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# Molecular Weight Distribution of Fluorinated Polymers with Long Chain Branching

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ABSTRACT: The molecular weight distribution (MWD) of branched fluorinated terpolymers made of vinylidene fluoride (VDF), hexafluoropropylene (HFP), and tetrafluoroethylene (TFE) has been investigated. These polymers, as well as all VDF-based polymers, have trifunctional long chain branches originated by the transfer to polymer mechanism. Furthermore, one of the samples here examined has a certain amount of tetrafunctional long chain branches produced by copolymerizing the sample in the presence of a fluorinated diolefin. The MWD of the polymers has been evaluated by combining the size exclusion chromatography data with the intrinsic viscosity of the whole polymer. To highlight the effect of branching over the MWD, the polymer samples have been fractionated and the high molecular weight fractions have been analyzed. The reliability of the adopted approach has been assessed by comparing the obtained values of weight-average molecular weight with the ones measured by the laser light scattering technique.

## 1. Introduction

The most common commercial fluoroelastomers are made of vinylidene fluoride (VDF), hexafluoropropylene (HFP), and sometimes tetrafluoroethylene (TFE). It is well-known that VDF-based copolymers are branched, and depending upon the polymerization conditions, gelled polymeric fractions can be detected.[1] Long chain branches are formed by transfer to polymer and propagation to terminal double bond reactions as well.[2] Both the reactions involve hydrogen abstraction from the backbone of the macromolecule and, thus, can occur only in the presence of VDF units.

This work is focused on a commercial fluoroelastomer, made of VDF, HFP, and TFE, whose trade name is TECNOFLON P757. This terpolymer is synthesized with the Ausimont proprietary *branching & pseudoliving* technology.[3,4,5] This new technology uses the pseudoliving kinetic evolution of the reaction together with a controlled branching mechanism to design the desired polymer molecular weight distribution (MWD). The polymerization reaction is carried out in the presence of a fluorinated diiodurate that ensures the pseudoliving conditions, and of a fluorinated diolefin through which a strictly controlled amount of long chain branches is formed. As a consequence, the frequency of long chain branches in the macromolecules can be significant because, besides the branching mechanisms typical of VDF-based polymers, branching points are also formed by the diolefin.

The processing as well as the mechanical properties of the terpolymer are deeply influenced by the branches from the diolefin. Actually, the broadness of the molecular weight distribution caused by the diolefin enhances the processing behavior of the polymer. Furthermore, the partially cross-linked structure obtained with the *branching & pseudoliving* technology guarantees better mechanical and sealing properties of the final product. However, if the amount of the diolefin in the polymer is too high, gelled fractions are produced, and the polymer is commercially useless. Accordingly, it is of great importance to have available a technique for evaluating with accuracy the amount of long chain branching in the polymer. In this connection, it is well-known that size exclusion chromatography (SEC) analysis is inadequate to provide accurate evaluation of the MWD of highly branched polymers. Actually, SEC separates the macromolecules according to hydrodynamic volume, and thus, a relationship between hydrodynamic volume and molecular weight is needed. A well-defined relationship exists only for linear polymers, while in the case of branched macromolecules, the relationship between hydrodynamic volume and molecular weight is complex and almost unpredictable. Several approaches have been proposed in the literature to evaluate the MWD of branched polymers. The most direct method uses SEC analysis with three detectors, namely refractive index, viscosimeter, and laser light scattering.[6] In the case of fluoropolymers, however, the refractive increment is very low and the use of an on-line laser light scattering is critical. Actually, the low intensity of the scattered light coupled with the low polymer concentration typical of the fractions coming from the SEC columns make the on-line laser light scattering measurements very difficult. Other approaches use SEC analysis with refractive index and viscosimeter detectors.[7] Finally, some methods use SEC with a single detector. In this case, indeed additional information relative to the entire polymer sample (usually intrinsic viscosity) is needed.[8,9]

Following the Ram−Miltz approach,[9] in this work the MWD of branched fluorinated polymers is obtained by combining SEC analysis with the measure of the intrinsic viscosity of the whole polymer. To highlight the effects of long chain branches, each polymer sample has been fractionated and the high molecular weight frac-

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**Table 1. Reaction Recipes**

| sample | initiator (g/L) | $C_6F_{12}I_2$ (g/L) | diolefin (g/L) | pressure (atm) | temp (°C) | conversion (g/L) |
|---|---|---|---|---|---|---|
| A | 0.10 | 3.0 | | 20 | 80 | 300 |
| B | 0.05 | 3.0 | | 20 | 80 | 300 |
| C | 0.05 | 3.0 | | 20 | 80 | 300 |
| D | 0.05 | 3.0 | 1.0[a] | 20 | 80 | 300 |
| L | 5 | 30.0[b] | | 30 | 50 | 50 |

[a] Introduced in 20 steps of 5% each, every 5% of conversion. [b] Introduced in 5 steps of 20% each, every 20% of conversion.

tions, as well as the entire sample, have been analyzed. The suitability of the adopted approach, has been verified by comparing the obtained value of weight-average molecular weight, $M_w$ with the absolute value of $M_w$ measured by laser light scattering technique (LLS).

## 2. Experimental Section

**2.1. Polymerization Reactions.** The polymerization reactions have been carried out in a 10 L pilot plant reactor (Ausimont laboratories, Bollate, Italy) made of 316 stainless steel. Details concerning the polymerization reactor are reported in Apostolo et al.[2]

During the polymerization reaction, a mixture with an appropriate composition of the gaseous monomers is continuously fed to the reactor in order to keep the pressure constant. This procedure allows the production of a copolymer with constant composition throughout the entire polymerization reaction.[10] The monomer feed flow rate is monitored on-line through a flowmeter. It is worth noting that, since the reaction is carried out at constant pressure and the monomer solubility in the reacting system is negligible, the monomer feed flow rate is substantially equal to the reaction rate. Thus, the flowmeter provides the on-line monitoring of the reaction conversion.

