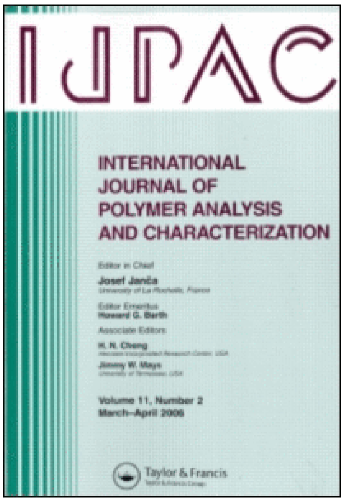

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# Analysis of Star-Branched Polymers with Triple Detection (Refractive Index, Viscometry, Light Scattering) Gel Permeation Chromatography

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This paper deals with the characterization of star-branched model copolymers. The polymer branches are composed of PMMA/PtBuA di-block copolymers of poly(methyl methacrylate) and poly(*tert*-butylacrylate) with well-controlled chemical composition and structure (very low polydispersity). When these copolymer branches are chemically coupled, they produce star-branched copolymers with various numbers of branches. Number-average molecular weights $M_n$ of stars and branches were used to calculate the number of branches of the star-branched copolymers. In order to determine the real structure of the star-branched copolymers, we have measured the branching parameter $g'$ and tested several hypothesis on the relationship which links the number of branches to the branching parameter $g$. The value of the exponent of the $g/g'$ relationship, which characterizes the type of branching, was determined at several conditions. Values were dependent on the branching relationship, however, it was not possible to find an exponent value of 0.5, corresponding to pure star-branched molecules. We could not conclude whether or not the technique of multidetection GPC was not accurate enough to obtain this kind of information or if the studied star-branched copolymers had a complex structure, more complicated than a simple star. Excellent agreement was found between light scattering values and from viscometry with universal calibration. These results demonstrate excellent performance for universal calibration, even for highly branched polymers with unusual viscometric behavior.

KEY WORDS Polymer characterization, size exclusion chromatography, viscometry, light scattering, long-chain branching

## INTRODUCTION

The technique of gel permeation chromatography is the most appropriate method for studying complex polymers with complicated structure. The use of multidetection greatly increases the power of characterization and makes multidetection GPC a useful approach for the characterization of complex polymers. Molecular mass detectors, like light scattering and viscometric detector, provide different information related to polymer structure.

A GPC unit using a refractive index (DRI) and single capillary viscometric detection coupled with an on-line light scattering detector was used for the characterization of star-

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branched model copolymers. The coupling of the DRI with light scattering detection provides average molecular weights, and the use of DRI with viscometric detection allows the determination of branching distribution and the calculation of average molecular weights using a universal calibration curve.

To determine the number of arms of star-branched copolymers, the number average $M_n$ is the key parameter. The light scattering detection is not the most appropriate method to determine this parameter because of the lack of sensitivity in the low-molecular-weight range, but can provide the weight average $M_w$ with better accuracy. Conversely, viscometric detection provides results assuming that universal calibration is valid. Due to the particular structure of the copolymers studied in this work, it was not obvious, at the beginning, that universal calibration could be strictly applied to those macromolecules. Consequently, we have used light scattering detection to determine $M_w$ and compared these values to the ones obtained using viscometric detection. The comparison of $M_w$ allows one to validate the use of universal calibration and, therefore, the use of the number average $M_n$ obtained from viscometric detection to characterize star-branched copolymers and branching information.

## EXPERIMENT

The chromatograph used for this study was a Waters GPC 150CV (Waters Corp., Milford, MA, USA) (differential refractometer (DRI) and single-capillary viscometer (SCV)), equipped with a light scattering (LALLS) detector Chromatix CMX 100 (Chromatix-TSP, Riviera Beach, FL, USA) inserted between the column set and the GPC 150CV detectors. The solvent was tetrahydrofuran (THF) at 40°C and a flow rate of 1 mL/min. THF was filtered using Millipore membrane type FH (Millipore, Bedford, MA, USA) and stabilized by Ionol at a concentration of 0.04 wt%. The columns used were a set of Waters Ultrastyragel ($10^3$, $10^4$, $10^5$ and $10^6$ Å, 1 ft). The narrow standards used for calibration were a set of narrow polystyrene (TSK from Toyo Soda, Japan) with molecular weights ranging from 3,000 to $3 \times 10^6$ g/mol.

The concentration detector was a differential refractometer "prototype #4". The reason for the special differential refractometer prototype is that it has been shown that the standard DRI detector may lead, in certain conditions, to erroneous results in viscosity calculations because of the occurrence of a small flow fluctuation, ("Lesec effect"), which distorts the experimental viscosity profile when the polymer flows across the detectors [1–3]. This effect is shown in Figure 1 where it has been exaggerated to produce a visible distortion. This very small flow fluctuation is induced by the change in viscosity and, accordingly, in pressure drop when the polymer solution flows through the detector and corresponds to the compliance of the GPC system when a change in pressure drop occurs. This small flow fluctuation is enough to produce a small peak distortion which looks like an apparent shift downstream of the viscometer peak. This effect leads to a small rotation of the viscosity-molecular weight relationship and a decrease of the Mark-Houwink exponent $a$ for linear polymers, as shown in Figure 2, or a distortion of the viscosity for branched polymers. The main consequence of this effect, which has been previously described [1–3], is an apparent shift downstream of the viscometer peak. One possible way to correct this effect is to manipulate the interdetector volume correction by applying a smaller value than the real one. By

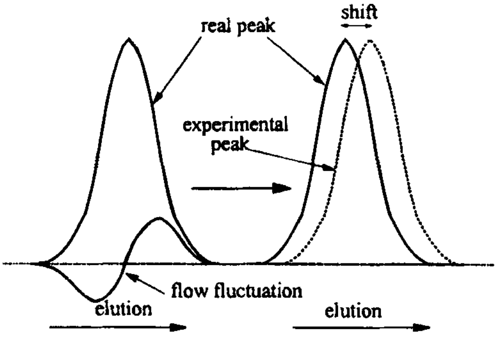


FIGURE 1 Viscometer profile distortion by a flow fluctuation.

