

High-Temperature Coupling of High-Speed GPC with Continuous Viscometry. II. Ethylene-Vinyl Acetate Copolymers

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Synopsis

An application of the high temperature coupling of a gel permeation chromatograph with a home-made continuous viscometric detector is described. It concerns the comprehensive characterization of ethylene-vinyl acetate copolymers. Suitable chromatographic conditions are chosen to enable a correct use of the universal calibration concept. Through analysis of poly(vinyl acetate) fractions and commercial polyethylene samples, a comparison is made with the results of classical measurements. Average molecular weights as well as intrinsic viscosity appear to be in good agreement within experimental error, which proves the system for the characterization of random ethylene-vinyl acetate copolymers. In attempting to obtain a reliable estimate of long chain branching frequency λ , a series of commercial samples has been selected, with the vinyl acetate weight fraction within the range 0–45%. As a rule, experimental viscosity law exhibits two parts, a straight line with a Mark-Houwink exponent 0.7 in the low molecular weight region and a curvature, well smoothed by a third-degree polynomial regression. Consequently, long chain branching does not appear before a limiting molecular weight of about 50,000. Beyond this limit, λ is 0.5×10^{-4} , with no dependence on molecular weight, which resembles low density polyethylene.

INTRODUCTION

We have related in a recent paper,¹ the coupling of a high temperature gel permeation chromatograph (Waters ALC/GPC 150-C) with a homemade continuous viscometer. This detector, first proposed by Ouano,² is the only suitable one for the application of universal calibration³ to high speed gel permeation chromatography (GPC). The viscometer^{4–9} is described in the previous paper.¹ In this configuration,¹⁰ it has proved efficient for the characterization of linear and branched polyethylenes.¹ Also time is saved, with regard to the classical GPC-discontinuous viscometry coupling.¹¹ Average molecular weights, intrinsic viscosity, and various branching parameters are obtained within 50 min, with good accuracy and perfect reproducibility.¹

Ethylene-vinyl acetate (EVA) copolymers in the range 0–45% vinyl acetate

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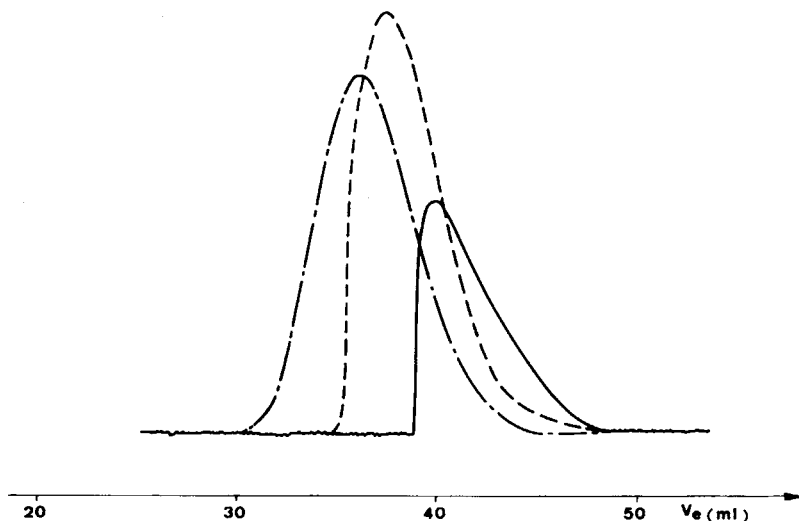


Fig. 1. Chromatogram shape of a poly(vinyl acetate) sample ($M = 60,000$) as a function of PEO 400 concentration in the mobile phase: (—) TCB; (---) TCB + 0.1% PEO 400; (- - -) TCB + 1% PEO 400.

(VA) weight fraction are of commercial interest. These products, synthesized by a high pressure polymerization process, consistently possess a random structure and do not need a third detector, such as the infrared photometer.

Although low density polyethylene (LDPE) and poly(vinyl acetate) (PVA) are branched, characterization¹² of their copolymers are also of interest.