The composition of all the polymer samples is 72/18/10 mol % VDF/HFP/TFE. The reaction recipes are shown in Table 1. The first three samples (A−C of Table 1) have been polymerized using the pseudo-living technique:[11] an iodine chain transfer agent is used to establish pseudo-living conditions and the reaction is carried out in microemulsion environment in order to obtain an acceptable reaction rate. A full description of this polymerization technique can be found in Apostolo et al.[12] In the case of sample D of Table 1, the polymerization reaction is performed in the presence of a controlled amount of a fluorinated diolefin (*branching & pseudo-living* technology[3]) in order to increase the number of long chain branches per macromolecule. It should be noted that, taking advantage of the on-line monitoring of polymer conversion, the addition of diolefin and, thus, the polymer branching can be strictly controlled.

Finally, to evaluate the parameters of the Mark Houwink equation (cf. eq 1) for the VDF/HFP/TFE 72/18/10 mol % terpolymer, a linear terpolymer has been synthesized (sample L). To reduce as much as possible the long chain branches, the polymerization has been carried out al low temperature (50 °C), high pressure (30 bar), and low conversion (50 g/L). To obtain a broad molecular weight distribution, suitable of fractionation in several fractions of different molecular weight, a big amount of iodine transfer agent was introduced in five steps (20% of transfer agent every 20% of conversion) during the polymerization reaction.

**2.2. Polymer Sample Fractionation.** According to the above-described mechanisms of long chain branching formation, the number of branches per macromolecule increases with the molecular weight of the polymer chain. Thus, to investigate the effect of long chain branching on the polymer MWD, the polymer samples have been fractionated by the solvent−nonsolvent method[13,14] using the pair methylethyl ketone−cyclohexane as described by Giannotti et al.[15] A single fraction of high molecular weight for each sample has been obtained (see Figure 1). In the following, we will refer to the high molecular weight fraction of samples A−D as samples A′−D′.

The same fractionation technology has been adopted for the linear terpolymer (sample L of Table 1). In this case, eight fractions of different molecular weight with polydispersity index between 1.1 and 1.3 have been collected (cf. Table 2).

**2.3. Polymer Characterization.** Size exclusion chromatography (SEC) was performed at 30 °C in tetrahydrofuran (THF) using a Waters pump (model 590), a refractive index detector (HP 1047A) and four packed columns, Ultrastyragel styrene−divinylbenzene, of porosities $10^3$, $10^4$, $10^5$, and $10^6$ Å, respectively. The eight fractions of the linear terpolymer, sample L, have been used to assess the required calibration curve as discussed in the next section.

Intrinsic viscosities in THF were determined on fractions and on unfractionated polymers at 30 °C in THF using an Ubbelohde viscosimeter coupled with a Schott Gerate AVS automatic viscosimeter. At least three concentrations were used with relative viscosities ranging between 1.2 and 1.8. Intrinsic viscosity was obtained by extrapolation to zero concentration of both specific and inherent viscosities.

The refractive index increment ($dn/dc$) was determined in THF at 25 °C at 546 nm by means of a Brice-Phoenix differential refractometer.

Light scattering measurements were carried out at 25 °C using a Spectra Physics 2020 argon-ion laser operating at 514.5 nm with a BI2030AT correletor and BI200SM goniometer (Brookhaven Instrument Co.). It should be noted that laser light scattering analysis on fluoropolymers is critical because the refractive increment of such polymers is very low. For this reason, to increase the intensity of the scattered light, the laser light scattering apparatus here adopted works with a green light source instead of the more usual red light. All the polymer solutions in THF were filtered through a 0.2 $\mu$m Millipore filter directly into a cylindrical cell located in a temperature bath circulating with a fluid having a refractive index matched to that of the scattering cells. Scattered intensities were measured at eight different angles in the range 30−135° and at different concentrations below the critical concentration $c^*$, where the polymer coils start to overlap. The value of $c^*$ has been evaluated as the inverse of the intrinsic viscosity.[16,17] The set of experimental data obtained at different concentrations and angles of observation were processed by the Zimm method,[18] and eventually, the absolute value of weight-average molecular weight has been obtained.

In all cases, the THF used was Baker RPE grade CAS[109-99-9]

$F^{19}$ NMR analysis of the polymer fractions was performed with a Varian Unity 300 instrument operating at 300 MHz to determine the polymer composition.

## 3. MWD and Long Chain Branching Evaluation

SEC analysis provides the distribution of the hydrodynamic volume ($v_i$) of the macromolecules because it separates the polymer chains according to their hydrodynamic volume. Benoit and co-workers[19] suggested that the hydrodynamic volume defined according to the Einstein law ($v_i$ proportional to the product between the molecular weight, $M$, and the intrinsic viscosity, $[\eta]$) could be used as a universal calibration parameter. This empirical suggestion turned out to correlate fairly well for a wide variety of polymers. The Einstein law, together with the empirical eq 1 (well-known as the Mark−Houwink equation) are then used to evaluate the MWD of *linear* polymers.

$$\ln([\eta]) = \ln(k) + \alpha \ln(M) \tag{1}$$

In eq 1, $k$ and $\alpha$ are the Mark−Houwink coefficients. In the following, this procedure will be called the *MH* approach.