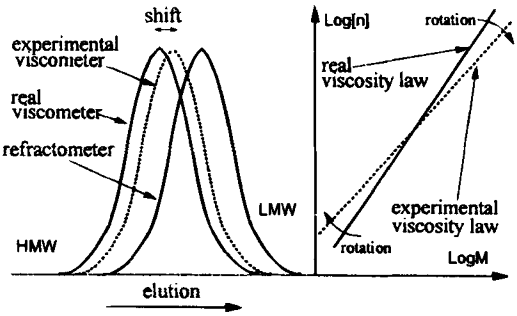


FIGURE 2 Viscometer peak shift and rotation of the Mark-Houwink law.

this way, the viscometer peak is roughly moved at the right place, but it is sometimes necessary to apply a negative volume correction, the viscometer peak shift being larger than the interdetector volume.

Unfortunately, this effect is very difficult to control since it is dependent on several parameters that are linked to sample conditions. It depends particularly on the sample specific viscosity (molecular weight and concentration) and on its polydispersity; the greater the specific viscosity, the greater the effect, as shown in Figure 3, and the lower the polydispersity, the smaller the effect as shown in Figure 4. Since conditions are different for every sample, it is obvious that the interdetector volume correction cannot be widely applied. The only real solution is to eliminate this effect. For this reason, DRI prototypes were designed to reduce this effect. A special geometry was used to reduce the pressure drop in the detector and also decrease the void volume. The prototype used in this study is "prototype DRI #4". A similar design is used in the new Waters GPC 150CVplus, details on this DRI design will be published later [4].

The GPC software used was the "Multidetector GPC software", a PC-DOS software written for triple detection GPC [5–6]. For data acquisition, the PC computer is connected to the 150 CV and the CMX. 100 through a IEEE488 board (CEC, Capital Equipment Corporation, Burlington, MA, USA) and a scanner multimeter Keithley 199 (Keithley, Cleveland, OH, USA). Molecular weights are calculated using both the LALLS detection and the viscometric detection with a combination of the classical molecular weight cali-

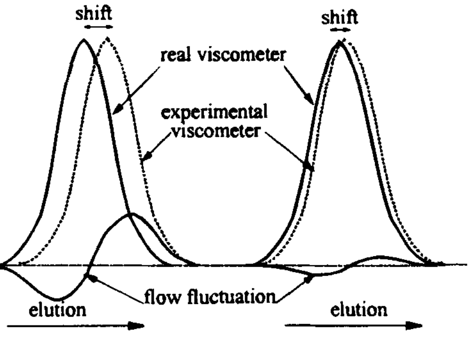


FIGURE 3 Influence of specific viscosity on apparent viscometer peak shift.

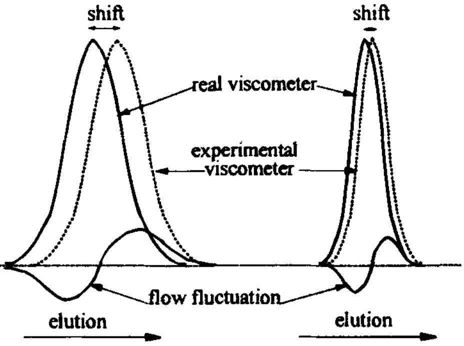


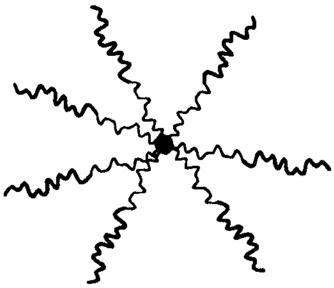
FIGURE 4 Influence of polydispersity on apparent viscometer peak shift.

bration curve and the Mark-Houwink relationship of the standards. This procedure is equivalent to the use of a unique universal calibration curve [5–6].

## MATERIALS

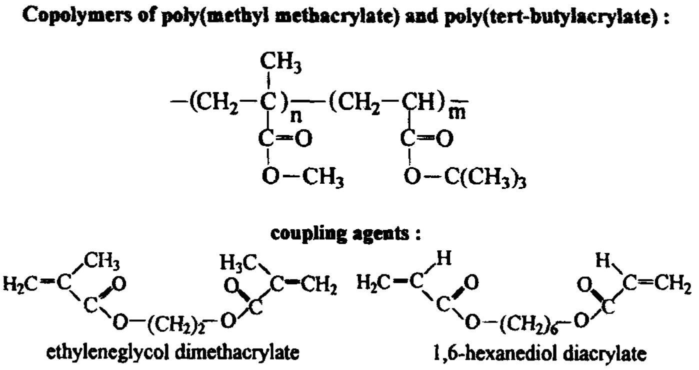
The star-branched polymers are copolymers of methyl methacrylate (PMMA) and *tert*-butylacrylate (PtBuA), their structure is represented in Figure 5. The polymer arms are composed of PMMA/PtBuA di-block copolymers with well-controlled chemical composition and structure. They were synthesized by *M*. Patin in the laboratory of P. Teyssié in Liège University (Belgium), using the usual sequential anionic addition polymerization which provides di-block copolymers with a low polydispersity [7–8]. The star-branched copolymers were obtained by coupling the living linear di-block copolymers by a coupling agent like ethylene glycol dimethacrylate (EGDMA) or 1,6-hexanediol diacrylate (HDODA), whose chemical structures are represented in Figure 6. Several well-defined star-branched copolymers were prepared with different arm lengths and different chemical compositions. Their characteristics are described in Table I.

Arm of PMMA and PtBuA di-block copolymer



Star-branched copolymer

FIGURE 5 PMMA-PtBuA arm and star representations.



$$-(CH_2-C(CH_3)(C{=}O\text{–}O-CH_3))_n-(CH_2-CH(C{=}O\text{–}O-C(CH_3)_3))_m-$$

FIGURE 6 Chemical structure of copolymers and coupling agents.