Preparative GPC technique in xylene at 60°C has been used by Barlow et al.¹³ in the study of two EVA resins, containing 16.5% VA and 25.5% VA, respectively. Fractions have been characterized by analytical GPC at 140°C, using 1,2,4-trichlorobenzene (TCB) as solvent, and by other classical methods. By comparing their experimental intrinsic viscosity-molecular weight relationship deduced from universal calibration with the one of linear polyethylene, they conclude that EVA copolymers exhibit a relatively high degree of long chain branching (LCB).

Salyer et al.¹⁴ have fractionated four samples (9%, 15%, 45%, and 70% VA) by solvent-nonsolvent precipitation methods. Viscosity-molecular weight equations have been established in xylene at 105°C (9% and 15% VA) and in methyl ethyl ketone at 30°C (45% and 70% VA). All four copolymers have a break in the viscosity law, a Mark-Houwink exponent of about 0.60 in the lower molecular weight region, and about 0.15 in the higher one, due to LCB. More recently, workers^{15,16} have focused their attention on the flow properties of a particular EVA sample, with 28% VA. Fourteen fractions have been obtained by fractional precipitation in carbon tetrachloride-methanol mixture at 25°C. GPC data and intrinsic viscosity have been obtained in THF at 20°C. As above,¹⁴ a break is observed in the viscosity plot, with a limiting molecular weight near 70,000.

The above contributions provide coherent information on EVA structure which is linear in the low molecular weight region, and relatively high long chain branched beyond a limiting value, located between 50,000 and 100,000. Nev-

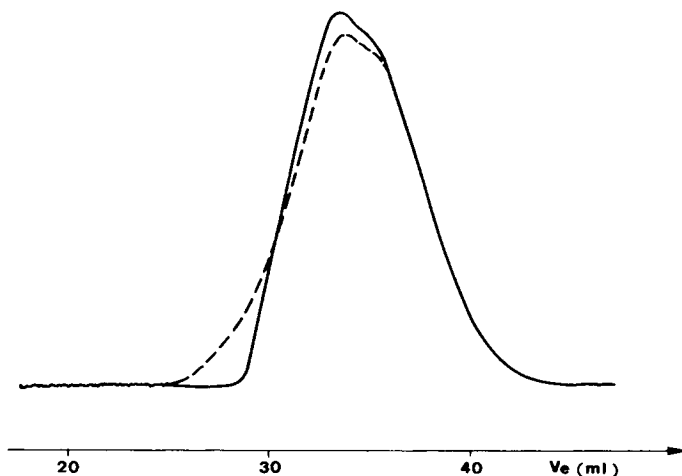


Fig. 2. Chromatogram shape of an EVA sample ($x = 0.28$) in pure TCB (—) and in TCB-G (1% PEO 400) (---).

ertheless, there is no fast and easy characterization method that can be applied to samples of all compositions. The main objective of this work is the development of such a method. Also, for more accuracy in the LCB frequency estimate, we have to establish the intrinsic viscosity–molecular weight relationships of hypothetical linear EVA samples, within the entire range of VA fraction.

EXPERIMENTAL

Gel Permeation Chromatography. The instrument used was a Waters 150C Liquid Chromatograph equipped with the continuous viscometer. Details of the coupling have been given elsewhere,¹ with the system of automatic data treatment. The columns were four micro-Styrigel of nominal pore size 10^3 , 10^4 , 10^5 , and 10^6 Å. For some experiments, the mobile phase was THF at 30°C , but high temperature measurements were carried out at 135°C with 1,2,4-trichlorobenzene as solvent. In every case, the flow rate was 1 mL/mn and the injected quantity was around 1 mg ($400\ \mu\text{L}$ at 0.25% w/v). Universal calibration was a linear relationship¹ for high temperature analysis:

$$\ln([\eta] \cdot M) = 38.651 - 0.704V$$

At ambient temperature, it was a third-degree polynomial deduced from polystyrene standards.

Viscosity Measurement. Dilute solution viscosities were measured using a classical Ubbelohde viscometer (for THF at 30°C) or a FICA Viscomatic for TCB at 135°C . Intrinsic viscosity was deduced from the classical way of double extrapolation to zero concentration.

