quantifying molecular weights, intrinsic viscosities and gyration radius, as well as the confident ranges. Reliable results were obtained despite the low LCB determined values.

A low density polyethylene was also included and compared. Discrepancies in the scaling laws for gyration radius and intrinsic viscosity reveal a strong effect of SCB which was confirmed by the structure factor and its dependence on molecular weight and comonomer content. However, the recently designed gpcBR index revealed to be nearly independent on the short chain branching and allowed detecting differences between apparently similar samples.

1. Introduction

Vinyl acetate ethylene copolymers, often referred as EVA copolymers, are thermoplastic materials resulting from the copolymerization of ethylene and vinyl acetate (VA). These copolymers are generally produced in high pressure and temperature bulk polymerization processes similar to those employed for the conventional high pressure free radical low density polyethylene (LDPE) production [1].

Three structural attributes of EVA copolymers largely determine the properties of any particular copolymer grade [2]: 1) weight % of vinyl acetate, 2) average molecular weight and molecular weight distribution, and 3) long (LCB) and short (SCB) chain branching.

In EVA copolymers, the primary effect of short chain branches, acetoxy groups from the vinyl acetate is to disrupt the crystallinity of the polyethylene (PE) segments. However, short chain branches have practically no impact on melt viscosity behaviour.

The long chain branching characterization is crucial to understand the viscoelastic behaviour of branched polymers in the melt flow, especially the viscosity at very low shear rate and the degree of shear thinning. Shear thinning is the phenomenon in which the viscosity decreases with increasing shear rate. The consequence of shear thinning is that the material exhibits lower viscosity and flows easier than expected when the flow rate is increased and branched materials require less pressure to be pumped at the same rate. LCB governs swell, melt strength, and environmental stress crack resistance in blow molding operations, bubble stability and lamellae orientation in film, sag resistance in pipe and geomembrane, and shear thinning and melt fracture in all extrusion processes [3]. Higher viscosity at lower shear rate for a polymer with long chain branching can enable easier fabrication via processes like profile, blown film, or foam extrusion [4]. Consequently, LCB is fundamental for the prediction of the processing behaviour [5]. However, number of long chain branches in EVA is quite low, usually under 2 per 1000 carbon atoms [1], and detection of such low values is very difficult by usual techniques [6].

Nuclear magnetic resonance (^{13}C NMR) and Fourier Transform Infrared (FTIR) are used for the determination of overall short chain branching levels in LLDPE samples, while Temperature Rising

---

* Corresponding author.
E-mail address: baudilio.coto@urjc.es (B. Coto).

http://dx.doi.org/10.1016/j.polymertesting.2016.04.014
0142-9418/

Elution Fractionation (TREF) and Crystallization Analysis Fractionation (CRYSTAF) are techniques widely used for the qualitative estimation of SCB distributions in semi crystalline copolymers [7–10].

Three methods allow LCB determination: rheology, nuclear magnetic resonance spectroscopy (NMR), and gel permeation chromatography (GPC) with triple detection (refractive index, DRI; viscometer, VIS; and a multi-angle laser light scattering, MALS) [11]. Rheology and NMR techniques determine the average LCB for the overall polymer sample while GPC technique allows determining the LCB distribution along the molecular weight distribution.

Combination of GPC-MALS allows determining both the molecular weight distribution and molecular dimension in solution in terms of the mean square radius of gyration (R_g) [12]. The branched polymer is more compact than linear polymer at any given molecular weight and consequently branches lead to smaller hydrodynamic volume, smaller radius of gyration and lower intrinsic viscosity ($[\eta]$). Thus LCB degrees can be determined by comparing branched polymers to a polydisperse linear reference sample. Ratios of the intrinsic viscosities (determined by GPC-VIS) or of the radius of gyration (determined by GPC-MALS) of branched samples compared to a linear reference can be used [13,14].

The branching indexes, g and g′, can be determined from R_g values by GPC-MALS and intrinsic viscosities by GPC-VIS, respectively, according to Equations (1) and (2):

$$g' = \left(\frac{[\eta]}{[\eta]_l}\right)_M \tag{1}$$

$$g = \left(\frac{R_g^2}{R_{g,l}^2}\right)_M \tag{2}$$

where the subscripts l refers to the corresponding value for a linear chain, and M represents that both values are taken at the same molecular weight. Values of g and g′ are 1 for linear samples and can decrease to 0.1 when LCB is increasing in the sample.

Branching index g, also called contraction factor [15], is related to the intrinsic viscosity index g′ by Equation (3):

$$g' = g^{\varepsilon} \tag{3}$$

where ε is a structure factor that determines the type of branching [16] and can be used to correlate the structure of the polymer with the properties and rheological behaviour of the material [17].