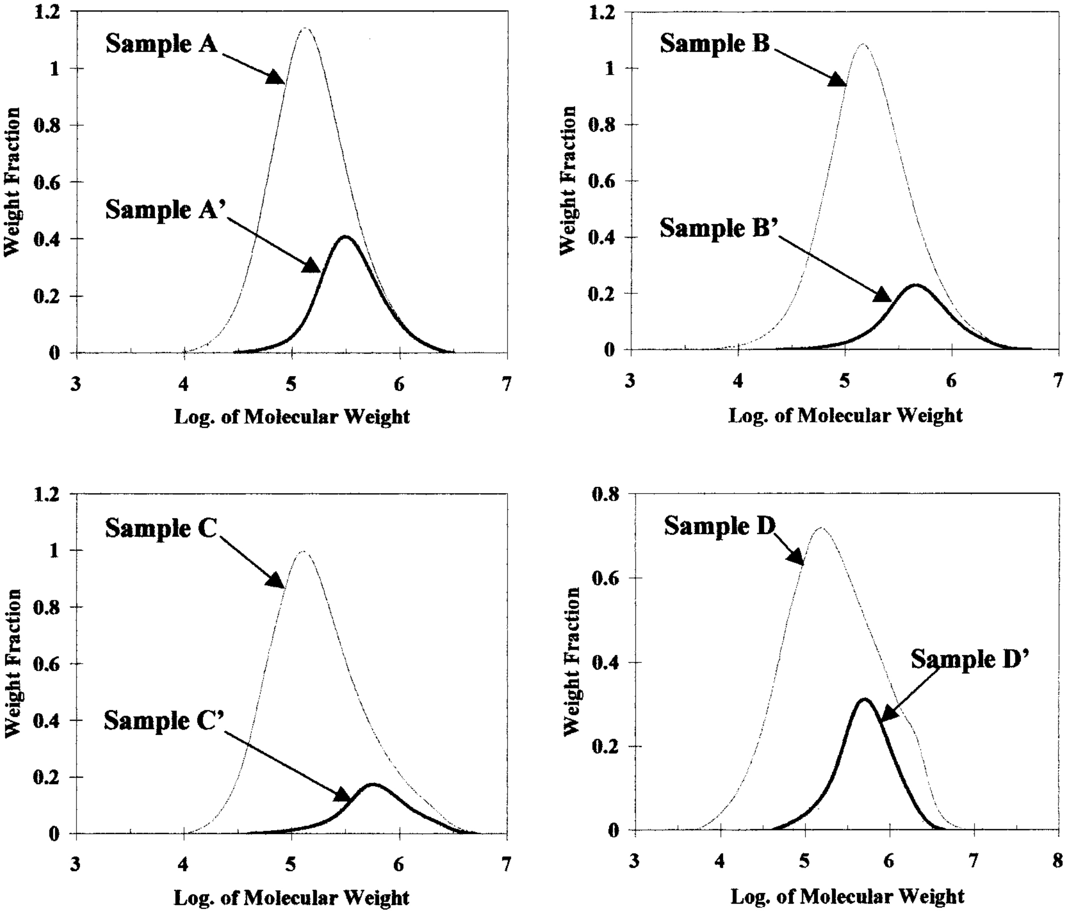

**Figure 1.** MWDs of polymer samples. Thin lines: Overall MWDs (samples A−D). Thick lines: MWDs of the high molecular weight fractions obtained by polymer fractionation (samples A′−D′).

**Table 2. Weight-Average ($M_w$) and Number Average ($M_n$)[a] Molecular Weights of Sample L Fractions**

| fraction | $M_n$ | $M_w$ | $M_w/M_n$ |
|---|---|---|---|
| 1 | 429 200 | 538 200 | 1.25 |
| 2 | 151 300 | 196 200 | 1.30 |
| 3 | 69 200 | 84 300 | 1.22 |
| 4 | 54 700 | 63 000 | 1.15 |
| 5 | 45 000 | 51000 | 1.13 |
| 6 | 38 300 | 43 000 | 1.12 |
| 7 | 32 400 | 36 300 | 1.12 |
| 8 | 28 000 | 30 600 | 1.09 |
| unfractionated | 35 400 | 208 000 | 5.88 |

[a] From GPC according to calibration curve of Figure 2.

In the case of a branched polymer, a unique relationship between the hydrodynamic volume and the molecular weight does not exist because the hydrodynamic volume of the polymer chain depends also on the number of long chain branches. To overcome this problem, in this work the Ram and Miltz approach[9] has been adopted. It is based on the observation that for a wide variety of branched polymers the relationship between the experimental values of $M$ and $[\eta]$ is well described by the following polynomial expression:

$$\ln([\eta]) = \ln(k) + \alpha \ln(M) + \beta \ln(M)^2 + \frac{\beta}{\ln(M_0)} \ln(M)^3 \tag{2}$$

where $M_0$ is the value of molecular weight below which all the polymer chains are assumed linear. Additional information for the whole polymer (usually the intrinsic viscosity) is used to evaluate through an iterative procedure the value of the unknown parameter, $\beta$. In the following this will be called the *MHM* approach.

The average number of long chain branches per macromolecule has been obtained by using the approach proposed by Zimm and Stockmayer.[20] During the VDF/HFP/TFE polymerization reaction some trifunctional branch units, $B_3$ can be produced by two different kinetic events: (i) the transfer to polymer reaction and (ii) the propagation to terminal double bond reaction.[2] The average number of $B_3$ units of each polymer fraction eluted by the GPC columns is calculated by solving the following equation:

$$g = \left[\left(1 + \frac{B_3}{7}\right)^{1/2} + \frac{4B_3}{9\pi}\right]^{-1/2} \tag{3}$$

Here $g$ is the ratio of the square radius of the branched macromolecule to that of a linear macromolecule. It should be noted that $g$ is equal to 1 when the polymer is linear, while it is less than 1 if the polymer is branched

$$g = 1 - \Delta g_3 \tag{4}$$

where $\Delta g_3$ is the deviation of $g$ from 1 due to the trifunctional branch points. Experimentally, the value of $g$ is readily obtained through the equation

$$g = \left[\frac{[\eta]_b}{[\eta]_1}\right]^{1/\epsilon} \tag{5}$$

where $[\eta]_b$ is the intrinsic viscosity of the branched polymer (calculated by eq 2), $[\eta]_l$ is the intrinsic viscosity of the polymer assumed linear (calculated by eq 1), and $\epsilon$ is an a dimensional coefficient lying between 0.7 and 1.3 (see Hamielec[7]).