Materials. EVA samples were all commercial products. A set of 10 resins was selected in order to give a comprehensive view of industrial production. Some of their characteristics are listed in Table I, except their origin. The wt % of VA was measured by infrared spectroscopy and by oxygen microanalysis

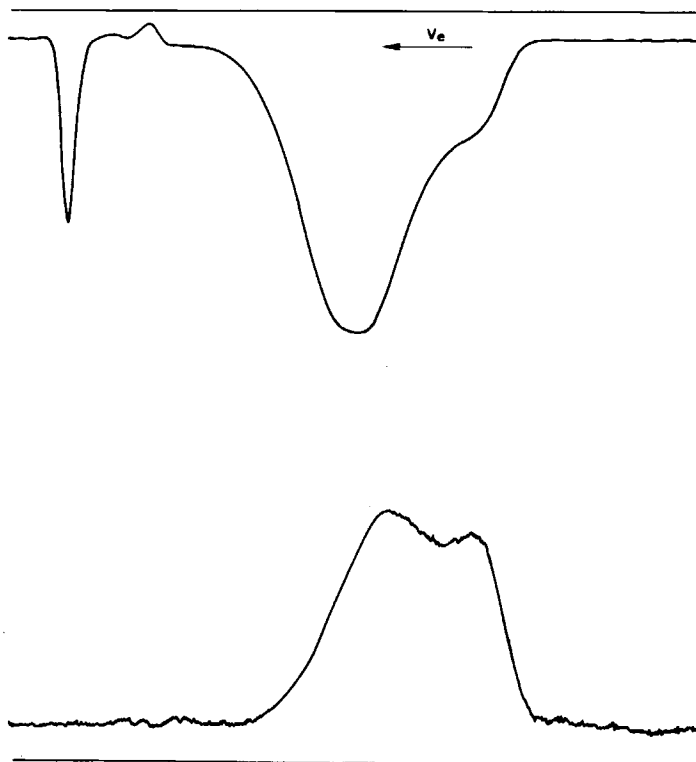


Fig. 3. Chromatograms of an EVA sample with a double distribution in TCB-G at 135°C. Upper trace: refractometer; lower trace: viscometer.

through the relationships

$$\% \text{ VA} = 2.69\% \text{ O}$$

Random character was proved in some experiments, performed by the coupling of 150C GPC with a Wilks infrared detector. The two chromatograms (refractive index change and carbonyl group absorption at 5.75 μm) exhibit perfect similarity.¹⁷

Linear PVA standards were purchased from the National Polymer Laboratory (Teddington, Middlesex, England). We used five Certified Reference Materials (part number M 19-17) covering a wide range of molecular weight. Methods of measurement and evidence for linearity of the macromolecular chains have been described by Dietz and co-workers.¹⁸⁻²⁰

Sample Preparation. Great care was exercised in sample dissolution, either in THF or in TCB. Copolymers are often less soluble than homopolymers, and branched structures less than linear ones. Experimentally, EVA branched copolymers followed these generalizations. Dissolution was carried out as follows: EVA in TCB at 135°C (whatever the composition), 4 h in an oven at 135°C with gentle, periodic stirring; EVA in THF at 30°C (for VA content greater than 25%), 6 h (more if possible) in an oven at 50°C; EVA with less than 25% VA are not soluble in THF at 30°C.

RESULTS

Characterization Method. A GPC method enabling the characterization of polyethylene, poly(vinyl acetate) and their copolymers at all compositions necessarily requires high temperature conditions. Consequently, we adopted, in a first trial, the same conditions as those for pure polyethylene analysis.¹ The unusual shape of chromatograms attracted our attention. EVA samples with relatively high VA content (>28%) exhibited high molecular weight side with steep slope, low molecular weight side being more classical as shown in Figure 1. For acetate group adsorption, we injected a commercial PVA sample under the same conditions. Figure 2 shows evidence of adsorption, whereas elution of the same sample through the same column set, but in THF at room temperature, perfectly obeys universal calibration.

Adsorption of EVA resins on silica packings is well recognized, and the use of mixed eluents has been often recommended.²¹ In the same way, increasing amounts of poly(ethylene oxide) (PEO) 400 were added to pure TCB. We can clearly observe in Figures 1 and 2 the chromatogram evolution, which occurs until the PEO concentration reaches approximately 1% (w/v). In further discussion, the mixed eluent TCB-1% PEO will be referred to as TCB-G. Vinyl acetate group adsorption on styrene-divinylbenzene gel is quite surprising. It may be caused by residual polar groups from synthesis, but more likely from a slow packing oxidation under high temperature conditions, since an increase in adsorption intensity was observed as a function of time.

