

High-Temperature Coupling of High-Speed GPC with Continuous Viscometry. I. Long-Chain Branching in Polyethylene

D. LECACHEUX, J. LESEC,* and C. QUIVORON, *Laboratoire de Physico-Chimie Macromoléculaire (Associé au CNRS N°278), E.S.P.C.I., 10 rue Vauquelin, 75231 Paris Cedex 05, France*

Synopsis

The coupling of a high-temperature liquid chromatograph (Waters 150C) with a home-made continuous capillary viscometer is described. This detector is the only one suitable for high-speed GPC when the small volume of the mobile phase prohibits the coupling with a classical viscometer. The pressure drop of the GPC effluent through the capillary is continuously measured along with the refractive index change. This dual detection leads to the determination of the intrinsic viscosity as a function of the elution volume, thus allowing a precise use of Benoit's universal calibration. The accuracy of our system is demonstrated in the case of the characterization of linear and branched polyethylene samples. The results concerning the average molecular weights as well as the branching factors (structure parameter g' and long-chain branching frequency λ) are in close agreement with those obtained by the classical way (coupling traditional GPC and discontinuous viscometry). It is well known that an estimate of the λ coefficient is extremely dependent on several hypotheses. However, for a set of commercial low-density polyethylenes, we obtained λ values about 0.5×10^{-4} , with no marked change along the molecular weight range.

INTRODUCTION

The use of the universal parameter $[\eta] \cdot M$ as a calibration concept¹ in gel permeation chromatography (GPC) requires the knowledge of the intrinsic viscosity $[\eta]$ throughout the chromatogram. Two kinds of viscometric detectors can fulfill such a purpose. The first one measures the flow time of aliquot fractions of the GPC effluent^{2,3} (Ubbelohde-type viscometer). It has proved to be very efficient, even at high temperatures, for the characterization of various polyolefins.⁴ But with modern packings, the volume of the permeating area is always too small to allow this coupling. The second type of viscometric detector has been first described by Ouano.⁵ It is based on the continuous measurement of the effluent pressure drop through a capillary tube. Assuming a laminar flow which obeys Poiseuille's law, the pressure drop P of the mobile phase is proportional to its absolute viscosity η and is given by

$$P = \frac{8}{\pi} \cdot Q \cdot \frac{l}{r^4} \cdot \eta$$

where Q is the flow rate, and l and r are the length and the radius of the capillary tube, respectively. As the concentration of the polymer issuing from the column

* To whom correspondence should be addressed.

set is very low, the intrinsic viscosity is continuously determined by

$$[\eta]_i = \frac{1}{c_i} \ln \frac{P_i}{P_0}$$

where c_i is the concentration given by the refractometric detector and P_0 is the pressure drop of pure solvent.

Thus, the coupling of modern GPC and dual detection (any concentration detector besides the continuous viscometer) enables the use of the universal calibration method, leading to accurate characterization of macromolecular samples.

Since 1976, the continuous viscometer has been studied in our laboratory,⁶ and a performance evaluation has been made recently.^{7,8} Our purpose is to extend its application to the high-temperature field near 140°C, which has not yet been done anywhere. The following results proceed from a preliminary study at ambient temperature, which will be published later.⁹

We describe here the fitting of the viscometer on the Waters ALC/GPC 150C chromatograph¹⁰ and the system of automatic data treatment. A few examples of linear (HDPE) and branched (LDPE) polyethylene analyses are given as a test of the validity of this method. We particularly emphasize the comparison of the results with those obtained by the classical GPC-viscometry coupling.

EXPERIMENTAL

The Continuous Viscometer¹¹

The main part of the viscometric detector consists of a stainless steel capillary tube inserted between the outlet of the column set and the inlet of the refractometer. Its characteristics are: inner diameter $\frac{9}{1000}$ in., outer diameter $\frac{1}{16}$ in., length 3 m. It is coiled in the column compartment, the diameter of the spires is about 16 cm.

The pressure drop through the capillary is measured by means of two pressure transducers (Sedeme,¹² C.M.A.C. 0–5 bars) located in the front of the pump compartment in the place of the internal solvent supply reservoir, which is easily removable. As shown in Figure 1, the pressure is transmitted from the "T" fittings to the transducers through $\frac{20}{1000}$ -in. I.D. tubing. A small tubing is brazed on the top of the transducer holder for the purge of the stationary solvent.

