Characterization of sparsely long chain branched polycarbonate by a combination of solution, rheology and simulation methods

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Synopsis

We characterize sparsely and randomly branched polycarbonate and fractions thereof by a combination of solution and rheological techniques, and we compare the observations with the results of Monte Carlo simulations as well as tube-based modeling. On-line coupling of size exclusion chromatography with intrinsic viscosity (SEC-IV) yields values for the viscosity branching index g', which deviate significantly from linear behavior above approximately 0.3 branches per chain. The experimental g' also follows closely the predictions for the geometric branching factor g calculated by Monte Carlo simulations of the polymer structure across the entire molar mass distribution ($g = g'$). The Monte Carlo simulations provide an explicit description of the molecular architectures present and can therefore in principle be used to test models suitable for sparsely branched polymers. Experimental dynamic moduli of unfractionated and fractionated samples are compared with predictions of a tube-based model recently published in van Ruymbeke *et al.* [J. Non-Newt. Fluid Mech. **128**, 7–22 (2005b)]. When the model is calibrated for polydisperse linear polycarbonate, discrepancies between the predicted and measured dynamic moduli are clearly observed at levels well below the detection limit of branching by the SEC-IV coupling method. The comparison between observed and predicted moduli is therefore a very sensitive method for the detection of sparse long chain branching in poorly and moderately entangled polymers, of which polycarbonate is a good example. © *2006 The Society of Rheology.* [DOI: 10.1122/1.2357188]

I. INTRODUCTION

It is well known that the presence of a small number of long chain branches, typically less than one per polymer chain, can significantly improve specific processability aspects

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of polymers, such as drawability, melt strength, etc., without detrimental effects on mechanical properties. Sensitive and accurate methods to detect long chain branching (LCB) of sparsely branched polymers are thus very important, especially those providing information on the number and length of the branches as well as their distribution across the molar mass distribution (MMD).

In order to determine LCB content, several techniques are known [Gabriel *et al.* (2002); Simon *et al.* (2001); Vega *et al.* (1999)]. The most direct ones are spectroscopic methods, in particular nuclear magnetic resonance. The current drawback of this technique is the limited branching length resolution. Branches longer than about six carbons cannot be distinguished by the best instruments [Shroff *et al.* (1999; 2001); Striegel *et al.* (2000); Gabriel *et al.* (2002); Janzen *et al.* (1999); Liu *et al.* (2004)], whereas branching length relevant for rheological properties is equal to at least twice the entanglement molecular weight, usually one order of magnitude higher. Rheology, on the other hand, is very sensitive to even minute levels of branching, but the rheological response alone is often ambiguous [Gabriel *et al.* (2002); Vega *et al.* (1999); Liu *et al.* (2004); Crosby *et al.* (2002); Lyu *et al.* (2001); Vega *et al.* (2002)]. Indeed, the rheological characteristics of a linear polymer with broad MMD and that of a long chain branched polymer can be quite similar [Doerpinghaus *et al.* (2003)]. Only a comparison of the experimental data with predictions of a quantitative model can eliminate the ambiguity if the true MMD is known [van Ruymbeke *et al.* (2005a)]. Solution characterization methods can provide unambiguous information on MMD and LCB when so-called coupled techniques are used, i.e., the simultaneous fractionation of the macromolecules by size exclusion chromatography (SEC), coupled viscometry, and/or light scattering characterization of the fractionated species [Janzen *et al.* (1999); Wang *et al.* (2004); Herz *et al.* (1972); Wyatt *et al.* (1993)]. However, the sensitivity of coupled solution techniques to LCB is clearly limited. LCB can only be detected by a small modification of the coil size at same MW or retention time, as detected by intrinsic viscosity (g' factor) [Gabriel *et al.* (2002); Zimm *et al.*(1949); Khasat *et al.* (1998); Bailly *et al.* (1986)] or light scattering (g factor). The sensitivity of solution methods can be enhanced by a fractionation of the samples at the semipreparative scale in order to concentrate the parts of the MMD with the highest branching content [van Ruymbeke *et al.* (2005a)].