GPC of EVA copolymers requires mixed eluents, and EVA chromatograms recorded in TCB-G, provide a true image of the distribution curves. Figure 3 represents the sample 5 chromatogram (see Table I) as an example of a lot of commercial resins. The double distribution appearance is probably due to a post-treatment for reducing the melt index. Most chromatograms have a Gaussian form.

Checking of the Method. When using either pure TCB or mixed TCB-G as eluent, no difference in polyethylene characterization was observed, since intrinsic viscosity as well as average molecular weights were the same. Therefore,

TABLE I
Characteristics of EVA Copolymers

EVA	% VA (in weight)		Melt index	\bar{M}_w^a (PEHD unit)	\bar{M}_w (real)	\bar{M}_w/\bar{M}_n
	IR	O ₂				
1	3.3	4.3	2.4	92	220	11
2	5.6	5.9	0.6	73	100	3.6
3	9	10	2.5	72	110	4.4
4	15	15.2	0.7	75	110	4.4
5	18.7	18.2	3	102	190	6.7
6	21	21.1	0.7	86	130	3.8
7	28	28	40	65	120	5.8
8	33	34.4	42	47	63	3.1
9	40	40.8	45	47	68	3.0
10	45	44.2	10	145	300	9.4

^a Molecular weight in thousands.

TABLE II
 Characteristics of the Set of Poly(vinyl Acetate)^a

PVAc	NPL Certificate			GPC/viscometry				
				THF 30°C			TCB-G 135°C	
	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n	\bar{m}_n	\bar{M}_v	\bar{M}_w	\bar{M}_n	\bar{M}_w
A	32	46	1.44	36	49	55	29	47
B	52	81	1.54	50	75	80	50	73
C	115	144	1.25	120	145	155	106	133
D	301	379	1.26	302	346	366	275	350
E	763	934	1.22	780	900	940	740	890

^a Molecular weight in thousands.

the previously established¹ universal calibration relationship has been kept for this study. The only change in routine conditions has been a weak increase (about 1%) of the pressure drop of mobile phase through the viscometer. On the other side, five PVA standards were thoroughly characterized. Average molecular weights were measured by GPC under the conditions to be checked, but also in THF at 30°C. The results (Table II) list a comparison with the values provided by the National Polymer Laboratory (\bar{M}_n by osmometry, \bar{M}_w by light scattering photometry). The agreement is satisfactory, especially when an attempt is made to estimate experimental errors. On the other hand, Mark-Houwink relationships have been established for linear PVA through viscometric-average molecular weights, deduced from GPC analysis. The following equations were obtained after least-square regression:

$$\text{THF/30°C: } [\eta] = 0.0149M^{0.698} \quad (1)$$

$$\text{TCB-G/135°C: } [\eta] = 0.0137M^{0.687} \quad (2)$$

Finally, comparisons were achieved on EVA copolymers. Intrinsic viscosities in TCB-G at 135°C measured by the 150C-viscometer coupling were compared with the results of classical viscometry. Agreement is again satisfactory (see Table III); however, a systematic underestimation of a few units occurs in the case of continuous viscometry, which can be explained by the neglected peak tails during chromatogram integration.

 TABLE III
 Intrinsic Viscosity of EVA Copolymers Measured by Classical Viscometry and by GPC in TCB-G at 135°C

EVA	% VA (in weight)	$[\eta]$ (mL/g) Ubbelohde	$[\eta]$ (mL/g) GPC
1	3.3	91	85
2	5.6	100	99
3	9	90	88
4	15	106	100
5	18.7	103	103
6	21	113	110
7	28	74	71
8	33	71	71
9	40	69	69
10	45	110	106

TABLE IV
GPC Molecular Weights of Some EVA in Different Conditions^a

EVA	% VA	THF 30°C		TCB-G 135°C	
		\bar{M}_n	\bar{M}_w	\bar{M}_n	\bar{M}_w
7	28	25	100	20	120
8	33	19	63	20	63
9	40	25	60	21	68
10	45	36	320	32	300

^a Molecular weight in thousands.