The number of branching points per chain of polymer, B_{3w} for tri-functional chains as those in PE, can be related to g factor by using the Zimm and Stockmayer relation given by Equation (4) [11,18]:

$$g = \frac{6}{B_{3w}}\left(\frac{1}{2}\left(\frac{2+B_{3w}}{B_{3w}}\right)^{1/2}\ln\left(\frac{(2+B_{3w})^{1/2}+B_{3w}^{1/2}}{(2+B_{3w})^{1/2}-B_{3w}^{1/2}}\right)-1\right) \tag{4}$$

LCB frequency is usually given in terms of λ or the number of long chain branches per 1000 carbon atoms and can be calculated, for each slice of the chromatogram, from the Equation (5).

$$\lambda = 1000\, M_0 \frac{B_{3w}}{M_i} \tag{5}$$

where M_0 is the molecular weight of the repeating unit (14 for $-CH_2-$ in polyethylene), B_{3w} is the number of branches per molecule and M_i is the molecular weight of the polymer at the slice i.

$$gpcBR = \left(\left(\frac{M_{W,LS}}{M_{W,GPC}}\right)^{\alpha}\left(\frac{[\eta]_l}{[\eta]}\right)\right) - 1 \tag{6}$$

where the subscript LS refers to light scattering, the subscript GPC refers to the values obtained from conventional GPC analysis assuming linear polymer, the subscript l refers to linear reference, and parameter α is the Mark-Houwink exponent for the same linear reference. This branching index takes advantage of the four most precise parameters that can be determined by GPC with triple-detection (concentration, viscometer, light scattering): the conventional M_w, the light scattering M_w and the intrinsic viscosity values.

In order to properly compare values for gpcBR to the rest of branching indexes, it is of interest to define such average index as a point by point index that describes the distribution along the molecular weight range.

In this work, a set of commercial EVA copolymers with different amount of vinyl acetate (VA) were analysed by GPC-VIS and GPC-MALS in order to determine both branching indexes (g and g′), the structure factor (ε), the LCB (λ) and the gpcBR index along the molecular weight distribution. Average values were obtained by including concentration values determined by DRI. All these results were compared with typical LDPE sample.

2. Experimental and data analysis

In this work, samples of EVA copolymer with different amounts of VA covering the range 3–20 wt% have been analysed. For comparison purposes, a LDPE sample with similar molecular weight was also studied. All these samples have been submitted by REPSOL. Along this work, these samples are named as LDPE and EVA followed by a number indicating the weight percentage of VA as can be seen in Tables 1–3.

GPC-VIS-MALS equipment was a gel permeation chromatograph (GPC, Waters Alliance 2000) equipped with refractive index and viscometer detectors combined with a multi-angle light scattering (MALS, DAWN EOS Wyatt Technology).

The GPC separation was carried out by using two columns from Polymer Laboratories 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, EMPOWER LOGIN 2002, from WATERS, allowed intrinsic viscosity acquisition from on-line viscometer and molecular weight determination from GPC and Universal Calibration carried out by using standard monodisperse polystyrene (PS) samples.

The MALS detector is equipped with a laser at 690 nm and 17 multi angle detectors. Temperature was also set at 145 °C. The DAWN EOS photometer system was calibrated with toluene, the detectors were normalized with a standard monodisperse PS ($M_w = 30$ kg/mol) which was also used to determine inter-detector volume [21]. The software used, ASTRA V 5.1.9.1, from Wyatt Technology, allowed on-line data acquisition of molecular weight and radius of gyration. Two injections were carried out of each sample in order to check the reproducibility.

The dn/dc values at the MALS wavelength and temperature (690 nm, 145 °C) were determined according to previously described method [22]. Value for LDPE was set equal to −0.101 mL/g, and those for EVA will be discussed later on.

Direct analysis of experimental R_g vs. M data is difficult because the extremely disperse data usually obtained by the MALS technique. The numerical iterative method previously developed [23] was used and yielded the ranges where data are confident. As all

Table 1
dn/dc values of EVA copolymers in 1,2,4-TCB.

Polymer	λ (nm)	dn/dc (mL/g)	T (°C)	Composition (wt% Ethylene)	Ref.
EVA	639	−0.1040	145	98.8	22
EVA	639	−0.1010	145	96.8	22
EVA	639	−0.0990	145	93.3	22
EVA	639	−0.0950	145	90.6	22
EVA	639	−0.0940	145	81.3	22
EVA	639	−0.0860	145	72.8	22
EVA	639	−0.0840	145	61.1	22
EVA	639	−0.0840	145	58.7	22
EVA3	810	−0.1020	145	97.0	This work
EVA9	810	−0.0987	145	91.0	This work
EVA14	810	−0.0975	145	86.0	This work
EVA20	810	−0.0932	145	80.0	This work

Table 2
Basic characterization values for all the studied samples.