Finally, the average number of trifunctional branches for the whole polymeric population, $\bar{B}_3$ is obtained by integrating the values related to each polymer fraction

$$\bar{B}_3 = \int_{\nu_i} \frac{fB_3}{M_n} \, d\nu_i \Bigg/ \int_{\nu_i} \frac{f}{M_n} \, d\nu_i \tag{6}$$

where $f$ is the normalized mass concentration detector response, $M_n$ is the average number molecular weight of the eluted fraction and $\nu_i$ is the elution volume.

When the polymerization reaction is carried out in the presence of the diolefin, besides the $B_3$ units, also tetrafunctional branch units, $B_4$, are produced. In this case, the deviation of the intrinsic viscosity/molecular weight relationship from the linearity (in the double logarithmic scale) is due to two different sources: the $B_3$ and the $B_4$ branches units as well. In other words, the value of $g$, which is equal to 1 for the case of linear polymers, is now less than 1 because of two different contributions: one ($\Delta g_3$) due to the trifunctional branching units, and another one ($\Delta g_4$) due to the tetrafunctional branching units. The relationship between $g$ and the two contributions, $\Delta g_3$ and $\Delta g_4$, is not known. In this paper, as a first assumption, we use the following linear relationship:

$$g = 1 - \Delta g_3 - \Delta g_4 \tag{7}$$

The utilization of such a linear equation is supported by the very low branching frequency of the fluoropolymers we are dealing with (cf. Table 5). Actually, in this narrow range of branching frequency, even if the relationship between $g$ and $\Delta g_3$ and $\Delta g_4$ should not be linear, it could be suitably linearized. To estimate the average number of tetrafunctional branching units, the following approach has been adopted. Two polymerization reactions with the same recipe but in one case with the diolefin and in the other case without the diolefin are carried out. The polymer from the reaction without the diolefin has only $B_3$ branch units, while the polymer with the diolefin has both $B_3$ and $B_4$ units. It is now reasonable to assume that, for each eluted fraction, the amount of $B_3$ units is the same in the two polymers because is not affected by the presence or absence of the diolefin. Accordingly, the polymer without the diolefin is used to evaluate the $B_3$ branch units amount and the value of $\Delta g_3 = 1 - g$. Then, the $\Delta g_3$ value so obtained is summed to the value of $g$ of the polymer with the diolefin, leading to a value, $g'$ where the contribution of the trifunctional branch points has been already accounted for

$$g' = g + \Delta g_3 = 1 - \Delta g_4 \tag{8}$$

The value of $B_4$ for each polymer sample eluted by the GPC columns is finally obtained by solving the equation[20]

$$g' = \left[\left(1 + \frac{B_4}{6}\right)^{1/2} + \frac{4B_4}{3\pi}\right]^{-1/2} \tag{9}$$

Again, the average number of tetrafunctional long chain branches per macromolecule in the whole polymer sample, $\bar{B}_4$ is obtained by integration:

$$\bar{B}_4 = \int_{\nu_i} \frac{fB_4}{M_n} \, d\nu_i \Bigg/ \int_{\nu_i} \frac{f}{M_n} \, d\nu_i \tag{10}$$

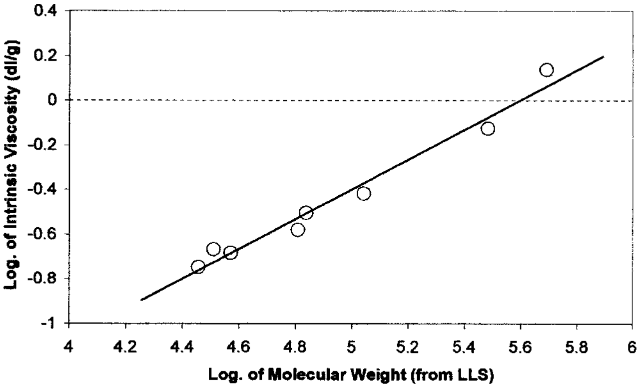

**Figure 2.** Intrinsic viscosity vs weight-average molecular weight from LLS measurements for the eight fractions of the linear terpolymer, sample L.

## 4. Results and Discussion

The fractions of linear terpolymer (sample L) have been used to estimate the Mark–Houwink parameters for the VDF/HFP/TFE 72/18/10 mol % terpolymer. In Figure 2, the intrinsic viscosity of each polymer fraction is plotted as a function of its weight-average molecular weight, $M_w$ obtained by laser light scattering. A linear regression over these data has allowed the estimation the Mark–Houwink parameters:

$$[\eta] = (1.83 \times 10^{-4})M^{0.67} \tag{11}$$

Here $[\eta]$ is expressed in dL/g. It should be noted that since the polymer fractions are almost monodisperse (cf. Table 2), the $M_w$ values of the terpolymer fractions coincide with their average viscosimetric molecular weights that *a rigori* appear in eq 11.

The Mark–Houwink parameters here obtained are very close to the same parameters for VDF/HFP 79/21 copolymers:[15]

$$[\eta] = (1.82 \times 10^{-4})M^{0.69} \tag{12}$$

It has been suggested[21] that the exponent of $M$ is somehow related to the interaction between polymer and solvent. Accordingly, the small diminution of the exponent of $M$ for terpolymers (0.67, cf. eq 11) with respect to that for copolymers (0.69, cf. eq 12) is possibly caused by the presence in the terpolymer of the TFE that reduces the affinity of the polymer with hydrogenated solvents such as THF.

Samples A–D and their high molecular weight fractions (samples A′–D′) have been characterized in terms of SEC and intrinsic viscosity. Furthermore, the composition of all the samples has been measured by $F^{19}$ NMR technique, and the LLS analysis of samples A′–D′ has been carried out.

The intrinsic viscosity, the refractive index, and the composition of the samples are reported in Table 3. The constancy of the polymer composition between the fractionated and unfractionated samples guarantees that the fractionation occurred only on the molecular weight basis and not by polymer composition.