EVA with more than 25% VA are soluble in THF at 30°C, which allows the comparison between GPC in THF and in high temperature conditions. Results related to samples 7, 8, 9, and 10 are given in Table IV, where number and weight average molecular weights are in close agreement. It proves the validity of high temperature chromatographic conditions for satisfactory characterization of EVA copolymers.

Long Chain Branching in EVA Copolymers. Long chain branching frequency measurement through GPC-viscometry coupling is based on the structure parameter g' :

$$g' = [\eta]_b / [\eta]_l \quad (3)$$

where¹ $[\eta]_l$ is the intrinsic viscosity of the linear species and $[\eta]_b$ that of the branched one with the same molecular weight M_b . $[\eta]_l$ is classically deduced from the Mark-Houwink relationship: $[\eta]_l = KM_b^a$. K and a values are obtained either from the literature or after experimental determination with linear standards. In the case of EVA copolymers, the Mark-Houwink coefficients depend on the VA fraction x , but there is no data in the literature and linear EVA standards are not available.

Fortunately, $\log [\eta] - \log M$ relationships for the EVA samples exhibit a particular shape (Fig. 4, sample 8). The curve is composed of two parts: the low molecular weight side, under a limiting molecular weight M_l of about 50,000, which is represented by a straight line, and the high molecular weight side, where the experimental points are smoothed by a third-degree polynomial regression. A qualitative agreement is thus reached with the previously mentioned papers.^{14,15}

As the linear part is always a straight line with a slope 0.7, whatever the VA content, and as Mark-Houwink exponents of HDPE and linear PVA in TCB at 135°C are, respectively, 0.7¹ and 0.69², we can assume that linear EVA fits the viscosity equation

$$[\eta] = K \cdot M^{0.7}$$

where K depends on the VA weight fraction x .

We determined through 10 EVA ($0 < x < 0.45$) the relationship for K as a function of x (Fig. 5)

$$K = 0.053(1 - 0.56x) \quad (4)$$

The structure parameter g' can thus be determined through the molecular weight

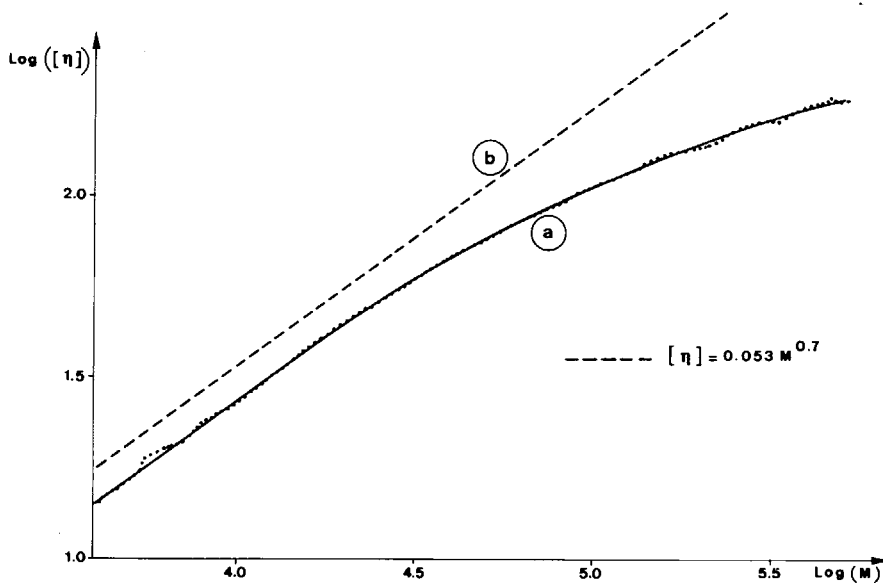


Fig. 4. Viscosity laws of an EVA sample (a) and of HDPE (b).