It has been mentioned elsewhere⁷ that such a viscometer is very sensitive to flow rate variations, so that three high-sensitivity filters¹⁰ must be added just after the pumping system so as to reduce the pressure pulses to an acceptable level. Under the typical conditions of polyethylene GPC characterization, i.e., 1,2,4-trichlorobenzene as solvent, flow rate 1 mL/min, and temperature 135°C, the pressure drop for pure solvent is 2.02 bars, and the baseline noise less than 2 millibars. The flow rate stability is excellent, and we have never observed any long-term drift over several months.

Data Acquisition and Treatment

We have realized a complete system of automatic data treatment with the following parts:

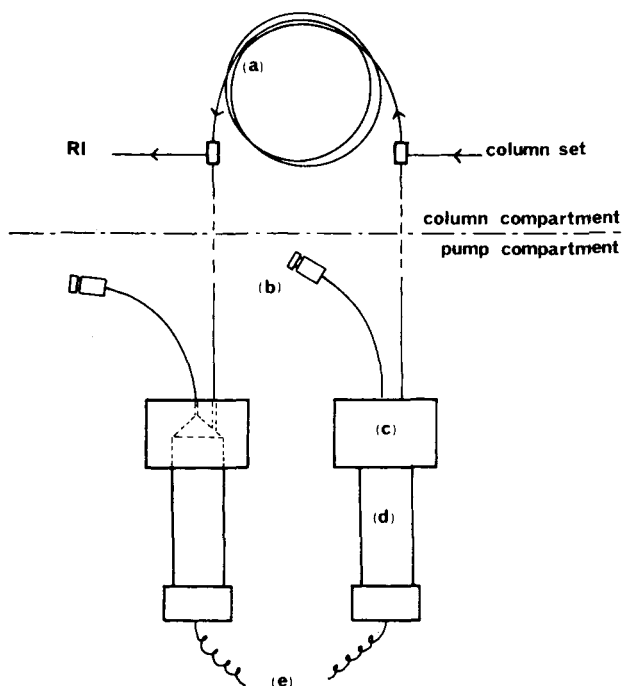


Fig. 1. Scheme of the continuous viscometer: (a) capillary tube; (b) purge; (c) transducer holder; (d) pressure transducer; (e) electronic units.

Hewlett Packard (H.P.) 9825 B desktop computer (64K memory).

H.P. 59313 A analog-to-digital converter.

H.P. 9872 A plotter.

Sedeme TS 27 transducers supply (two units).

A homemade electronic system was designed to perform the following requirements:

Choice between reading either of the transducers for adjustment or directly the differential value ($P = P_1 - P_2$, where subscripts 1 and 2 are referring respectively to each transducer).

Start of the real-time clock (H.P. 98035A) when injection is achieved, using the "injection switch" of the 150C.

This complete system permits automatic acquisition and recording of the chromatograms. At the end of each injection, the chromatograms are saved on the data cartridge allowing the next injection. After the last one (1 to 16 samples per run), calculations and graphic output are performed within a few minutes. The injection runs are usually programmed over night.

Chromatographic Conditions

The Waters 150C was equipped with 4 μ -Styragel columns of nominal pore sizes 10^3 , 10^4 , 10^5 , and 10^6 Å. TCB (1,2,4-trichlorobenzene) used as mobile phase was purchased from the Société des Solvants (SDS-FRANCE). It was carefully purified in three steps just before use: (1) filtration through activated alumina layer; (2) addition of 0.1% (w/v) 2,6-di-*tert*-butyl-4-methylphenol (ionol) as antioxidant; and (3) filtration on FH Millipore membranes (0.45 μ m).