**Table 3. Intrinsic Viscosity ([$\eta$]), Refractive Index (d$n$/d$c$) and Composition by F$^{19}$ NMR of Samples A−D and A′−D′**

| | full samples | | | fractionated samples | | | |
|---|---|---|---|---|---|---|---|
| | A | B | D | A′ | B′ | C′ | D′ |
| [$\eta$] (dL/g) | | 0.771 | 0.943 | 1.073 | 1.421 | 1.623 | 1.240 |
| d$n$/d$c$ | | | | 0.0285 | 0.0270 | 0.0248 | 0.0290 |
| F$^{19}$ NMR | | | | | | | |
| VDF (mol %) | 71.5 | | 71.3 | 71.3 | 72.2 | 71.0 | 72.0 |
| HFP (mol %) | 18.0 | | 17.4 | 18.3 | 17.6 | 18.7 | 17.6 |
| TFE (mol %) | 10.5 | | 11.3 | 10.4 | 10.2 | 10.3 | 10.4 |

**Table 4. Number Average Molecular Weight ($M_n$) and Weight Average Molecular Weight ($M_w$) of Samples B, D, and A′−D′**

| | full samples | | fractionated samples | | | |
|---|---|---|---|---|---|---|
| $M_{n,w}$ ($\times 10^3$) | B | D | A′ | B′ | C′ | D′ |
| $M_n$ from MH | 130 | 108 | 331 | 410 | 486 | 459 |
| $M_n$ from MHM | 131 | 110 | 346 | 422 | 505 | 546 |
| $M_w$ from MH | 306 | 476 | 522 | 726 | 929 | 807 |
| $M_w$ from MHM | 312 | 504 | 555 | 757 | 985 | 1040 |
| $M_w$ from LLS | | | 617 | 798 | 1060 | 1080 |

The SEC analyses of all the samples are collected in Figure 1. The effect of the diolefin on the MWD is clearly visible in sample D of Figure 1: the shape of the MWD in the high molecular weight region testifies the presence in the polymer of a population of very high molecular weight resulting from the long chain branching produced by the diolefin.

When considering the evaluation of the MWD by MHM approach, a remark should be made about the value of $M_0$, i.e., the molecular weight value below which all the polymer chains are assumed to be linear. In the literature, approaches based on a double iteration over $\beta$ and $M_0$ have been proposed.[22] Accordingly, the value of $M_0$ is not an input parameter, but it is a result of the iteration procedure. For the system under examination here, however, a sensitivity analysis has shown that the effect of $M_0$ on the MWD is substantially negligible. As an example, in the case of sample D′, if a value of $M_0 =$ 5000 instead of 1500 is chosen, the change of $M_w$ and $M_n$ is less than 0.2%, while the variation on the average number of branches per macromolecule is less than 5%. For this reason, in all the simulations here performed, the value of $M_0$ has been chosen to be equal to 1500 and the iteration procedure has been performed only on $\beta$.

The $M_w$ and $M_n$ of samples A−D obtained using the MHM approach are compared in Table 4 to the values calculated by the MH approach. It clearly appears that the effect of long chain branching on the MWD is negligible, even in the case of sample D that has been synthesized with the diolefin. This feature is further illustrated in Figure 3, where the MWDs of sample D obtained with MH and MHM methods are superimposed.

On the contrary, in the case of samples A′−D′, the effect of long chain branching on the MWD is not negligible. This feature is detailed in Table 4, where the weight-average molecular weight and the number-average molecular weight obtained by the two approaches (MH and MHM) are compared. In particular it results that the MWD of sample D′ is strongly affected by long chain branches. This is not surprising because, as already said, sample D′ has been synthesized by introducing the fluorinated diolefin during the polymerization reaction. In Figure 4, the MWDs of samples A′−D′ calculated by using the MHM and MH approach are compared. It appears that the long chain branches affect especially the region of high the molecular weights, as expected.

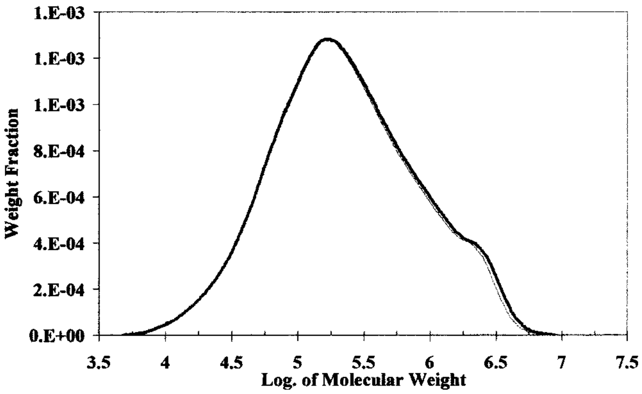

**Figure 3.** MWD of sample D. Thin lines: MWD calculated assuming linear the polymer chains (*MH* approach). Thick lines: MWD calculated assuming branched the polymer chains (*MHM* approach).

In all the four cases examined, the MH approach, by assuming linear the polymer chains, underestimates the high molecular weight fractions. To verify the reliability of the MHM approach, the absolute value of weight-average molecular weight of samples A′−D′ has been estimated by means of the LLS technique. The Zimm plots of the four samples are reported in Figure 5. It is worth noting that, despite the low refractive index value (cf. Table 3), the trend of the double extrapolation is very clear. The measured $M_w$ values are reported in Table 4. It appears that the $M_w$ values from LLS measurements are closer to those obtained using MHM approach than those measured with the MH methodology. This feature is particularly evident in the case of sample D′, where the amount of long chain branching is rather high due to the use of the diolefin during the polymerization reaction. It should be noted that light scattering provides also another way to evaluate the $g$ factor and it could be interesting to compare the $g$ values from LLS with the ones from off-line viscosimetry. However, due to the low refractive index of fluoropolymers, the $g$ values from light scattering turned out to be affected by an error greater than 50%, and thus, they could not be properly compared with the $g$ values from viscosimetry.

The trend of the $g$ factor as a function of the molecular weight of the polymer is shown in Figure 6. The deviation from the value of $g = 1$ (i.e., linear polymer) increases with the molecular weight and is similar for samples A′−C′, while it is much higher for sample D′, that is, the polymer with the diolefin, thus indicating a higher amount of branches per macromolecule.