distribution, and the number n of long branches can be calculated with the two relationships $g'-g$ and $g-n$, where g is the ratio of the mean square radii of gyration $\langle R_G^2 \rangle$ of branched and linear species with the same molecular weight and n the number of branches per macromolecule:

$$g = \langle R_G^2 \rangle_b / \langle R_G^2 \rangle_l$$

Owing to the lack of any response in the literature, we decided to maintain the hypothesis made for LDPE¹

$$g' = g^{1.2} \quad (5)$$

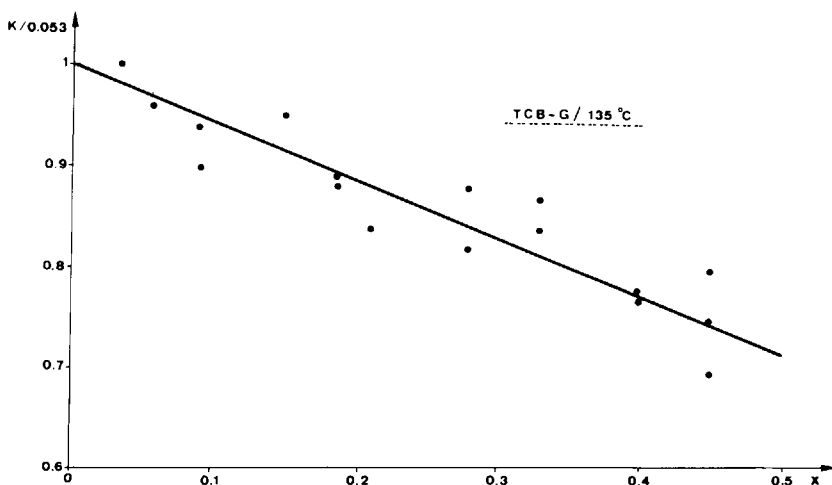


Fig. 5. Experimental determination of the relationship K as a function of the VA weight fraction x .

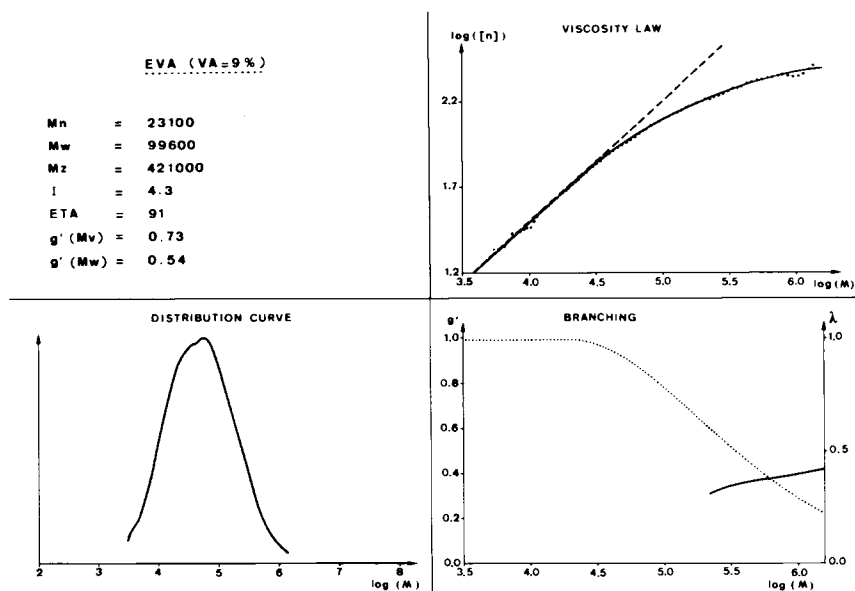


Fig. 6. Computer report of the characterization of an EVA sample (VA = 9%).

$$g = \frac{3}{2}(\pi/n)^{1/2} - 5/2n \quad (6)$$

All the results related to EVA sample 3 are collected in Figure 6. The viscosity relationship (dotted line) is deduced from (4). Agreement with experimental values is rather satisfactory. In this example, LCB frequency λ is about 0.4×10^{-4} beyond M_L , with a small increase in molecular weight. Nevertheless, when comparing the 10 commercial EVA, marked dependence is not observed on molecular weight or on the process. Thus, the only difference between EVA and LDPE, with regard to branching, is the persistent linear structure for EVA in the low molecular weight region.