TABLE I

Composition of the different star-branched copolymers.

| Sample | $M_n$ PMMA | $M_n$ PtBuA | % PMMA in arm |
|---|---|---|---|
| PM4 | 4150 | 18250 | 22.5 |
| PM1 | 6390 | 21130 | 23.2 |
| PMA | 8120 | 9980 | 44.7 |
| PM25 | 20200 | 20900 | 49.2 |
| PM2 | 16730 | 14460 | 53.6 |
| PM3 | 16530 | 7400 | 68.2 |

During the synthesis, an aliquot of the reaction medium was drawn from the reactor before the coupling reaction and purified to obtain a small amount of the pure linear copolymer corresponding to the arm of the star-branched copolymer for every sample. These compounds were carefully characterized by GPC and were used to interpretate GPC experiments the on star-branched copolymers.

Since the coupling reaction is not fully efficient, the star-branched copolymers were not pure and contained a non negligible amount of uncoupled linear copolymer. A purification step was necessary to reduce the amount of linear chains and to obtàin the star-branched copolymers as pure as possible. Linear copolymer chains were extracted by fractional precipitation using different solvent/non-solvent methods [7–8].

## METHODS

The problem of determining the average number of branches of a star-branched polymer is theoretically simple. It is the ratio of the number average molecular weight $M_n$ of the star polymer to that of the uncoupled linear arm. In fact, the problem is more complicated experimentally since the branched copolymers contain a residual amount of unused linear branches, even after purification. Fortunately, these two materials have significantly different molecular weights and they elute separately as shown in Figure 7. Consequently, it is possible to perform the GPC analysis of the star peak only without interference from linear molecules. The important issue is that the branched copolymer contains uncoupled linear arms as an "impurity" and this weight must be taken into account. Accordingly, the real concentration of the star copolymer is not known exactly, which can result in significant errors when using molecular mass detectors.

We have used a method for determining the sample concentration independent of knowing the exact sample concentration. This method consists of calibrating the DRI response *R* using a polystyrene sample (Dow 1683) with a well-known refractive index increment *dn/dc* to determine the DRI *K* constant. The relationship is given below where *K* is the calibration constant and *c* the sample concentration:

$$R = K \bullet dn/dc \bullet c \tag{1}$$

By using *K*, it is then possible to measure the *dn/dc* of each arm copolymer since they are pure and their concentrations are known. Finally, assuming that the *dn/dc* of the star copolymer is close to the one of the arms (there is only a few amounts of coupling agent), it is just necessary to set the software in the "concentration correction" mode to determine the correct slice concentration using the DRI signal, *K* and *dn/dc*. This corrected slice concentration is then used in light scattering calculations to determine the molecular weights, and in viscosity calculations to obtain the right slice intrinsic viscosity and also molecular weights. The *dn/dc* of the different branch copolymers are represented in Figure 8 as a function of the PMMA content.

Figure 7 shows that the star-branched copolymer PM25 gives a broad GPC peak which indicates a high polydispersity, the same holds true for the other samples. The only possible explanation is that star-branched copolymers are a mixture of different stars with a various number of arms. In that case, as the composition, and accordingly the *dn/dc*, of the

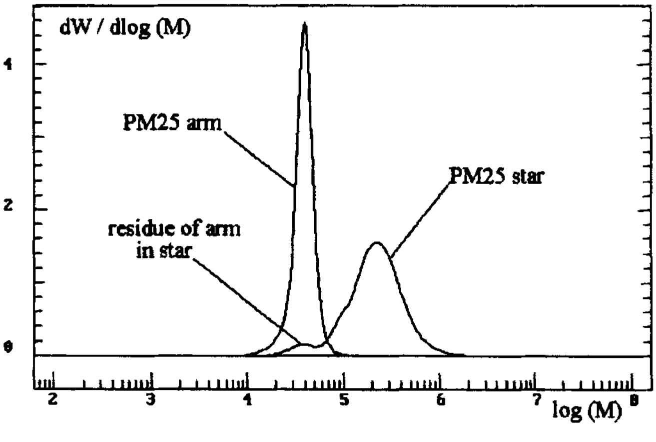


FIGURE 7 Overlay of the distributions of the PM25 arm and the PM25 star.

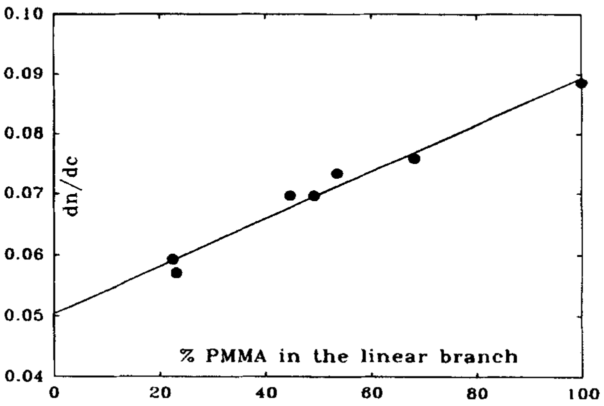


FIGURE 8 *dn/dc* variations of arm copolymers as a function of PMMA content.

arm is well-controlled, the star-branched copolymers should have the same *dn/dc* as the corresponding arm. That means that we can assume that *dn/dc* is constant along the distribution and use it in light scattering calculations.

The GPC instrument was calibrated using TSK narrow standards to provide a universal calibration curve. To check the GPC system, especially the performance of the viscometric detector and the refractometer "prototype #4", we compared the polystyrene Mark-Houwink coefficients obtained using the TSK narrow standards, represented in Figure 9, and the one obtained with a linear broad molecular weight polymer, polystyrene Dow 1683 represented in Figure 10, where interdetector volume correction was applied using the exact interdetector volume. Similar Mark-Houwink exponents *a* were obtained (0.715 and 0.717), confirming the reliability of this GPC instrument and the parameters used for calibration [9].