This is clearly seen in Figure 7, where the number of long chain branching per macromolecule is plotted versus the molecular weight of the polymer chain. The calculation of the branching frequency has been carried out assuming $\epsilon = 1$ (see eq 5). Figure 7 shows that the polymers A′−C′ have a similar behavior, with the content of long chain branches that slightly increases with the molecular weight from 0.2 to about 1.5 branches per macromolecule. On the contrary, sample D′ exhibits an evident higher amount of branching frequency: from 0.5 to 4 branches per polymer chain. As already discussed, this is due to the presence of the diolefin in the polymer.

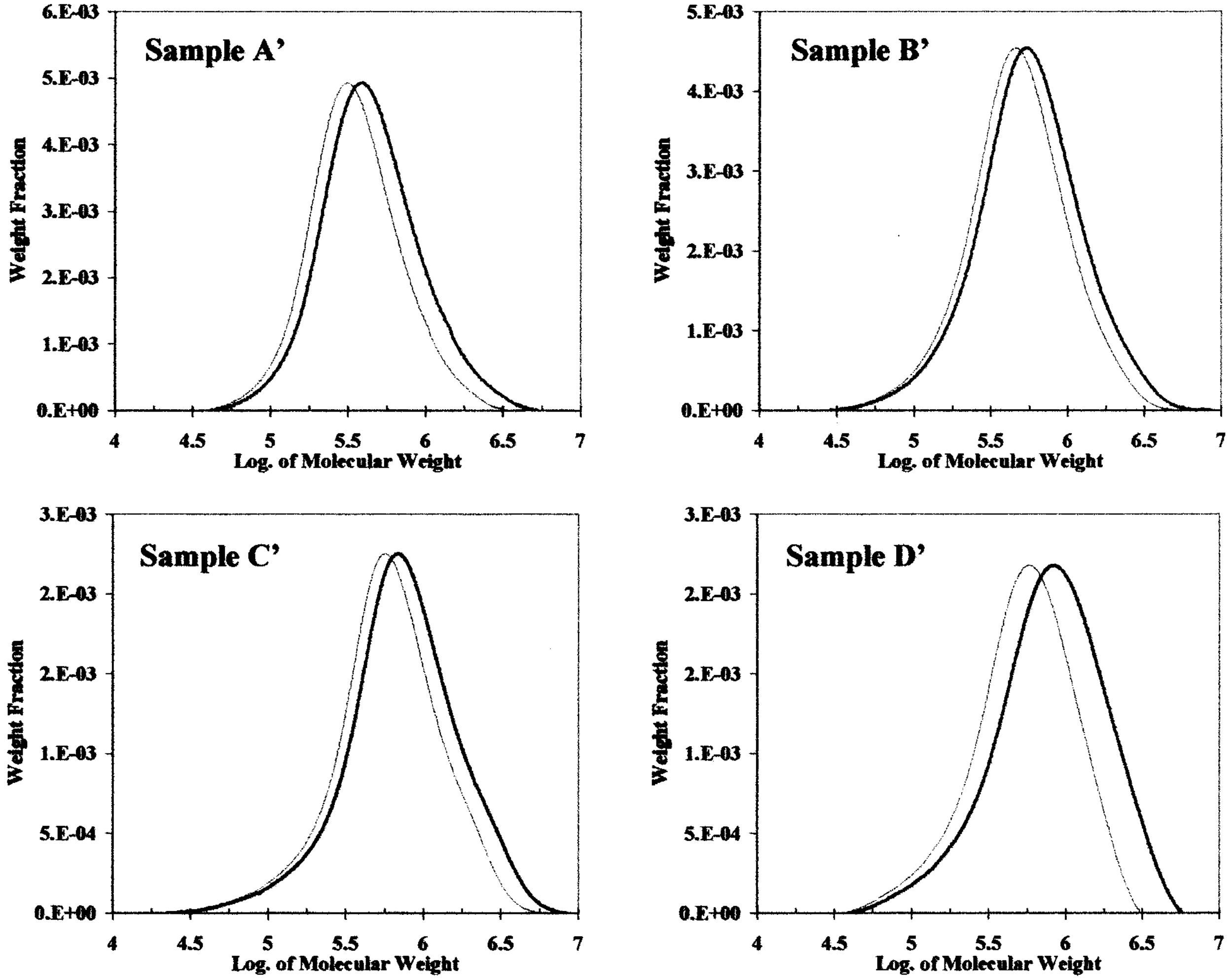

**Figure 4.** MWDs of samples A′−D′. Thin lines: MWD calculated assuming linear the polymer chains (*MH* approach). Thick lines: MWD calculated assuming branched the polymer chains (*MHM* approach).

The average number of long chain branching per macromolecule is reported in Table 5. As described above, all the branches of samples B and A′−C′ are of the trifunctional type. In the case of samples D and D′, indeed, the presence of the diolefin caused the formation also of tetrafunctional branch points. Following the approach depicted in the previous section, sample B and sample C′ have been used to determine the amount of the trifunctional branch points of samples D and D′, respectively. Then, the residual deviation of $g$ from the unity has been attributed only to the tetrafunctional branch units.

The comparison between the number of branches per macromolecule of sample B and B′ as well as D and D′ shows clearly that the polymer fractions at high molecular weight have a tangible higher amount of branches. This is particularly evident for the tetrafunctional branches of samples D and D′, thus suggesting a higher amount of the diolefin in the high molecular weight polymer chains.

It also appears from the data in Table 5 that for the three polymers without the diolefin (samples A′−C′) the branching frequency is comparable, lying between 0.48 and 0.76 branches per macromolecule. On the contrary, in the polymer D′, there is about 1 tetrafunctional branch point per chain besides about 0.66 of the trifunctional branch type.