A. Solution characterization

The viscometric parameter characterizing LCB is g' equal to $([\eta]_{br}/[\eta]_{lin})_M$, where $[\eta]_{br}$ and $[\eta]_{lin}$ are the intrinsic viscosities of, respectively, branched and linear polymers of the same molar mass M. The correlation of a global g' with an average LCB content has been attempted in a few publications for polycarbonate (PC) [Zimm *et al.* (1949); Bailly *et al.* (1986); Douglas *et al.* (1990)]. This approach mostly fails, mainly because of the lack of adequate models for the correlation. Better methods are based on the coupling of SEC with viscometry (SEC-IV), which allows "local" branching characterization from knowledge of g'_i for each chromatographic slice.

Because SEC-IV is an indirect technique, a procedure is required to transform g' into a branching density or overall number of branches. The only theoretical formulas relating the influence of chain architecture to solution properties have been developed by Zimm and Stockmayer [Zimm *et al.* (1949)]. They link the geometric structure factor g (defined as the ratio between the radii of gyration of the branched and linear polymers of the same molar mass, respectively) with the number of branches per chain, for several architectures. These formulas are only valid in theta solvent. Moreover, a formula to transform g' into g is required. Although a power law is usually assumed for the transformation, the

value of the exponent is ill-defined (reported values ranging from 0.5 to 1.5) [Khasat *et al.* (1998); Zimm *et al.* (1959); Stockmayer *et al.* (1953); Frater *et al.* (1997); Hadjichristidis *et al.* (2000)]. In order to eliminate these two problems, some studies have been performed on model polymers with a known branching structure and content. Douglas and Freed [Douglas *et al.* (1990)] as well as Balke *et al.* (2002) have proposed experimental formulae for monodisperse star polymers, which directly link g' to the number of arms.

We have recently established a relationship between g' and the number of long chain branches of a polydisperse polymer for a model system consisting of polydisperse linear polystyrene blended with a small and known fraction of monodisperse 3-arm stars [Kaivez (2004)]. We have shown that semiquantitative detection of the branched fraction can be obtained from the Mark-Houwink plot. The link between local g'_i and a long chain branching index (LCBI) expressed as the number of long chain branches per chain has been established [Netopilik *et al.*(2003)]:

$g'_i > 0,92$: quasilinear chains (LCBI $\leqslant 0.25$)
$0,85 \leqslant g'_i \leqslant 0,92$: slightly branched chains ($0.3 \leqslant$ LCBI $\leqslant 0.5$)
$g'_i < 0,85$: pure 3-arm stars (LCBI$=1$)

In this work, we try to extend these observations to randomly branched polycarbonate.

B. Rheological characterization

Many studies [Gabriel *et al.* (2002); Vega *et al.* (1999); Liu *et al.* (2004); Crosby *et al.* (2002); Vega *et al.* (2002); Lyu *et al.* (2001); van Ruymbeke *et al.* (2005a); He *et al.* (2004); Wood-Adams *et al.* (2000)] have shown that the presence of LCB in a well-entangled polymer melt has a dominant influence on linear viscoelasticity. The relaxation of a long chain branched polymer is in most cases much slower than the relaxation of a linear polymer with the same MMD. Following tube theory, this is understood by a completely different balance between reptation and fluctuations relaxation processes for the two architectures. Tube-based models predicting linear viscoelasticity for linear polymers have reached an excellent level of quantitative agreement with experiments [Leonardi *et al.* (2000); Likhtman *et al.* (2002); van Ruymbeke *et al.* (2002); Pattamaprom *et al.* (2000)]. Therefore, discrepancies between the experimental relaxation of a given long chain branched sample and its predicted relaxation, calculated assuming that the polymer is linear, can give important qualitative information about the presence of LCB [van Ruymbeke *et al.* (2005a); He *et al.* (2004); Wood-Adams *et al.* (2000)]. The confident use of such a model requires an excellent knowledge of the true MMD. On the other hand, no quantitative tube models exist for complex polymers characterized by polydispersity in molar mass and architecture, including sparsely branched polymers such as the ones used in this study. Hence, direct quantification of LCB based on reptation models remains elusive at the moment.