Sample	VA (wt%)	dn/dc (mL/g)	Sample	M_w (kg/mol)	P.I.
LDPE	0	−0.101	LDPE-1	342	19.7
			LDPE-2	345	19.3
			LDPE-3	348	20.0
EVA3	3	−0.0999	EVA3-1	240	12.5
			EVA3-2	245	12.9
EVA9	9	−0.0977	EVA9-1	256	11.6
			EVA9-2	252	13.4
EVA14	14	−0.0957	EVA14-1	253	10.8
			EVA14-2	249	12.7
EVA20	20	−0.0935	EVA20-1	105	6.7
			EVA20-2	104	6.7

Table 3
Average values for $\overline{\lambda}$, $\overline{\varepsilon}$ and $\overline{gpc_{BR}}$ calculated for all samples studied.

Sample	VA (wt%)	Sample	$\overline{\lambda}$	$\overline{\varepsilon}$	$\overline{gpc_{BR}}$
LDPE	0	LDPE-1	0.261	1.812	2.050
		LDPE-2	0.225	2.170	2.067
		LDPE-3	0.272	1.802	2.053
EVA3	3	EVA3-1	0.216	2.294	0.934
		EVA3-2	0.218	1.553	0.961
EVA9	9	EVA9-1	0.150	2.315	0.743
		EVA9-2	0.151	2.063	0.746
EVA14	14	EVA14-1	0.170	0.981	0.645
		EVA14-2	0.149	1.198	0.630
EVA20	20	EVA20-1	0.285	0.904	0.696
		EVA20-2	0.234	0.899	0.634

the magnitudes have to be simultaneously confident, final ranges are typically very restrictive.

Along such data analysis, each magnitude of interest is finally explained as a function of the retention time. The experimental data from the several detectors allow obtaining the mathematical fitting function for next magnitudes:

a) $\log(M)_{l,\,LS}$: M for a linear polymer determined by MALS
b) $\log(M)_{LS}$: M for each polymeric sample determined by MALS
c) $\log(R_g)_l$: R_g for a linear polymer determined by MALS
d) $\log(R_g)$: R_g for each polymeric sample determined by MALS
e) $\log(M)_{l,\,GPC}$: M for a linear polymer determined by GPC and Universal Calibration
f) $\log(M)_{GPC}$: M for each polymeric sample determined by GPC and Universal Calibration
g) $\log([\eta])_l$: $[\eta]$ for a linear polymer determined by GPC on-line viscometer
h) $\log([\eta])$: $[\eta]$ for each polymeric sample determined by GPC on-line viscometer

It is important to note that such functions are always obtained from experimental values. Linear polymers were used as reference and their functions obtained by the analysis of linear standard polyethylene samples. Such functions can be used to compute the corresponding magnitudes for a given retention time, number of repeating units, or molecular weight. According to the previous definitions, g) and h) values are involved in the calculation of g′; c) and d) values are involved in the calculation of g and λ; c), d), g) and h) values are involved in the calculation of ε, and a), f), g) and h) values are involved in the calculation of gpcBR.

Original formulation of gpcBR was carried out for average properties, in this work such index was formulated for being computed point by point, according to above definition and determined functions, $gpcBR_i$ value for slice i is calculated according to

$$gpcBR_i = \left(\left(\frac{M_{i,LS}}{M_{i,GPC}} \right)^{\alpha} \left(\frac{[\eta]_{i,1}}{[\eta]_i} \right) \right) - 1 \tag{7}$$

Where the subscript i refers to slice i, and the rest of subscripts have the same meaning as in Equation (6).

From the distribution of the different properties calculated (λ, ε, gpcBR), an average value can be calculated. In this paper, weight average value was determined according to the next equation:

$$\overline{y} = \frac{\sum c_i y_i}{\sum c_i} \tag{8}$$

where c_i is the concentration for each slice in the chromatogram, and y_i represents the involved magnitude (λ_i, ε_i, $gpcBR_i$) determined for each slide.

In addition, listed magnitudes allow the determination of the dimension of the macromolecules in solution as a function of the molar mass. Accurate determination of the radius of gyration and of the intrinsic viscosity vs molar mass power law, generally known as Mark-Houwink-Sakurada (MHS), are of fundamental importance [24] because molecular architectures of the polymers in solution are usually investigated with the scaling laws relating R_g and $[\eta]$ with M_w:

$$R_g = Q \cdot M^q \tag{9}$$

$$[\eta] = Q\prime \cdot M^{q\prime} \tag{10}$$

where q and q′ are shape parameters which depend on the polymer, the solvent, and the temperature and reveals information about the polymer conformation in solution. Generally, q has a value of 0.33 for globular polymers, 0.5 for random coil polymers at theta conditions, and up to 0.6 for random coil polymers in good solvents [14,25,26]. Typical values for q′ are 0 for compact sphere, 0.65–0.85 for random coil or 1.8 for very stiff chain).

3. Results

3.1. Determination of EVA copolymers dn/dc

dn/dc values are required in any MALS study, and they are scarce properties for most copolymer systems. Most of the copolymer properties depend on its composition and consequently the dn/dc values have to be experimentally determined for EVA copolymers.

dn/dc values for EVA copolymers at 639 nm, 145 °C and different compositions are available in the literature [27]. New values were determined in this work by GPC at 810 nm and 145 °C. Table 1 list dn/dc values of EVA copolymers at a given λ, temperature and copolymer composition.