The average number of tetrafunctional branches per polymer chain measured for sample D is about 0.1. This value can be used to estimate the efficiency of the diolefin with the following procedure. First, by performing the ratio between the polymer produced and the average number molecular weight, $M_n$, the overall number of polymer chains is obtained. Then, the overall number of tetrafunctional branches is calculated by simply multiplying the average number of the tetrafunctional branches per macromolecule by the overall number of macromolecules. From the data of Tables 1 and 4, a value of $2.7e^{-4}$ mol/L of tetrafunctional branches is obtained. This value should be compared to the moles of the diolefin introduced in the reactor. This quantity, which is equal to $2.8e^{-3}$ mol/L, is readily obtained by dividing the amount in grams per liter reported in Table 1, by the molecular weight of the diolefin (i.e., 354 gr/mol). From a comparison of the number of tetrafunctional branches ($2.7e^{-4}$ mol/L) and the number of diolefin molecules introduced in the reactor ($2.8e^{-3}$ mol/L), it appears that only the 10% of the diolefin has produced tetrafunctional branches.

As a final consideration, a mathematical model for the evaluation of the full MWD and the branching distribution of fluorinated polymers produced with the pseudo-living polymerization process has been presented elsewhere by Apostolo et al.[12] The model was there applied to the VDF/HFP 79/21 mol % copolymer system. The application of the model to the system investigated here, that is, the VDF/HFP/TFE 72/18/10 mol % terpolymer, should require the evaluation of the

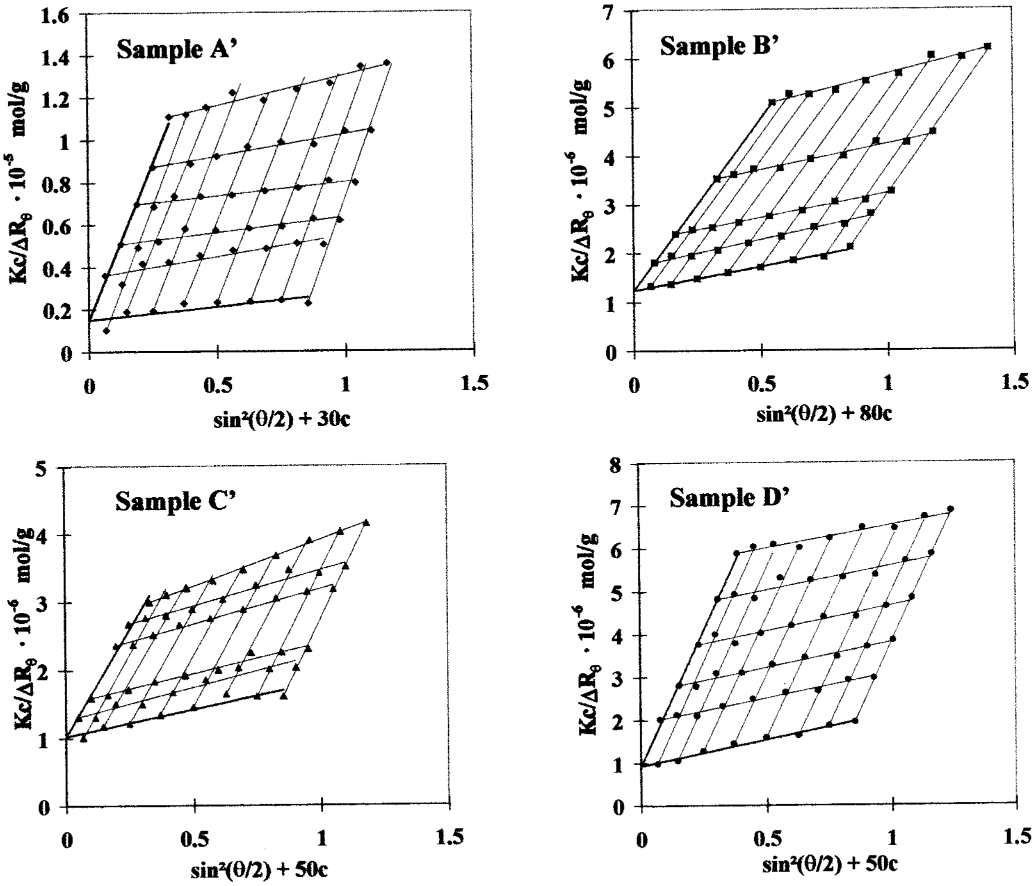

**Figure 5.** Zimm plot of samples A′−D′.

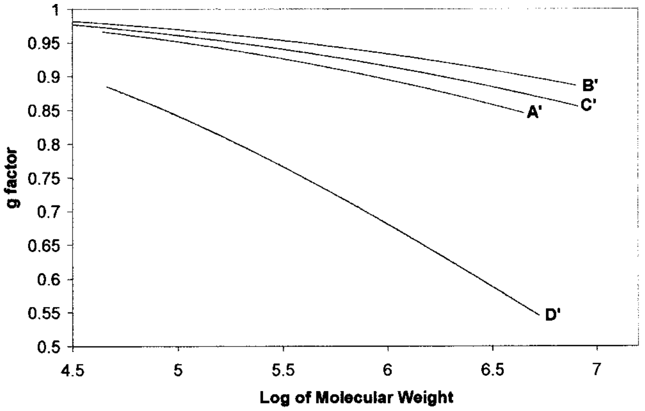

**Figure 6.** Evolution of the *g* factor as a function of the molecular weight for samples A′−D′.

full set of kinetic parameters of TFE and is beyond the objectives of this work. However, a critical examination of the results reported in the cited reference provides some interesting considerations. Actually, the polymerization recipe for reaction B (Table 1) was very close to that of Apostolo et al., with the copolymer composition being the only main difference. The amount of VDF in the polymer is particularly important because the transfer to polymer, which is the most significant source of trifunctional long chain branching, requires the abstraction of hydrogen from the VDF units in the polymer.