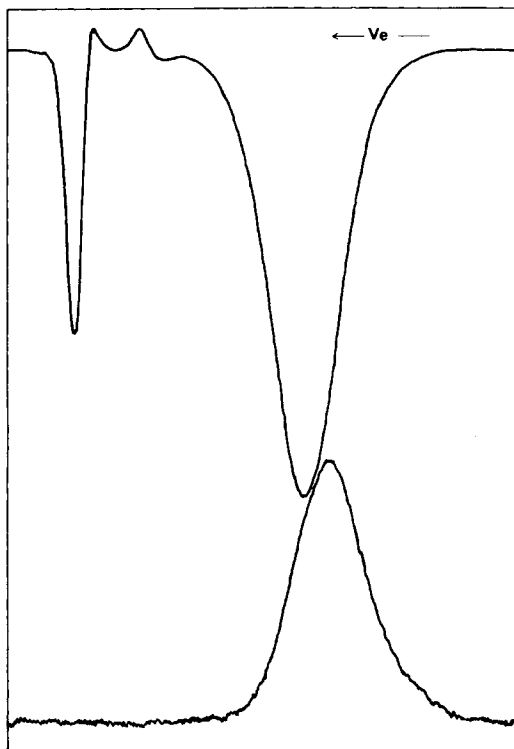


Fig. 2. Chromatograms of SRM 1475 linear polyethylene. Upper trace: refractometer; lower trace: viscometer.

The temperature was kept constant at 135°C, except in the pump compartment, which was at about 50°C. Increase or decrease in temperature was always performed at a rate of 5°C/h to avoid a loss of resolution of the column set. The flow rate was 1 mL/min; and according to the pressure trace, deviations did not exceed 10^{-3} mL/min. For all injections, we chose to keep constant the injected volume (0.4 mL) as well as the solute concentration (0.25% w/v). All solutions were filtered using the internal device of the 150C.

Polymers

The series of six low-density polyethylenes (LDPE) mentioned in this article are whole polymers. They were obtained by classical commercial continuous polymerization process, and they are manufactured by ATO-Chimie.¹³

RESULTS

Principles of Calculations

Column calibration was established by means of three whole linear polyethylenes: the well-known SRM 1475 (National Bureau of Standards, U.S.A.) and two high-density polyethylenes used by the S.N.E.A. (P.)¹⁴ as domestic standards, herein referred to as A and B. Figure 2 shows the two chromatograms

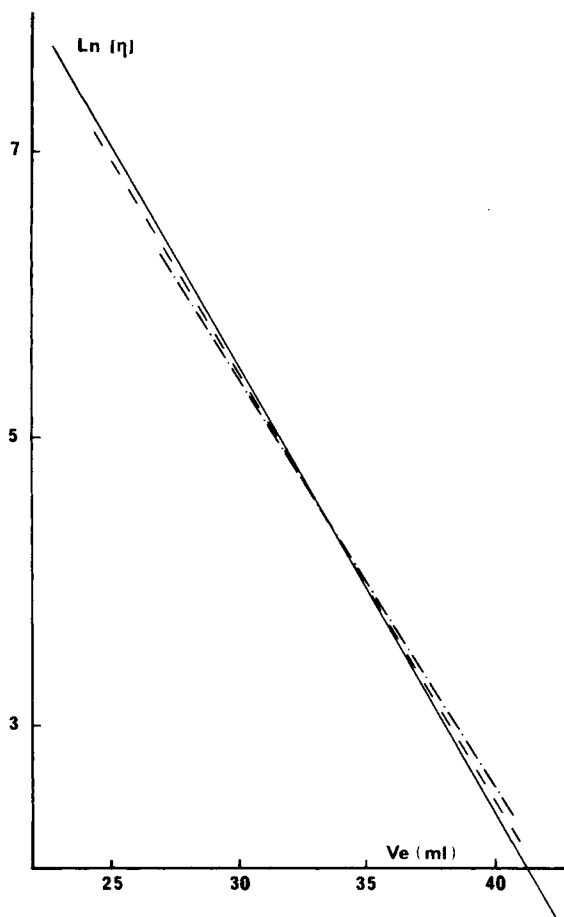


Fig. 3. Plot of $\ln [\eta]$ vs. elution volume for SRM 1475 (---), sample B (- · - · -), and sample A (—).