Dependence of dn/dc with composition and wavelength has been studied following a procedure developed in previous study for ethylene-propylene copolymers [21].

Both dependences can be expressed simultaneously by Equation (11):

$$\frac{dn}{dc} = a + a'w + \frac{b + b'w}{\lambda^2} \tag{11}$$

where a, a′, b and b′ are considered fitting parameters that minimize the objective function:

$$F = \sum \left[(dn/dc)_{\mathrm{exp}} - (dn/dc)_{cal} \right]^2 \tag{12}$$

The fitted parameters were $a = -1.303 \times 10^{-1}$, $a' = 4.179 \times 10^{-4}$, $b = 3.2010 \times 10^{+4}$ and $b' = -3.809 \times 10^{+2}$, with a standard deviation between experimental and calculated dn/dc values of $\sigma = 0.003$. As σ value is similar to the experimental uncertainty, the equation can be used to extrapolate a confident dn/dc value for a copolymer at a given composition and wavelength.

Table 2 lists basic characterization of each EVA copolymer used in this study: VA comonomer content, calculated dn/dc values at $\lambda = 690$ nm, average molecular weight and polydispersity indexes for each injection.

3.2. Study of dimension of macromolecules in solution by GPC-VIS and GPC-MALS

Fig. 1a) plots radius of gyration and viscosity as a function of molecular weight for EVA14 sample obtained along 2 different injections. Similar results were obtained for the different samples and the reproducibility between the injections can be considered excellent.

Scaling laws given by Equations (9) and (10) were applied in the range of confident values both for R_g and [η]. Obtained q and q′ values for EVA copolymers in comparison with LDPE are plotted in Fig. 2 as a function of VA comonomer weight percent. A branched chain is more compact than a linear one and its dimension decreases as the degree of branching increases at constant molecular weight [28]. The q value was 0.22 for LDPE, representing a compact globular polymer, and increases to 0.42 for EVA20, showing how the second monomer favoured to adopt a random coil chain configuration that can be related with the size of VA comonomer and its polarity.

However, when similar study is carried out with GPC-VIS data, obtained q′ values are nearly independent of the comonomer content and similar to that for LDPE (around 0.40) as can be seen in Fig. 2. These values confirm how the melt flow behaviour, especially the viscosity at very low shear rate and the degree of shear thinning behaviour, is affected by long chain branches while short chain branches have practically no impact.

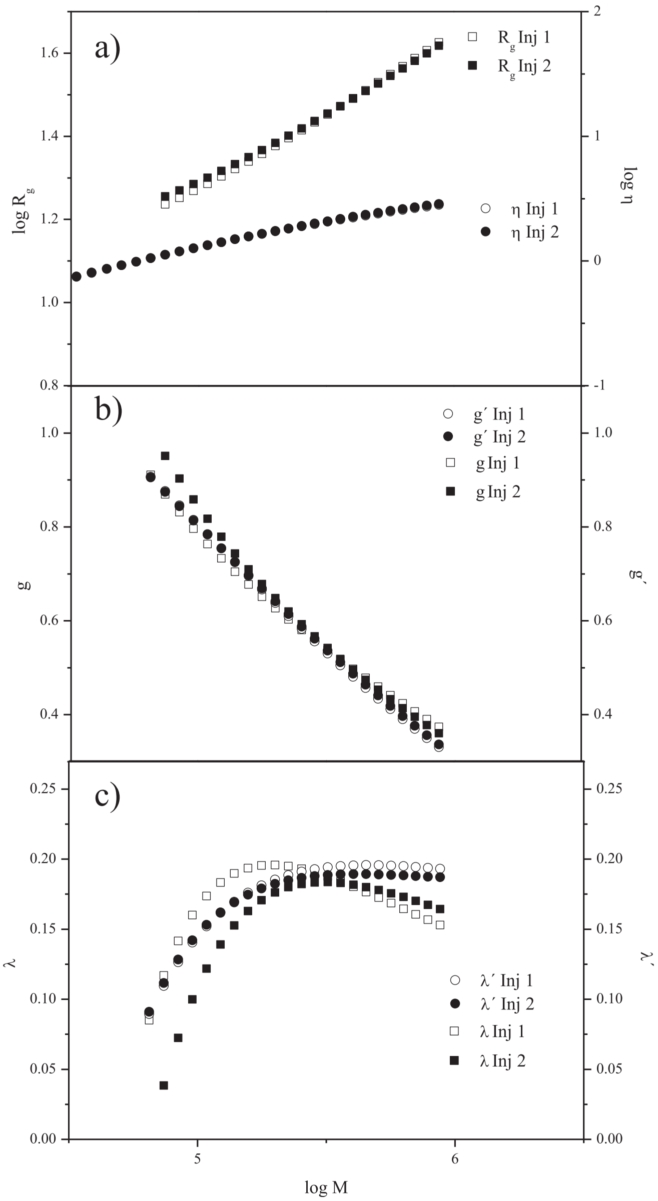

Fig. 1. Plot determined properties versus molecular weight for EVA14 sample: a) radius of gyration and viscosity, b) branching indexes g and g′, c) LCB λ and λ′.