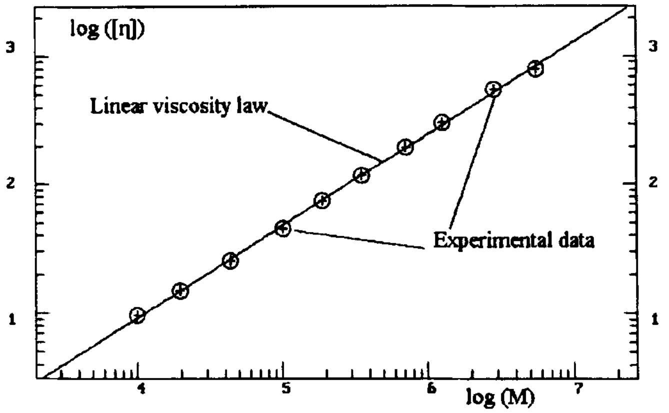


FIGURE 9 Viscosity law of TSK narrow polystyrene standards. (log ($K$) = −1.8995, $a$ = 0.715)

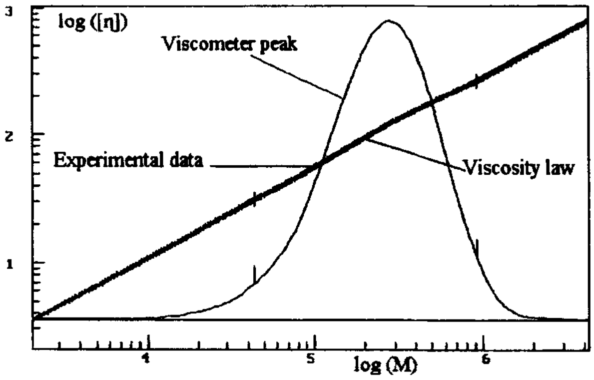


FIGURE 10 Viscosity law of the linear broad polystyrene Dow 1683. (log ($K$) = −1.8367, $a$ = 0.717)

## RESULTS

The chromatograms of the linear-arm copolymer corresponding to sample PM1 are represented in Figure 11. The three peaks nearly overlay completely, which indicates a low polydispersity, experimentally measured as 1.06. Conversely, the chromatograms of the star-branched sample PM1 are represented in Figure 12 and look completely different. The LALLS peak is normally shifted towards the high-molecular-weight region, but the viscometer peak is extremely close to the DRI peak, which is very unusual. Usually, the viscometric response is close to the light scattering response, the former response being proportional to $c \cdot [\eta]$ (that is $c \cdot M^{0.7}$), the latter response being proportional to $c \cdot M$ ($[\eta]$ is the intrinsic viscosity), as shown in Figure 13 for the linear broad-molecular-weight polystyrene Dow 1683. The particular behavior of these star-branched copolymers is due to the high degree of long-chain branching that tremendously reduces their viscosity behavior as a function of molecular weight.

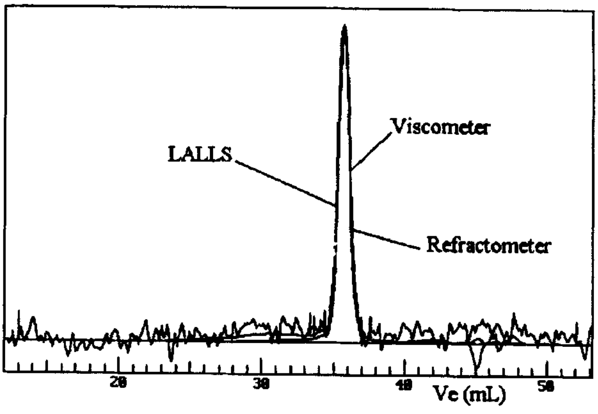


FIGURE 11 Chromatograms of the arm copolymer corresponding to PM1.

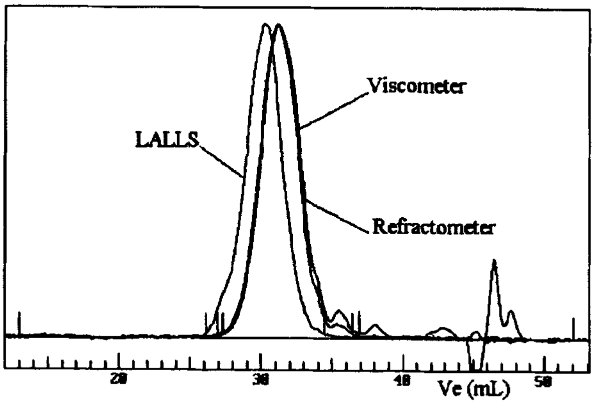


FIGURE 12 Chromatograms of the star-branched copolymer PM1.

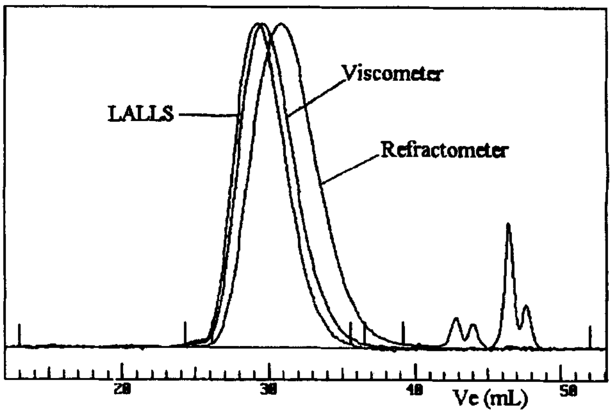


FIGURE 13 Chromatograms of the linear broad polystyrene Dow 1683.

Intrinsic viscosity variations of PM1 star-branched copolymer versus elution volume are represented in Figure 14. A highly distorted curve occurs with regard to linear macromolecules, due to the high degree of long-chain branching of this sample. The same occurs for intrinsic viscosity variations versus *logM* which are plotted in Figure 15 where the experimental viscosity/molecular weight relationship is compared to the one of the arm (linear) to determine the branching distribution $g'_i$ (where $g'_i = [\eta]_{br}i/[\eta]_{lin}i$ intrinsic viscosities of the branched and the linear polymer respectively, at the same molecular weight $M_i$). These plots confirm the highly branched behavior of these molecules since $g_i$ strongly decreases to around zero for high molecular weights.