(viscometric and refractometric) of the SRM 1475. For those three standards, the $[\eta]$ -vs.-elution volume relationships are plotted together in Figure 3 after a linear regression on experimental points. It is obvious that a single straight line may provide a satisfactory calibration with regard to other experimental errors.¹⁵ Thus, assuming the Mark-Houwink relationship¹⁶

$$[\eta] = 0.053 \bar{M}_v^{0.7} \quad (\text{mL/g})$$

in good agreement with the proposal of Cervenka,¹⁷ we have deduced the universal calibration curve:

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

All calculations were performed without any correction. Specially, axial dispersion was neglected. Results related to branched polyethylene samples are based on Benoit's universal calibration concept, which has been often verified in this case.^{18,19} Each chromatogram was digitalized into about 80 points; and after a smoothing of the raw data, the various mean values (average molecular

TABLE I
Intrinsic Viscosities of Linear and Branched Polyethylenes

Sample	[η], mL · g ⁻¹	
	Our results	Classical coupling
HDPE SRM 1475	100	99
HDPE A	163	170
HDPE B	121	127
LDPE 1	107	108
LDPE 2	107	104
LDPE 3	95	99
LDPE 4	86	84
LDPE 5	83	80
LDPE 6	79	81

weights and intrinsic viscosities) were calculated through the classical formulas

$$\bar{M}_n = \frac{\sum_i C_i}{\sum_i \frac{C_i}{M_i}} \quad \bar{M}_w = \frac{\sum_i C_i M_i}{\sum_i C_i} \quad [\eta] = \frac{\sum_i [\eta]_i C_i}{\sum_i C_i}$$

Check of the Method

In Table I are collected the intrinsic viscosities of linear and branched polyethylenes. Our results (first column) are compared with those obtained by the classical GPC-flow time viscometry coupling.¹⁴ (On the NBS certificate of SRM 1475, the intrinsic viscosity obtained by classical viscometry is 101 mL/g.) It is obvious that the agreement is quite good; discrepancies do not exceed a few percent. Accordingly, the effect of the high shear rate in the capillary,⁹ which is about 8500 s⁻¹, seems to be negligible in this molecular weight range within experimental error. In addition, the reproducibility has been found to be $\pm 2\%$. These results give proof once again of the validity of the continuous viscometer as a molecular size detector in high-speed GPC.

As an example, Figure 5 shows the experimental viscosity law of LDPE sample 2 whose chromatograms are reproduced in Figure 4. A very good correlation between the experimental points is observed, except in the low-molecular-weight range ($M < 10^4$) because of the loss of sensitivity inherent in the molecular size detectors in this case. For further calculations, the $\ln [\eta]$ - $\ln M$ relationship is smoothed by a third-degree polynomial regression. The excellent fitting (see Fig. 5) corroborates what is often an *a priori* hypothesis in the literature.²⁰

In the same way, number- and weight-average molecular weights are compared in Table II. The agreement is again satisfactory, although variations are greater than in the viscometric results. The fast linear calibration procedure (described above) is probably responsible mainly. Moreover, the hydrodynamic correction for long-chain branching is a second source of discrepancies between laboratories in the characterization of LDPE. The consequence of this correction is well perceptible in Figure 6: for each sample of the series, the ratio of the real weight-average molecular weight to the apparent one is near 2.

Consequently, the GPC-continuous viscometer coupling appears to be a very

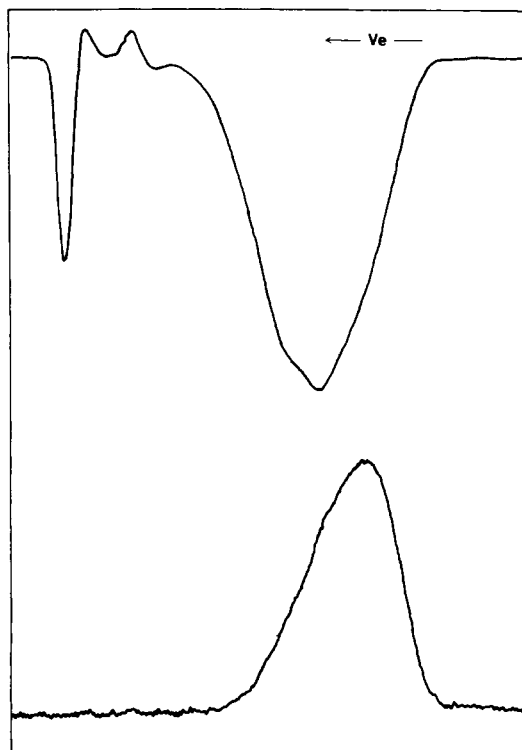


Fig. 4. Typical chromatograms of LDPE sample 2. Upper trace: refractometer; lower trace: viscometer.