Consequently, scaling law allows obtaining q values from GPC-MALS results is affected by comonomer size and polarity (SCB and LCB) but on the contrary intrinsic viscosity obtained by GPC-VIS is only affected by LCB.

3.3. Study of the branching index

Fig. 1b) compares the branching indexes (g′ and g) calculated from Equations (1) and (2) as a function of molecular weight. High reproducibility can be checked for both magnitudes in two injections. Similar values were obtained for both parameters with the highest differences for the lower molecular weights.

The relation between branching indexes g and g′ is given by Equation (3) through the ε factor. Different values of this factor have been described as a function of the LDPE synthesis method: a value

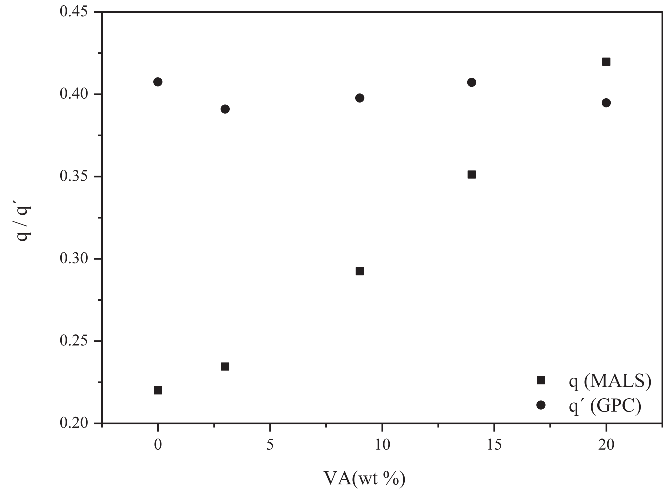

Fig. 2. Plot of q and q′ values versus VA % for studied EVA copolymers and LDPE.

of ε = 0.5 was obtained by Stockmayer for star branched molecules, Berry assumed ε = 1.5 for comb shaped molecules with small branches, Kuhn and Kromert determined ε values of 1.2 and 2.0 for one zone autoclave and tubular LDPE, and Scholte found ε values ranging from 1.0 to 0.5 with increasing molecular weight for autoclave and tubular products [29]. In a previous work [30], the dependence of this parameter with molecular weight was studied for different LDPE samples and a clear decrease of ε towards a limit value of 1.0 was obtained when molecular weight was increased along a range similar to that covered in the present work.

In Fig. 3 ε values for all samples are plotted as a function of molecular weight. It can be observed a clear decrease of ε with the increase of molecular weight for all samples towards a limit value of 1. The values reached at low molecular weights are related with the comonomer content; similar behaviour was previously obtained when dimension of macromolecules in solution is studied.

3.4. Study of LCB

Fig. 1c) plot LCB distributions (λ and λ′), determined using Equations (4) and (5), versus molecular weight for EVA14 sample. It can be seen how these samples present distributions where LCB increases with molecular weight. Small differences in g or g′ lead to higher differences in the values for λ and λ′, and values obtained by GPC-VIS are more reproducible than those obtained by GPC-MALS, with the highest deviations at low molecular weight.

In order to improve the quantification of the LCB, the new gpcBR LCB index has been determined following Equation (7). This new LCB index was created to allow a direct comparison with the LCB index used in the rheological tests [19]. The definition of gpcBR takes advantage of the most precisely measured parameters in the experiments i.e., the light scattering $M_{w,LS}$, the viscometer [η], and the conventional GPC $M_{w,GPC}$ and $M_{v,GPC}$ values, where $M_{w,GPC}$, [η] and $M_{v,GPC}$ are the weight-average molecular weight, intrinsic viscosity, and viscosity-average molecular weight, respectively. The theoretical value of gpcBR is 0.0 for linear polyethylene and it can range up to 4.0 for typical LDPE resins.

Fig. 4 plotted these values for each sample analysed as a function of molecular weight. The small error bars plotted represent a high reproducibility for this parameter when it is compared with previous values of λ and λ′ calculated from g and g′. From Fig. 4 it is possible to check how these branching indexes are increasing with molecular weight for all samples independent of the comonomer content. EVA copolymers and LDPE behaviour is similar and both present higher amounts of branches at high molecular weight, despite EVA copolymers show lower branching than LDPE in the whole molecular weight range.

In order to give a more quantitative sense to above results, average values have been determined. Fig. 5 plots together the slice concentration (left axis), and ε, gpcBR and λ (right axis) values versus molecular weight for EVA14 sample. The range plotted is that determined with confidence. This figure allows to confirm that average values can be considered confident because the concentration values are high enough in the covered range and because most properties fails to very small values when concentration increases.