For comparison, we have plotted in Figure 16 the same branching representation for a well-known long-chain branched polymer, the low-density polyethylene NBS 1476 [9]. The comparison shows the difference in long-chain branching between the two samples, the PM1 sample being obviously more branched than the NBS 1476.

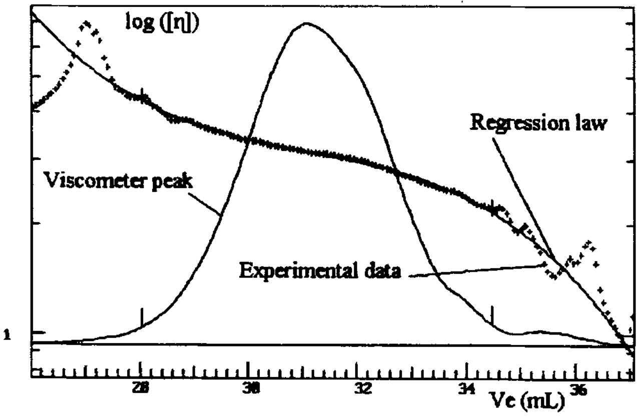


FIGURE 14 Viscosity variations of the star-branched polymer PM1. PM1 viscosity peak and log $[\eta]_i$ versus elution volume.

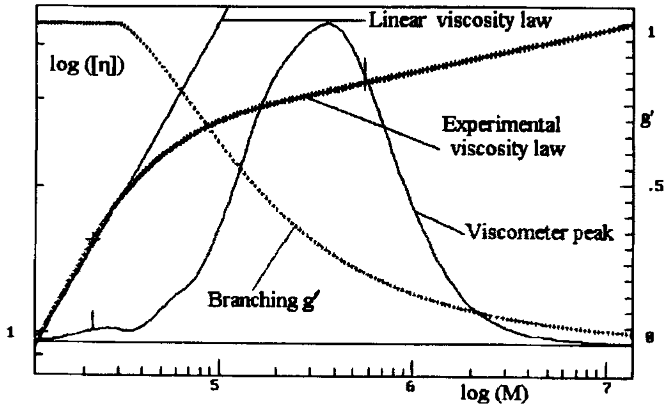


FIGURE 15 Viscosity law of the star-branched polymer PM1. log $[\eta]_i$ and $g'_i$ branching distribution versus molecular weight. (log $K = -1.8550$, $a = 0.698$)

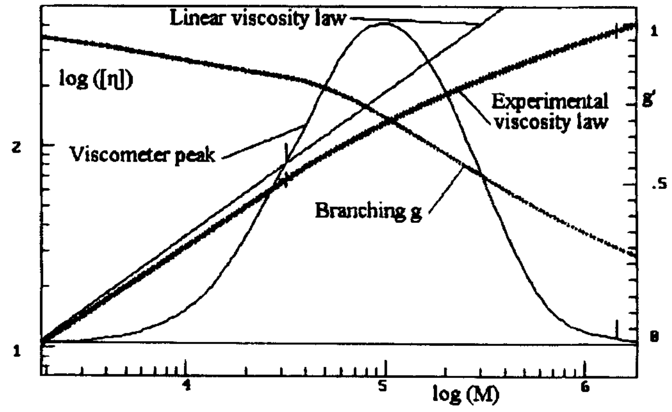


FIGURE 16 Viscosity law of the branched polyethylene NBS 1476. log [$\eta$], and $g'$, branching distribution versus molecular weight. (log $K = -1.3087$, $a = 0.715$)

The results of the analysis of the arm starting material copolymers ($M_n$, $M_w$, and polydispersity $I_w$) are given in Table II for both the viscometric ($V$) and the light scattering ($L$) detectors. Excellent agreement is found between these values, and the polydispersity was low which confirms the highly controlled structure of the linear copolymers.

The results of the analysis of star-branched copolymers are given in Table III for both the viscometric ($V$) and the light scattering ($L$) detectors. The numerical values are in good agreement, especially for the $M_w$ values. These results confirm that universal calibration is perfectly valid for branched molecules, even for a high degree of long-chain branching. Measured polydispersities $I_w$ vary from 1.3 to 2.3, which confirms that star-branched copolymers are composed of different stars, having a various number of arms.

It is interesting to point out that light scattering detection is usually not very accurate for the analysis of polydisperse copolymers since $dn/dc$, which is a key parameter in light scattering experiments, generally varies along the molecular weight distribution. In the particular case of these star-branched copolymers, the composition of the arm is well controlled and the molecular weight polydispersity only comes from the polydispersity in the number of arms. That means that we can assume that $dn/dc$ is constant along the distribution and use it in light scattering calculations. That also explains the good agreement between the values from viscometry and light scattering.

Although the light scattering detection is not the most appropriate method to measure $M_n$, because of the low scattered light intensity in the low-molecular-weight range, the agreement looks reasonable for both $M_w$ and $M_n$ values from GPC/viscometry and GPC/LALLS. These results confirm that universal calibration works well for this type of branched macromolecule.

The $M_n$ values for the six different samples for arms (*lin*) and stars (*st*) are represented in Table IV. The number of branches per star $n_{br}$ are calculated by dividing the number-average molecular weight of the star-branched polymer $M_{n,st}$ by the number-average molecular weight of the linear arm $M_{n,lin}$. The values obtained by GPC/viscometry ($V$) and by GPC/LALLS ($L$) are in good agreement and approximately lead to the same number of branches per star $n_{br}(V)$ and $n_{br}(L)$.