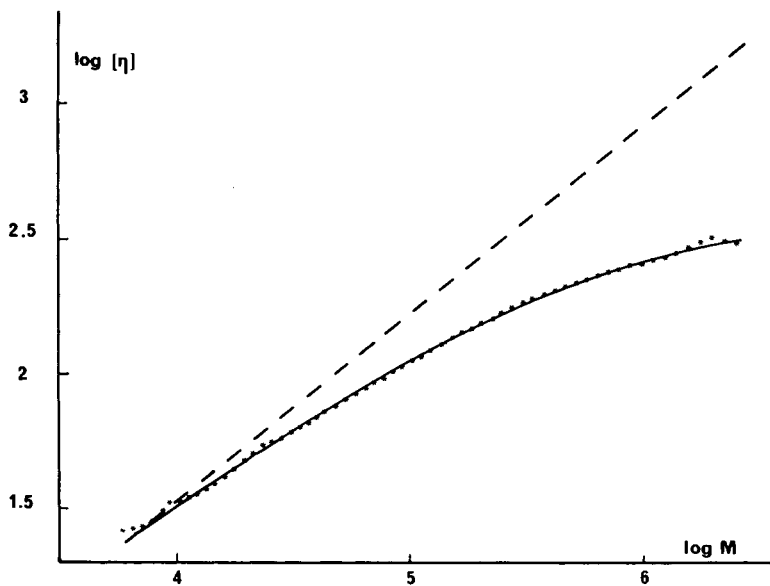


Fig. 5. LDPE sample 2: plot of experimental viscosity law (***) and comparison with the Mark-Houwink relationship for linear polyethylene (- - -).

TABLE II
Average Molecular Weights of Linear and Branched Polyethylenes

Sample	Our results		Classical coupling	
	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$
HDPE SRM 1475	23	55	18	54
HDPE A	15	141	13	148
HDPE B	19	84	12	92
LDPE 1	31	271	26	293
LDPE 2	28	189	27	209
LDPE 3	25	183	22	167
LDPE 4	23	145	23	131
LDPE 5	22	88	20	78
LDPE 6	21	123	18	103

efficient method for the characterization of branched polyethylene at high temperature. The results are comparable with those obtained by the classical coupling, but the method is three or four times less time consuming.

Long-Chain Branching Frequency λ

The estimate of the long-chain branching frequency in low-density polyethylene has been achieved by many workers (see the review of Small²¹). But large discordances in the reported results are observed, proceeding mainly from the various assumptions admitted *a priori*. In every case, the starting value is the structure parameter g' :

$$g' = \frac{[\eta]_b}{[\eta]_l}$$

where $[\eta]_b$ is the intrinsic viscosity of the branched species and $[\eta]_l$ is that of the linear one with the same molecular weight $M_b \cdot [\eta]_l$ given by

$$[\eta]_l = KM_b^g$$

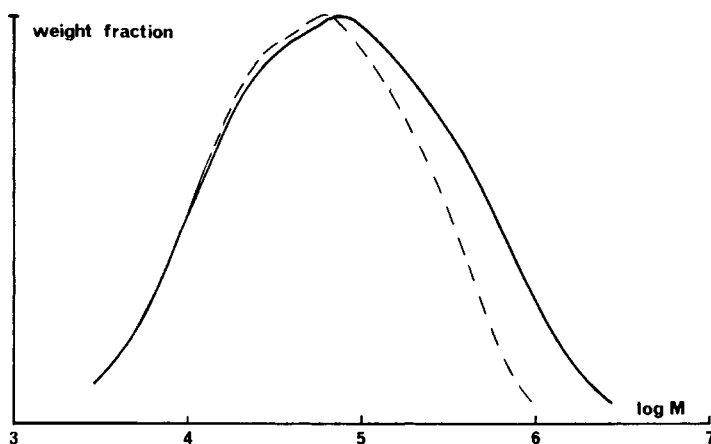


Fig. 6. Apparent molecular weight distribution (in linear polyethylene units) of LDPE sample 2 (- - -) compared with that (—) deduced from universal calibration.