From the distribution of λ, ε and gpcBR and the slice concentration obtained by GPC average values were calculated according to Equation (8). Obtained values are listed in Table 3 for each sample and injection. Fig. 6 shows the $\overline{gpcBR}$ and $\overline{\lambda}$ for each injection as a function of the comonomer weight percent. A slightly and continuous dependence with comonomer content is found for $\overline{\lambda}$ with a minimum value around 10 wt%. Reproducibility in $\overline{\lambda}$ is reasonable but differences between injections increase with VA weight percent. However, a different plot is obtained for the $\overline{gpcBR}$,

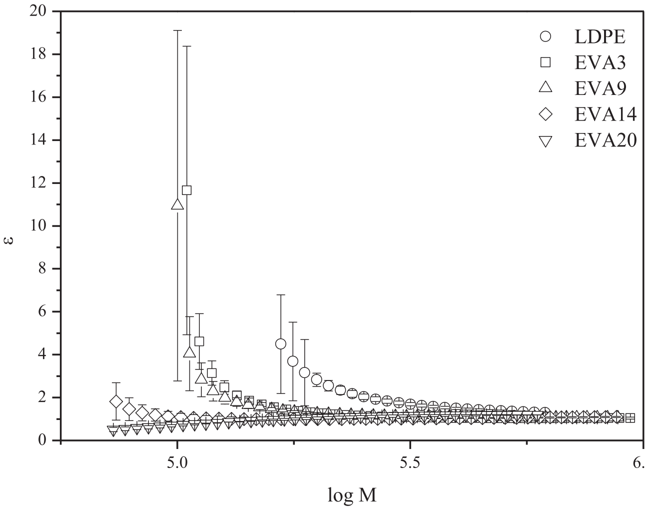

Fig. 3. Structure factor ε versus molecular weight for the studied samples.

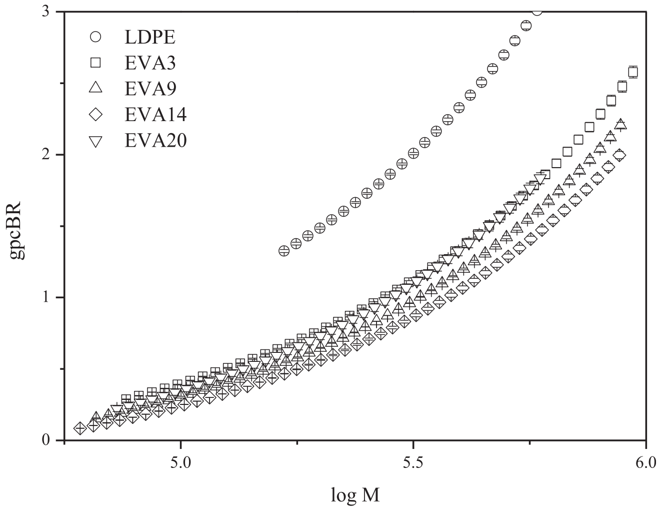

Fig. 4. Plot of gpcBR index versus molecular weight for the studied samples.

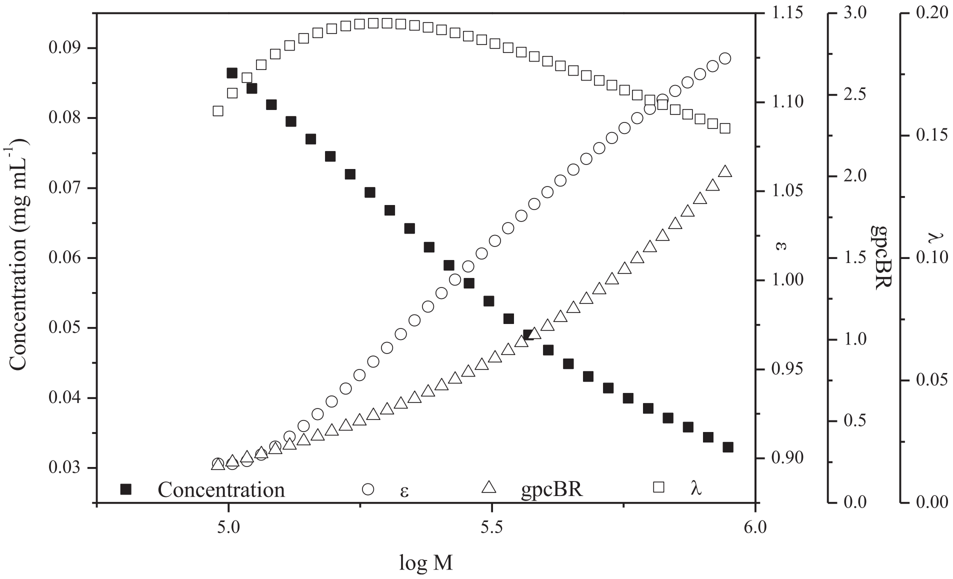

Fig. 5. Concentration, ε, gpcBR and λ parameters in the whole molecular weight range for EVA14 sample.