TABLE II

Characterization of arm copolymers. ($I_w$ = polydispersity)
($V$ and $L$ indicate viscometry and light scattering, respectively)

| Sample | $M_{w,lin}(V)$ | $M_{w,lin}(V)$ | $I_w(V)$ | $I_w(L)$ | $M_{n,lin}(L)$ | $M_{w,lin}(L)$ |
|---|---|---|---|---|---|---|
| PM4 | 20350 | 20990 | **1.03** | **1.03** | 18960 | 19490 |
| PM1 | 26010 | 27160 | **1.04** | **1.03** | 23730 | 24490 |
| PMA | 17500 | 18090 | **1.03** | **1.01** | 17480 | 17730 |
| PM25 | 36940 | 39630 | **1.07** | **1.07** | 37480 | 40110 |
| PM2 | 24510 | 24990 | **1.02** | **1.02** | 23050 | 23520 |
| PM3 | 20190 | 20600 | **1.02** | **1.02** | 19810 | 20300 |

TABLE III

Characterization of star-branched copolymers. ($I_w$ = polydispersity)
($V$ and $L$ indicate viscometry and light scattering, respectively)

| Sample | $M_{w,st}(V)$ | $M_{w,st}(V)$ | $I_w(V)$ | $I_w(L)$ | $M_{n,st}(L)$ | $M_{w,st}(L)$ |
|---|---|---|---|---|---|---|
| PM4 | 137100 | 205800 | **1.50** | **1.57** | 120400 | 189600 |
| PM1 | 270800 | 554700 | **2.05** | **2.30** | 253600 | 582200 |
| PMA | 220500 | 743200 | **3.37** | **3.76** | 223800 | 842400 |
| PM25 | 202200 | 282900 | **1.40** | **1.43** | 190900 | 272900 |
| PM2 | 94690 | 136900 | **1.45** | **1.68** | 88720 | 148700 |
| PM3 | 123100 | 133900 | **1.36** | **1.34** | 112800 | 151500 |

TABLE IV

Number of branches per star by GPC/viscometry and GPC/LALLS.
($V$ and $L$ indicate viscometry and light scattering respectively)

| Sample | $M_{n,lin}(V)$ | $M_{n,st}(V)$ | $n_{br}(V)$ | $n_{br}(L)$ | $M_{n,lin}(L)$ | $M_{n,st}(L)$ |
|---|---|---|---|---|---|---|
| PM4 | 20350 | 137100 | **6.74** | **6.35** | 18960 | 120400 |
| PM1 | 26010 | 270800 | **10.41** | **10.69** | 23730 | 253600 |
| PMA | 17500 | 220500 | **12.60** | **12.80** | 17480 | 223800 |
| PM25 | 36940 | 202200 | **5.47** | **5.09** | 37480 | 190900 |
| PM2 | 24510 | 94690 | **3.86** | **3.85** | 23050 | 88720 |
| PM3 | 20190 | 123100 | **6.10** | **5.69** | 19810 | 112800 |

Considering the results from Table III and Table IV, it is difficult to determine which detector (viscometry and light scattering) seems the most appropriate to characterize these copolymers. The average numbers of branches $n_{br}(V)$ and $n_{br}(L)$ of star-branched copolymers were found to be similar and roughly vary from 4 to 13.

## DISCUSSION

The viscometric detection allows the calculation of average intrinsic viscosities $[\eta]_{br}$ and $[\eta]_{lin}$ for both linear and star-branched copolymers. The values are reported in Table V. The ratio $[\eta]_{br}/[\eta]_{lin}$ of the intrinsic viscosity of the star and the intrinsic viscosity of the linear molecule used to synthesize the star, was found to be almost constant and equal to approximately two. This interesting result has already been observed for some other star-

TABLE V

Intrinsic viscosity and branching parameter $<g'>$ by GPC/viscometry

| Sample | $[\eta]_{lin}$ | $[\eta]_{br}$ | $[\eta]_{br}/[\eta]_{lin}$ | $<g'>$ |
|---|---|---|---|---|
| PM4 | 11.89 | 21.52 | **1.81** | 0.4385 |
| PM1 | 13.49 | 27.08 | **2.07** | 0.3105 |
| PMA | 10.70 | 19.75 | **1.85** | 0.1780 |
| PM25 | 18.13 | 33.93 | **1.87** | 0.5024 |
| PM2 | 12.85 | 23.87 | **1.86** | 0.6096 |
| PM3 | 12.06 | 21.88 | **1.81** | 0.4367 |

branched polymers [10]. It indicates that the size of a star-branched polymer is independent of the number of arms and seems to be twice the value of the linear macromolecule. The star-branched polymer should have a more compact structure as the number of arms increases.

The GPC software also calculates $g'_i$, ratios of intrinsic viscosities $[\eta]_i$ of the branched macromolecules to the corresponding linear ones at the same molecular weight at every peak slice. It also calculates the average branching parameter $<g'>$ of star-branched copolymers, $<g'> = [\eta]_{br}/[\eta]_{lin}$, by integration using $[\eta]_i$ and intrinsic viscosity of the corresponding linear arm, calculated by the Mark-Houwink relationship, at the same molecular weight. We have also reported in Table IV the values of $[\eta]_{br}/[\eta]_{lin}$ which are the ratios of intrinsic viscosities of the star-branched copolymer ($[\eta]_{br}$) and its corresponding arm ($[\eta]_{lin}$), respectively. Their corresponding values are reported in Table V.

Figure 17 represents the variations of the branching parameter $<g'>$ as a function of the number of arms in the star. The $<g'>$ value, plotted on a logarithmic scale, decreases linearly when the number of arms $n_{br}$ in the star increases. Good agreement is observed between GPC/viscometry and GPC/LALLS values, the slope of variation being approximately –0.061.

In fact, the branching parameter $<g'>$, measured by GPC/viscometry, cannot be directly linked to the number of arms $n_{br}$, but to the number of branching points $m_{br}$, which is the number of branches $n_{br} - 2$. There are several relationships which have been established by Zimm and Stockmayer [11] and reviewed by Drott and Mendelson [12]. They are based on the branching parameter $<g'>$ defined with the radius of gyration $<R_g^2>^{1/2}$ usually measured by multi-wide-angle light scattering. In that case, a simple relationship links $<g'>$and $<g>$:

$$<g> = <g>^x \quad \text{with} \quad <g> = \frac{<R_g^2>_{\text{br}}}{<R_g^2>_{\text{lin}}} \tag{2}$$

where the exponent $x$ depends on the branching structure : $x = 0.5$ for star-branched polymers, $x = 1.5$ for comb-like branched polymers and $0.5 < x < 1.5$ for intermediate branching.