C. This work

The overall objective of this paper is to show that the combined use of fractionation, solution characterization, rheological measurements, and modeling can provide unambiguous and highly sensitive information on the branching structure of a model long chain branched polymer with very low level of branching (less than 1 branching point per 10 chains on average) and a low to moderate number of entanglements (in this specific case: from $M_w=3$ to 16 entanglements). The model polymer used for this study is bisphenol-A polycarbonate (PC) obtained by melt transesterification from bisphenol-A

and diphenyl carbonate. Branches result from a side reaction leading to the random incorporation of trifunctional monomer units [Hagenaars *et al.* (2001)]. The choice for this system is based on two main considerations.

(i)   A method for continuous preparative fractionation (CPF) has recently been developed for PC [Hagenaars *et al.*(2001)]. Through this technique, preparative size fractions of polydispersity index around 1.5 can be obtained in a short time with limited use of solvent. For linear PC, the CPF method fractionates according to molar mass (MM) only. For sparsely branched PC, this is also predominantly the case because, at very low level of branching, solution properties are only marginally perturbed with respect to the linear polymer [Hagenaars *et al.*(2001) and (2005)]. It is thus possible to confirm and refine results obtained for broad, unfractionated samples, by analyses of narrow fractions.

(ii)   Because melt transesterification of PC is an equilibrated reaction, the resulting distribution for the linear polymer is of the "most probable" or "Flory" type [Flory (1946); Hagenaars *et al.* (2002)]. Moreover, branching of this system can be considered as a random process. Therefore, a Monte Carlo simulation method can be used to predict the statistical molecular structure of melt branched PC [Shida *et al.*(1998); Karayiannis *et al.*(2003); Lee *et al.*(2001)].

The paper is divided in four sections following this Introduction. In Sec. II, we recall the main features of our new tube model, which will be used to highlight LCB in some of the PC samples, and we present a Monte Carlo simulation approach, which allows an explicit and quantitative description of the chain architectures present in the sample. Section III is devoted to a description of the experimental techniques used and samples tested. In Sec. IV, we present and discuss the results of the solution and rheological analyses and compare them to the output of the Monte Carlo simulations. In particular, we show that the model presented in Sec. II leads to quantitative predictions for truly linear PC, while very small levels of LCB are readily visible from a discrepancy between the experiments and the predictions. Conclusions are drawn in Sec. V.

II. THEORY AND SIMULATIONS

A. Rheological model

For the rheology predictions, we have used a new model based on tube theory, which has been recently published in van Ruymbeke *et al.* (2005b). Starting from a classical description of reptation, fluctuations, and constraint release processes, the model is able to predict the linear viscoelastic behavior of mixtures of (asymmetric) star and linear polymers from knowledge of their structure. As our aim is to highlight a discrepancy between measured dynamic moduli and predictions based on the assumption of linearity of the molecules, we can here limit the application of the model to linear polydisperse polymers. A complete description has been published in van Ruymbeke *et al.* (2005b).

According to tube theory, each entangled molecule in a polymer melt can be pictured as if it were confined by a virtual tube [de Gennes (1971); Doi and Edwards (1986)]. The tube represents the entanglement constraints on the observed molecule by the surrounding chains. In order to relax after a deformation, a test molecule has to move out of its original tube. In this way, the memory of the orientation is lost and the chain recovers an equilibrium coil conformation. This memory loss is described by the relaxation function $F(t)$, defined as the unrelaxed fraction of the polymer melt at time t. In our model, it is taken as the weighted sum of the probabilities that any chain segment is not yet relaxed at the observed time t,

$$F(t) = \sum_i \varphi_i \int_0^1 (p_{rept}(x_i,t)p_{fluc}(x_i,t)p_{envir}(x_i,t)) dx_i, \tag{1}$$