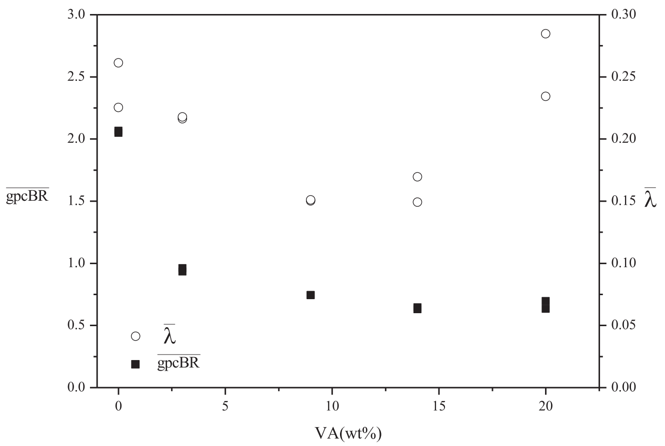

Fig. 6. Plot of $\overline{gpcBR}$ and $\overline{\lambda}$ values versus comonomer weight percent.

a value higher than 2 is obtained for LDPE sample, but values lower than 1 are obtained for EVA samples and with very low VA % dependence.

These results clearly show the higher dependence of $\overline{\lambda}$ with SCB in comparison with $\overline{gpcBR}$.

4. Conclusions

Analysis of EVA copolymers has been carried out using GPC-VIS and GPC-MALS techniques following experimental and numerical procedures previously developed. The range of application of GPC-VIS covers lower molecular weights than GPC-MALS and the full analysis was limited to the region were all the experimental data were confident, i.e. log(M_W) ranging 4.5 to 6.

Scaling laws for R_g and [η] vs. M_W were determined with very different values for q and q′ parameters, thus confirming how MALS is sensitive to SCB while viscometer is not affected by such comonomer content. Branching indexes, g and g′, and the branching frequencies, λ and λ′, reveal the same difference, and lead to a structure factor, ε, highly dependent both in M_W and in the conomomer content, even considering that uncertainty is higher in the low M_W range.

λ and ε average values were determined using the experimental slice concentration. Despite no confident values are available for the full range, the covered M_W range can be considered significant enough. Average λ values range from 0.15 to 0.29, thus describing very low branched samples but dependent of SCB. On the opposite, average ε values range from 0.9 to 2.3, and they increase according to the increase of comonomer content, in agreement with the differences found between q and q′ values.

Calculated values for gpcBR index are very low and few sensitives to comonomer content, according to the definition of that index. Average values range from 0.6 to 0.9 in agreement with low λ values.

For comparison purposes, a LDPE sample with similar M_W and synthesis procedure was included in the study. Despite similar q′ values, that sample presented the lowest q value, and the highest λ, ε and gpcBR values. Value for gpcBR was about 2 and consistent with a long chain branching sample where SCB has no influence.

On the opposite, low LCB in EVA samples (with gpcBR lower than 1), has to be considered influenced by the content and nature of the polar SCB and consequently the real λ values should be even lower. However, gpcBR index is not affected by SCB and differs in samples that in principle should be expected very similar.

Acknowledgments

The authors grateful acknowledge samples from REPSOL.

References

[1] J. Peón, J.F. Vega, M. Aroca, J. Martínez-Salazar, Rheological behaviour of LDPE/EVA-c blends. On the effect of vinyl acetate comonomer in EVA copolymers, Polymer 42 (2001) 8093.
[2] A.M. Henderson, Ethylene-vinyl acetate (EVA) copolymers: a general review, IEEE Electr. Insul. Mag. 9 (1) (1993) 30.
[3] Q. Yang, M.D. Jensen, M.P. McDaniel, Alternative view of long chain branch formation by metallocene catalysts, Macromolecules 43 (2010) 8836.
[4] K. Anderson, Branching in Ethylene Vinyl Acetate (EVA) Copolymers, 2012. http://www.vitaldose.com/blog/branching-in-ethylene-vinyl-acetate-eva-copolymers/.
[5] E. Ruymbeke, V. Stéphenne, D. Daoust, P. Godard, R. Keunings, C. Bailly, A sensitive method to detect very low levels of long chain branching from the molar mass distribution and linear viscoelastic response, J. Rheol. 49 (6) (2005) 1503.

[6] A. Malmberg, C. Gabriel, T. Steff, H. Münstedt, B. Löfgren, Long-chain branching in metallocene-catalyzed polyethylenes investigated by low oscillatory shear and uniaxial extensional rheometry, Macromolecules 35 (2002) 1038.

[7] S.R. Torabi, N. Fazeli, A rapid quantitative method for determination of short chain branching content and branching distribution index in LLDPEs by DSC, Polym. Test. 28 (2009) 866.