It is then necessary to assume a relationship between g' and the ratio g of the mean square radius of giration $\langle R_G^2 \rangle$ of the same species²²:

$$g = \frac{\langle R_G^2 \rangle_b}{\langle R_G^2 \rangle_l}$$

In accordance with several studies,^{23,24} we have used

$$g' = g^{1.2}$$

Finally, the number n of branches per macromolecule is obtained by one of the Zimm-Stockmayer relationships.²⁵ The two following are the most often encountered:

$$g = \left[\left(1 + \frac{n}{7} \right)^{1/2} + \frac{4n}{9\pi} \right]^{-1/2} \quad (1)$$

$$g = \frac{6}{n} \left[\frac{1}{2} \cdot \left(\frac{2+n}{n} \right)^{1/2} \cdot \ln \left(\frac{(2+n)^{1/2} + n^{1/2}}{(2+n)^{1/2} - n^{1/2}} \right) - 1 \right] \quad (2)$$

But it seems²¹ that either of the two should be well fitted to the size exclusion mechanism (fractions with a given hydrodynamic volume and random branching). Owing to the lack of theoretical basis, we have used a third equation, numbered (40b) in Ref. 25:

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

which has been demonstrated for fractions with a given molecular weight M and a constant number of branches ($n > 5$). Anyway, we checked the three different relationships. Their results are not very different with regard to the expected precision, mainly, when eqs. (1) and (3) are compared.

Figure 7 shows the case of LDPE sample 2. The long-chain branching frequency λ ($\lambda = n/M$) is about 0.5×10^{-4} , with no significant change along with the molecular weight. We came to the same conclusion for the six samples studied.

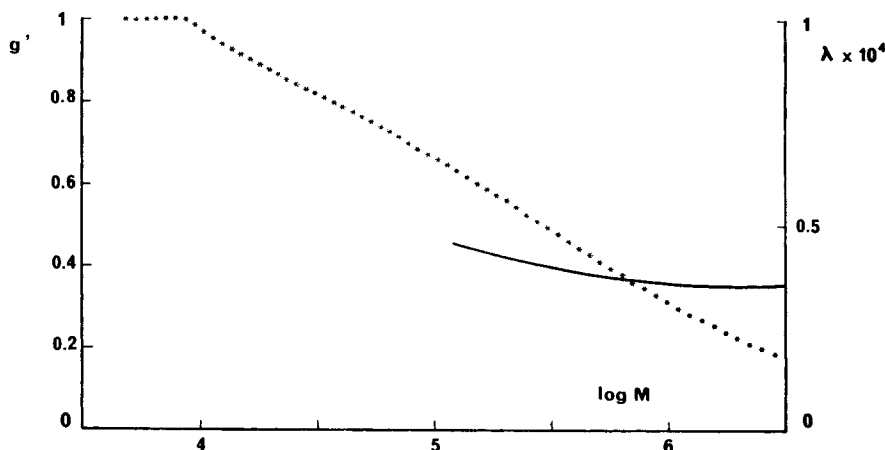


Fig. 7. LDPE sample 2: plot of structure parameter g' (***) and long-chain branching frequency λ (—) vs. molecular weight.

In spite of the doubts regarding the above assumptions, our results are in close agreement with the results of Bovey et al.²⁶ Using the ¹³C-NMR technique, they obtained λ values of the same order of magnitude (0.4 and 0.6×10^{-4}) and no marked change with molecular weight. It is satisfactory to note that Jackson,²⁷ studying chain transfer under typical ethylene polymerization conditions, calculated an estimate of λ of 0.25×10^{-4} . It is certain that particular processes may change this average. However, a sudden increase of λ in the high-molecular-weight field as is sometimes encountered in the literature, with values of more than 10×10^{-4} , is probably due to wrong assumptions in the calculation method.

CONCLUSIONS

The characterization of linear and branched polyethylene samples is easily performed with an automatic gel permeation chromatograph coupled to a continuous viscometric detector. The average molecular weights, intrinsic viscosities, and branching parameters are in good agreement with those obtained the classical way. The main interest is the time saving of high-speed GPC. This system may be safely employed at higher temperature (145°C) for the analysis of polypropylene. At last it is possible to achieve a precise characterization of complex polyolefins such as ethylene-vinyl acetate copolymers, which we shall describe in a future communication.²⁸

This work was supported by a grant from the Société Nationale Elf Aquitaine (Production). The authors wish to thank Dr. R. Panaris and Dr. R. Prechner for helpful discussions. Prof. H. Benoit is gratefully acknowledged for his interest in this work.

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Received March 2, 1982

Accepted July 14, 1982