Since the branching parameter $<g'>$ was measured by GPC/viscometry and the number of branching points $m_{br}$ by GPC/viscometry and GPC/LALLS, we have tried to study the branching structure of the star-branched copolymers by determining the $x$ exponent which characterizes the branching structure. Unfortunately, there are several Zimm-Stockmayer relationships depending of the type of branching.

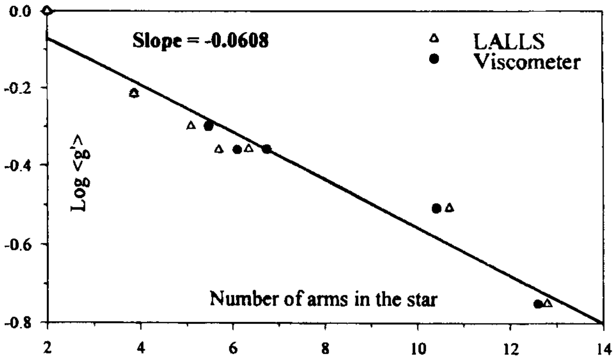


FIGURE 17 Variations of log $<g'>$ as a function of the number of arms in the star.

In the case of polydisperse systems, assuming trifunctional branching points, the relationship which links $<g>$ to the number of branching points $m_{br}$, being the number of branches $n_{br} - 2$, is:

$$<g> = \frac{6}{m_{br}}\left[\left(\frac{2+m_{br}}{4m_{br}}\right)^{1/2} \bullet \log_e\left(\frac{(2+m_{br})^{1/2}+m_{br}^{1/2}}{(2+m_{br})^{1/2}-m_{br}^{1/2}}\right)-1\right] \tag{3}$$

Figure 18 represents the variations of log $<g'>$ as a function of log $<g>$, assuming a trifunctional branching model. A linear variation is observed with a slope $x = 1.45$, which does not correspond to a star-branched structure but rather to comb-like branched polymers. Sample PMA, which is the more branched sample, was not taken into account in the regression since it seems to exhibit a peculiar behavior, probably due to a more complex branching structure.

Since the star-branched polymer structure is probably not well represented by trifunctional branching points, we have tried another relationship, valid for polydisperse systems, but assuming tetrafunctional branching points, that is closer to a star-branched structure. In that case, the relationship which links $<g>$ to $m_{br}$ is:

$$<g> = \frac{1}{m_{br}}\left[\log_e(1+m_{br})\right] \tag{4}$$

Figure 19 represents the variations of log $<g'>$ as a function of log $<g>$, assuming a tetrafunctional branching model. Again, a linear variation is observed but the slope $x$ of this variation is now found around 0.87, that is, closer to a star-branched structure but still far from the theoretical value of 0.5. Again, sample PMA was not taken into account in the regression.

It is obvious that, if our copolymers have really a star-branched structure, the two previous relationships do not represent the right relationships between the branching parameter $<g>$ and the number of branching points $m_{br}$. We have tried another model, specific to star-branched molecules and assuming a random walk model. Another relationship links $<g>$ to the number of arms $n_{br}$ of the star:

$$<g> = (3n_{br} - 2)/n_{br}^2 \tag{5}$$

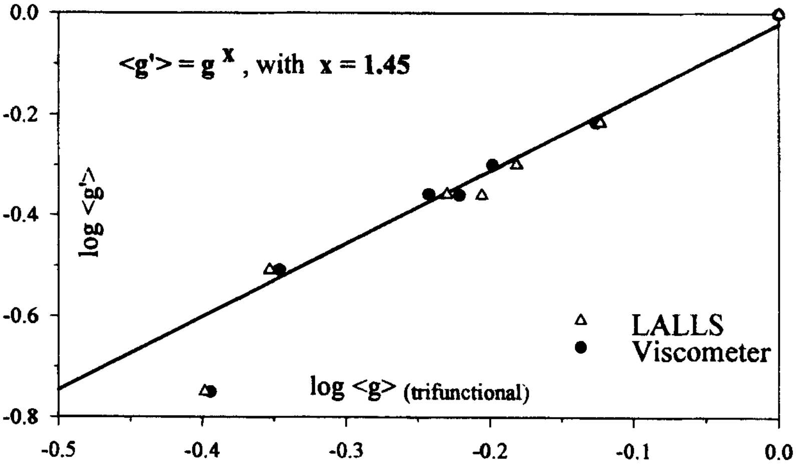


FIGURE 18 Variations of log <*g*'> as a function of log <*g*> assuming a trifunctional branching model.

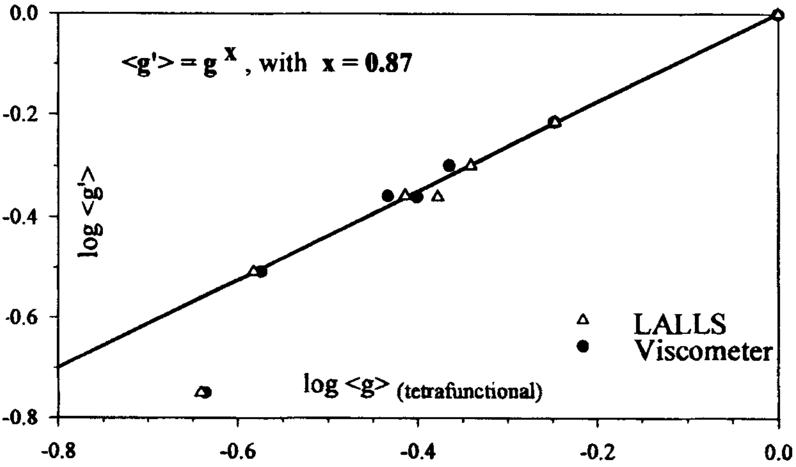


FIGURE 19 Variations of log <*g*'>as a function of log <*g*> assuming a tetra-functional branching model.