[8] B. Monrabal, Temperature rising elution fractionation and crystallization analysis fractionation, in: R.A. Meyers (Ed.), Encyclopedia of Analytical Chemistry, John Wiley&Sons Ltd, 2000, p. 8074.

[9] B. Monrabal, Chemical composition distribution analysis in polyolefins. Introduction to crystallization analysis fractionation CRYSTAF, in: S. Hosoda (Ed.), New Trends in Polyolefin Science and Technology, Research Signpost, 1996, p. 126.

[10] A. Albrecht, R. Bruell, T. Macko, F. Malz, H. Pasch, Comparison of high-temperature HPLC, CRYSTAF and TREF for the analysis of the chemical composition distribution of ethylene-vinyl acetate copolymers, Macromol. Chem. Phys. 210 (2009) 1319.

[11] Y. Yu, P.J. DesLauriers, D.C. Rohlfing, SEC-MALS method for the determination of long-chain branching and long-chain branching distribution in polyethylene, Polymer 46 (2005) 5165.

[12] R. Medrano, M.T.R. Laguna, E. Saiz, M.P. Tarazona, Analysis of copolymers of styrene and methyl methacrylate using size exclusion chromatography with multiple detection, Phys. Chem. Chem. Phys. 5 (2003) 151.

[13] C. Kim, J. Sainte Beuve, S. Guilbert, F. Bonfils, Study of chain branching in natural rubber using size-exclusion chromatography coupled with a multi-angle light scattering detector (SEC-MALS), Eur. Polym. J. 45 (2009) 2249.

[14] K. Tribe, G. Saunders, R. Meißner, Characterization of branched polyolefins by high temperature GPC utilizing function specific detectors, Macromol. Symp. 236 (2006) 228.

[15] W. Burchard, Solution properties of branched macromolecules, Adv. Polym. Sci. 143 (1999) 115.

[16] P.F.N Rui Mário Costa, R.C.S. Dias, Prediction of mean square radius of gyration of tree-like polymers by a general kinetic approach, Polymer 48 (6) (2007) 1785.

[17] P. Taekx, J.C.J.F. Taex, Chain architecture of LDPE as a function of molar mass using size exclusion chromatography and multi-angle laser light scattering (SEC-MALLS), Polymer 39 (14) (1998) 3109.

[18] B.H. Zimm, W.H. Stockmayer, The dimension of chain molecules containing branches rings, J. Chem. Phys. 17 (2) (1949) 1301.

[19] W.W. Yau, Examples of using 3D-GPC-TREF for polyolefin characterization, Macromol. Symp. 257 (2007) 29.

[21] Y. Liu, S. Bo, Y. Zhu, W. Zhang, Determination of molecular weight and molecular sizes of polymers by high temperature gel permeation chromatography with a static and dynamic laser light scattering detector, Polymer 44 (2003) 7209.

[22] B. Coto, J.M. Escola, I. Suarez, M.J. Caballero, Determination of dn/dc values for ethylene-propylene copolymers, Polym. Test. 26 (5) (2007) 568.

[23] I. Suárez, B. Coto, Quantification of uncertainties involved in the conformational study of polymers by light scattering, Eur. Polym. J. 47 (2011) 2331.

[24] R. Mendichi, L. Soltes, A.G. Schieroni, Evaluation of radius of gyration and intrinsic viscosity molar mass dependence and stiffness of hyaluronan, Biomacromolecules 4 (2003) 1805.

[25] S. Podzimek, T. Vlcek, Characterization of branched polymers by SEC coupled with a multiangle light scattering detector. II. Data processing and interpretation, J. Appl. Polym. Sci. 82 (2001) 454.

[26] H.M. Huang, I.C. Liu, Tsiang R. Chien-Chao, Studies of hydrodynamic properties for characterizing star-shaped poly(ethylene-co-propylene), Polymer 46 (2005) 955.

[27] D.C. Bugada, R. Gagnon, A. Rudin, Specific refractive index increments of ethylene–vinyl acetate copolymers in trichlorobenzene solutions at 145°C, J. Appl. Polym. Sci. 34 (2) (1987) 501.

[28] N. Hadjichristidis, M. Xenidou, H. Iatrou, M. Pitsikalis, Y. Poulos, A. Avgeropoulos, S. Sioula, S. Paraskeva, G. Velis, D.J. Lohse, D.N. Schulz, L.J. Fetters, P.J. Wright, R.A. Mendelson, C.A. García-Franco, T. Sun, C.J. Ruff, Well-defined, model long chain branched polyethylene 1. Synthesis and characterization, Macromolecules 33 (2000) 2424.

[29] Y. Othman Alothman. Processing and Characterization of High Density Polyethylene/Ethylene Vinyl Acetate Blends with Different VA Contents. Advances in Materials Science and Engineering Volume 2012.

[30] I. Suárez, B. Coto, Determination of long chain branching in PE samples by GPC-MALS and GPC-VIS: comparison and uncertainties, Eur. Polym. J. 49 (2) (2013) 492.