Thus, it is reasonable to assume that the branching frequency, calculated in Apostolo et al.[12] for the polymer with 79 mol % of VDF, could be applied to the terpolymer B of this work if the different amounts of VDF in the two polymers are somehow taken into account. This is here done by simply renormalizing, on the different amounts of VDF in terpolymer B, the branching frequency calculated for the copolymer. Accordingly, the value of about 0.5 long chain branches per macromolecule calculated for the VDF/HFP 79/21 mol % copolymer (when conversion is 300 g/L) is modified to about 0.45 branches per macromolecule for the VDF/HFP/TFE

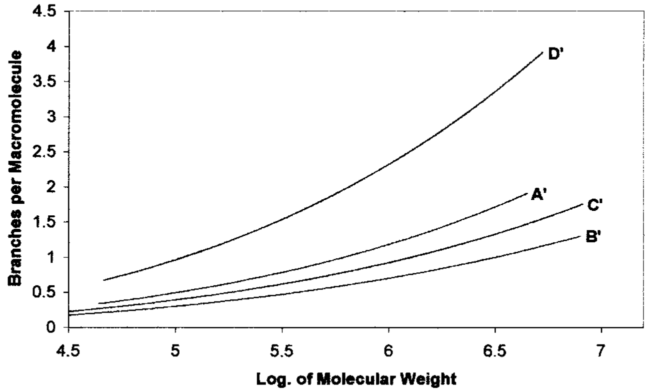

**Figure 7.** Evolution of the average number of long chain branches per macromolecule as a function of the molecular weight for samples A′−D′.

**Table 5. Number Average Long Chain Branching Per Macromolecule of Trifunctional ($\bar{B}_3$) and Tetrafunctional ($\bar{B}_4$) Type of Samples B, D, and A′−D′**

| branches per macromolecule | full samples |  | fractionated samples |  |  |  |
|---|---|---|---|---|---|---|
|  | B | D | A′ | B′ | C′ | D′ |
| $\bar{B}_3$ | 0.22 |  | 0.76 | 0.48 | 0.66 |  |
| $\bar{B}_3 + \bar{B}_4$ |  | 0.30 |  |  |  | 1.70 |

72/18/20 terpolymer. It turns out that this value is of the same order of magnitude of the one obtained in this work for the polymer B, i.e., 0.22 branches per macromolecule (cf. Table 5). This provides another strong support to the reliability of the approach adopted for the branching frequency evaluation.

## Conclusions

In this paper, it has been shown that size exclusion chromatography data coupled with intrinsic viscosity measurements can be used to evaluate the molecular weight distribution and the long chain branching of VDF/HFP/TFE terpolymers. For this purpose, the algorithm formerly applied by Ram and Miltz to the branched hydrogenated polyolefin has been adopted. The reliability of the approach has been validated comparing the weight-average molecular weights with those obtained by laser light scattering technique.

The long chain branching frequency measured using the Ram and Miltz approach has been compared with the values calculated by a mathematical model of the polymerization of fluorinated monomers presented elsewhere by Apostolo et al. The reasonable agreement obtained provides a further support to the consistency of the adopted approach.

Finally, in the case of the polymer sample synthesized in the presence of a diolefin, a procedure able to evaluate separately the amount of tri- and tetrafunctional branching points has been presented. The measured long chain branching frequency has been used to estimate the efficiency of the diolefin to produce tetrafunctional long chain branches.

## References and Notes

(1) Logothetis, A. L. *Prog. Polym. Sci.* **1989**, *14*, 251−296.

(2) Apostolo, M.; Arcella, V.; Storti, G.; Morbidelli, M. *Macromolecules* **1999**, *32*, 989-*1003*.

(3) Arcella, V.; Brinati, G.; Apostolo, M. *Chim. Ind.* **1997**, *79*, 345−351.

(4) Arcella, V.; Brinati, G.; Albano, M.; Tortelli, V.; U.S. Pat. 5 585 449, 1994.

(5) Arcella, V.; Brinati, G.; Albano, M.; Tortelli, V.; U.S. Pat. 5 612 419, 1995.

(6) Zammit, M. D.; Davis, T. P. *Polymer* **1997**, *38*, 4455−4468.

(7) Hamielec, A. E. *Pure Appl. Chem.* **1982**, *54*, 293−307.

(8) Drott, E. E.; Mendelson, R. A. *J. Polym. Sci. A-2* **1970**, *8*, 1361−1371.

(9) Ram, A.; Miltz, J. *J. Appl. Polym. Sci.* **1971**, *15*, 2639−2644.

(10) Apostolo, M.; Morbidelli, M. *Chim. Ind.* **1997**, *79*, 361−367.

(11) Tatemoto, M. in *Proceedings of IX International Symposium on Fluorine Chemistry;* Daikin Koygo Co., Ltd.: Osaka, Japan, 1979.

(12) Apostolo, M.; Arcella, V.; Storti, G.; Morbidelli, M. To be published, 2000.

(13) Flory, P. *Priciples of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.

(14) Kamide, K. *Thermodynamics of Polymer Solutions*; Elsevier Ed.: Amsterdam, 1990.

(15) Gianotti, G.; Leolini, C.; Borghi, D. *Chim. Ind.* **1991**, *73*, 463−468.

(16) Ying, Q.; Chu, B. *Macromolecules* **1987**, *20*, 362−366.

(17) Brown, W. *Dynamic Light Scattering*, Clarendon Press: Oxford, England, 1993.

(18) Zimm, B. H. *J. Chem. Phys.* **1948**, *16*, 1099−1116. Reprinted in: *Light Scattering from Dilute Polymer Solution;* McIntyre, D., Gornick, F., Eds.; Gordon and Breach: New York, 1964; pp 157−174.

(19) Grubisic, Z.; Rempp, P.; Benoit, H. *J. Polym. Sci., Polym. Lett. Ed.* **1967**, *5*, 753−759.

(20) Zimm, B. H.; Stockmayer, W. H. *J. Chem. Phys.* **1949**, *17*, 1301.

(21) Van Krevelen, D. W. *Properties of Polymers*; Elsevier Ed.: Amsterdam, 1976.

(22) Chiunshan, J.; Qipeng, G. *J. Appl. Polym. Sci.* **1990**, *41*, 2383−2390.

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