The results by GPC/viscometry (*V*) and GPC/LALLS (*L*), using the star-branch random walk model, where *x* is the experimental exponent of the <*g*'>/<*g*> relationship, are represented in Table VI.

Figure 20 represents the variations of log <*g*'> as a function of log <*g*>, assuming a random walk branching model. Again, a linear variation is observed and, surprisingly, the slope *x* of this variation was found to be 0.87, that is exactly the same value as with the previous relationship assuming tetrafunctional branching points. This result is closer to a star-branched structure but still far from the 0.5 value. For the same reasons, sample PMA was not taken into account in the regression.

It is very difficult to make any definite conclusions about the structure of these samples because the numerical results are very dependent on the hypothesis made on the branch-

TABLE VI

$\langle g' \rangle / \langle g \rangle$ relationship using the random walk model. ($V$ and $L$ indicate viscometry and light scattering respectively)

| Sample | $\langle g' \rangle$ | $n_{br}(V)$ | $\langle g \rangle(V)$ | $x(V)$ | $n_{br}(L)$ | $\langle g \rangle(L)$ | $x(L)$ |
|---|---|---|---|---|---|---|---|
| PM4 | 0.4385 | 6.74 | 0.4011 | 0.90 | 6.35 | 0.4228 | 0.96 |
| PM1 | 0.3105 | 10.41 | 0.2697 | 0.89 | 10.69 | 0.2631 | 0.86 |
| PMA | 0.1780 | 12.60 | 0.2255 | 1.16 | 12.80 | 0.2222 | 1.15 |
| PM25 | 0.5024 | 5.47 | 0.4816 | 0.94 | 5.09 | 0.5122 | 1.03 |
| PM2 | 0.6096 | 3.86 | 0.6430 | 1.12 | 3.85 | 0.6443 | 1.13 |
| PM3 | 0.4367 | 6.10 | 0.4380 | 1.00 | 5.69 | 0.4655 | 1.08 |

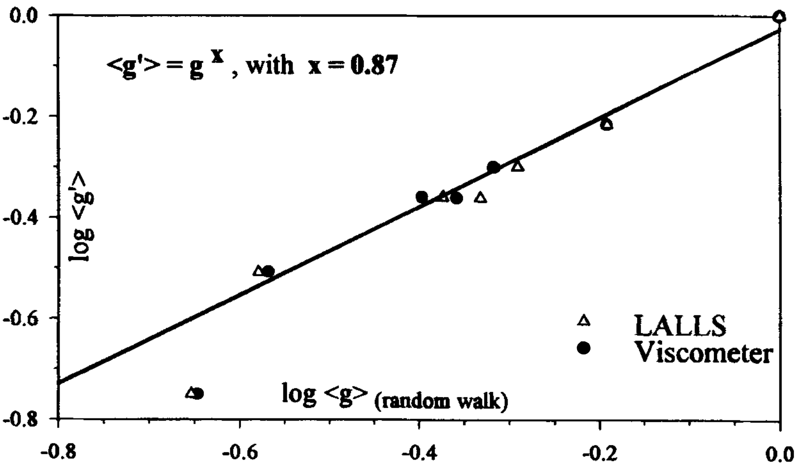


FIGURE 20 Variations of log $\langle g' \rangle$ as a function of log $\langle g \rangle$ assuming a random-walk model for star-branched molecules.

ing structure. Values of $\langle g' \rangle$, $m_{br}$ and $n_{br}$ are determined experimentally, but the $\langle g \rangle$ values depend on the $\langle g \rangle / n_{br}$ or $m_{br}$ relationship which is used in the calculations. However, the $x = 0.5$ value, which corresponds to a pure star-branched polymer according to theory, has never been experimentally observed. It is impossible to conclude to a lack of precision of the established relationships or to a structure more complicated than a pure star-branch model for our samples. For example, sample PMA, which is the more branched sample, seems to exhibit a particular behavior and does not follow the same law than the other samples. This is probably due to a more complex branching structure, intermediate between star and comb model.

## CONCLUSION

The characterization of star-branched polymers has been performed using the triple detection SEC system since it was not obvious, at the beginning of this study, that universal calibration could be applied to star-branched polymers. In fact, the GPC software used handles experimental data as separate GPC/viscometry and GPC/LALLS detection systems as well as a triple detection system. Experimentally, excellent agreement between these two sets of data was obtained, that is, GPC/viscometry using a universal calibration curve and GPC/LALLS without a molecular weight calibration curve. These results demonstrate that universal calibration works well with long-chain branched polymers, even with unusual viscometric behavior.

The calculation of the number of arms was performed by the ratio of the number average molecular weight of the star polymer to that of the uncoupled linear molecules. The use of $M_n$ from GPC/viscometry and $M_n$ from GPC/LALLS leads approximately to the same number of arms in the star-branched copolymers. The ratio $[\eta]_{br}/[\eta]_{lin}$, between the intrinsic viscosity of the star and the intrinsic viscosity of the linear molecule used to synthesize the star, was found to be approximately constant and equal to 2, which has already been observed for other star-branched polymers [10].

Different relationships have been used to calculate the branching parameter $<g>$ using the number of arms $n_{br}$ of the star or the number of branching points $m_{br}$, which is the number of branches $n_{br} - 2$. The trifunctional approach leads to an $x$ exponent of the $<g'>/<g>$ relationship around 1.45, which does not correspond to a star-branched structure but rather to comb-like branched polymers. The tetrafunctional approach and the star-branch hypothesis, assuming a random-walk model, both lead to the same $x$ exponent value of 0.87, which is closer to a star-branched structure but still far from the 0.5 value. We have never experimentally observed this value due in part to a lack of precision of the multidetection GPC method. The structure of these copolymers may be more complicated than a pure star-branched model. For example, sample PMA does not follow the same law as the other samples. This sample is the more branched (13 arms) and it may have a more complex structure intermediate between the star-model and comb-model.

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