DISCUSSION

It is usual to compare experimental results on A-B type copolymers with the properties of the two A and B homopolymers at the same molecular weight M . As an example, a polymer blend will obey

$$[\eta] = x_A[\eta]_A + x_B[\eta]_B \quad (7)$$

where x_A and x_B are the respective weight fractions of A and B. A similar rule between the mean square radii of gyration has been applied to linear copolymers under θ conditions, when there is no A-B interaction,

$$\langle R_G^2 \rangle = x_A \langle R_G^2 \rangle_A + x_B \langle R_G^2 \rangle_B \quad (8)$$

and according to Flory's theory,

$$[\eta] = (x_A \cdot [\eta]_A^{2/3} + x_B \cdot [\eta]_B^{2/3})^{3/2} \quad (9)$$

Block copolymers²²⁻²⁹ perfectly obey the former relationship, whereas random

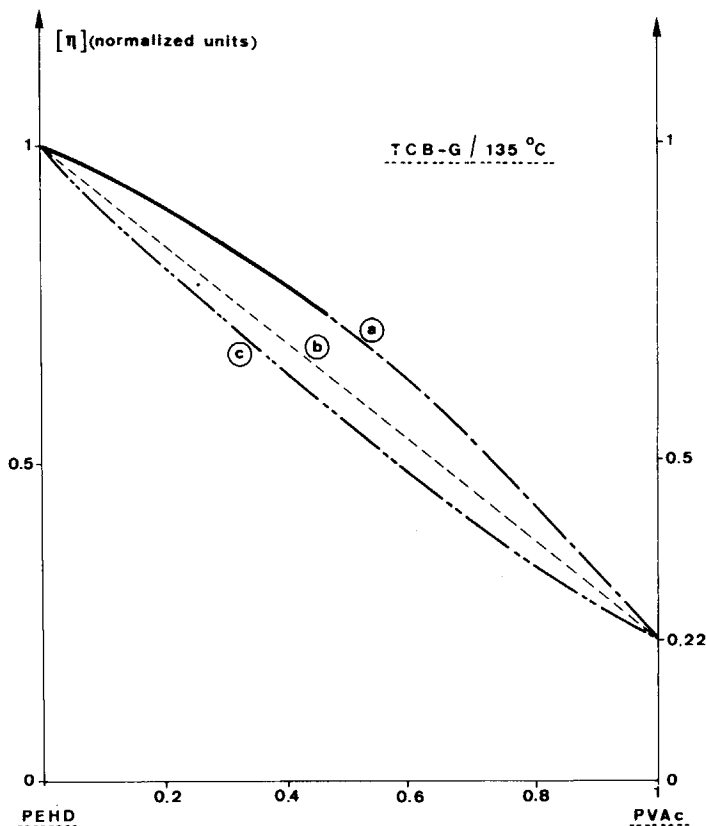


Fig. 7. Variations of intrinsic viscosity of an EVA sample ($\bar{M}_w = 100,000$) as a function of the VA weight fraction: (a) = experimental results; (b) relationship (7); (c) relationship (9).

copolymers exhibit real intrinsic viscosity higher than the expected value: the stronger the incompatibility, the larger the discrepancy. The system ethylene/vinyl acetate is represented in Figure 7 for a molecular weight of 100,000. Our experimental results (in arbitrary units) are reported together with relationships (7) and (9). A difference is actually observed, due to the random character of EVA copolymers and to a certain incompatibility between ethylene and vinyl acetate monomers.

Although we did not dispose of EVA with x greater than 0.45, the likely symmetry of the diagram (Fig. 7) enabled us to fit the K - x relationship along the entire range of composition, by a second-degree polynomial,

$$K = 0.053(1 - 0.46x - 0.32x^2) \quad (10)$$

Such a proposal surely offers a good approximation before further experiments.

CONCLUSION

Our results demonstrate the usefulness of the high temperature coupling of gel permeation chromatography with continuous viscometry as a fast and easy

characterization method for ethylene/vinyl acetate copolymers with any composition. The viscometer has given proof of its ability in enabling the determination of Mark-Houwink relationship for hypothetical linear EVA, thus allowing long chain branching estimates in commercial resins. In the future, this system would surely bring deeper insight into long-chain branching, and would yield information such as the long chain branched character of EVA, appearing only beyond a molecular weight of 50,000 in contrast with LDPE.

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