where x_i is a parameter describing the position of a primitive chain segment along a chain "i;" x_i goes from 0 at the end of a chain to 1 at the center; $\varphi(i)$ represents the volumetric fraction of chain i, and $p(x_i,t)$ represents the survival probability of segment x_i, at time t. Each segment can relax in three different ways, which will be explained below: by reptation, by fluctuations, or by rearrangement of the environment. This way of taking into account the different relaxation mechanisms does not require dividing time into different regions linked to the relaxation state of each molecule. Therefore, it can be easily used for predicting the linear viscoelasticity (LVE) of polydisperse polymers. The relaxation modulus $G(t)$, which is directly linked to the experimentally accessible dynamic modulus through mathematical transformations, is the product of $F(t)$ and the plateau modulus G_N^0. In order to obtain $F(t)$, we use a time-marching algorithm, which calculates, at each time step, the polymer fraction already relaxed by reptation or by fluctuations, called $\Phi(t)$. This is often essential because the relaxed fraction can in some cases speed up the characteristic relaxation times. Because of this feedback effect of the relaxed part on relaxation times, no analytical solution can usually be found for the relaxation function of polydisperse linear polymers. In the specific case of polydisperse linear chains, the polymer fraction already relaxed will act as a solvent in the reptation process of longer chains only if their relaxation times are well separated in time [see Eq. (3)], as defined by the "Graessley criterion," explained in detail in van Ruymbeke *et al.* [(2005b) and (2006)]; Struglinski *et al.* (1988). This means that only linear polymers with a large polydispersity will see a solvent effect coming from the reptation of the smallest chains.

The term p_{rept} in Eq. (1) represents the probability that a given tube segment located at x_i is not relaxed by reptation at time t. This is the main relaxation process of a linear chain. Based on the work of Doi and Edwards (1986), we can calculate the survival probability by reptation of a given tube segment, after a time interval Δt,

$$p_{rept}(x_i,\Delta t) = \sum_{p\ odd} \frac{4}{p\pi} \sin\left(\frac{p\pi x_i}{2}\right) \exp\left(\frac{-p^2\Delta t}{\tau_{rept}(M)}\right), \tag{2}$$

where τ_{rept} is the reptation time of the observed molecule. For linear polydisperse chains, τ_{rept} is only a function of molar mass and of the entanglement relaxation time τ_e,

$$\tau_{rept}(M) = 3\tau_e\left(\frac{M}{M_e(0)}\right)^3 \Phi_{active}(t,M), \tag{3}$$

with $M_e(0)$ being the molecular weight between two effective entanglements at time $t = 0$ and $\Phi_{active}(t,M)$ being the unrelaxed part of the polymer at time t, which does not act as a solvent during the reptation process of the observed molecule. As explained in van Ruymbeke *et al.*, (2006), it is equal to $\Phi(t/Z)$, the unrelaxed part of the polymer at time t/Z (with Z the number of entanglements of the observed molecule). We use a time-marching algorithm to calculate survival probabilities along a discretized time axis

$$p_{rept}(x_i,t_k) = p_{rept}(x_i,t_{k-1})p_{rept}(x_i,[t_{k-1},t_k]). \tag{4}$$

The survival probability after reptation, at time t_k, is the product of the survival probability at time t_{k-1} and the survival probability during an interval Δt comprised between t_{k-1} and t_k. The latter can be calculated from Eq. (2).

The term p_{fluc} in Eq. (1) determines the probability that an initial tube segment is not yet relaxed by tube length fluctuations. Fluctuations shortening the occupied tube length will relax part of the orientation. The effective equilibrium length of a chain, which is associated to the effective molecular weight between two entanglements $M_e(t)$ [van Ruymbeke *et al.* (2005b), (2006)], depends on the relaxed fraction,

$$L_{eq}(t) = L_{eq,0} \cdot (\Phi(t))^{\alpha/2}, \tag{5}$$

where L_{eq0} represents the effective equilibrium length of the observed chain at time 0 and α is the dilution exponent, taking values between 1 and 4/3 [Park *et al.* (2004); Colby *et al.* (1990); Raju *et al.* (1981)] and fixed to 1 in this work. The time for a segment to relax by fluctuations increases exponentially with a fluctuation potential that results from the balance of the chain entropic spring force and the tube constraint [Milner *et al.* (1997)]. Including the idea of dynamic dilution [Marrucci (1985); Ball *et al.* (1989)], Milner and McLeish (1997) have proposed an expression to calculate the dependence of the potential U and the fluctuations time τ_{fluct} on the fluctuations depth x_i,

$$\frac{\partial \ln \tau_{fluc}(x_i)}{\partial x_i} = \frac{\partial(U(x_i)/kT)}{\partial x_i} = 3 \cdot Z_i \cdot x_i \cdot \Phi(x_i)^{\alpha}, \tag{6}$$

where $\Phi(x_i)$ is the unrelaxed polymer fraction if the fluctuations depth of the arm i is x_i. and Z_i is the number of entanglements of chain "i." The prefactor of this equation has been corrected according to Larson *et al.* (2003). Using the Graessley criterion [Struglinski *et al.* (1985); (1988)], we can show that, for the analysed molecules, $\Phi,(x_i)$ is affected by fluctuations but not by reptation. Therefore, the parameter $\Phi(x_i)$ is defined as proposed by Milner and McLeish (1997); van Ruymbeke *et al.* (2005b),

$$\Phi(x_i) = \sum_j \varphi_j(1 - x_j), \tag{7}$$

where φ_j is the volumetric fraction of chains with a molecular weight of M_j and x_j is potentially equivalent to x_i.

For segments close to the chain end, fluctuations are not controlled by the potential but by unconstrained Rouse motions of the chain end,

$$\tau_{early}(x_i, t_k) = \frac{9\pi^3}{16}\left(\frac{M_a}{M_{e,0}}\right)^2 \tau_{R,chain} x_i^4, \tag{8}$$

where $\tau_{R,chain}$ is the Rouse time of the chain, M_a the molar mass of the "arms" (i.e., half the molar mass of the chain), and $M_{e,0}$ the undiluted molecular weight between entanglements. Up to now, it was not clear if this expression had to consider $M_e(t)$, the effective molecular weight between two active entanglements, or its initial value, $M_{e,0}$. Since in the present case, this difference does not significantly affect the predictions, we choose $M_{e,0}$, as proposed by Milner-McLeish (1997) or Park-Larson (2004) [van Ruymbeke *et al.* (2006)].

The transition between these "early" fluctuations and those controlled by the potential occurs at a transition segment where the potential is equal to kT,

$$\tau_{fluc}(x_i) = \tau_{early}(x_i) \quad for \ x_i < x_{trans,i}, \tag{9}$$

$$\tau_{fluc}(x_i) = \tau_{early}(x_{trans,i})\exp\left(\frac{\Delta U(x_{trans,i} \rightarrow x_i)}{kT}\right) \quad for \ x_i > x_{trans,i}, \tag{10}$$

where $x_{trans,i}$ is the fluctuation depth corresponding to a potential level equal to kT.

The fluctuation survival probability between t_k and $t_k + \Delta t$ can be calculated from knowledge of the fluctuation time $\tau_{fluc}(x_i, t_k)$,

$$p_{fluc}(x_i, \Delta t) = \exp \frac{-(\Delta t)}{\tau_{fluc}(x_i, t_k)}. \tag{11}$$

The fluctuation survival probability can be updated at increasing times in the same way as the reptation process [Eq. (4) with p_{fluc} replacing p_{rept}].

The term p_{envir} in Eq. (1) describes the probability that the test segment is not relaxed by the effect of the relaxation of surrounding molecules. This describes a thermal constraint release mechanism. It is convenient and reasonably accurate to consider that the probability to lose an entanglement in this way is identical for all the segments in the polymer melt. Therefore, p_{envir} is equal to the probability that a segment taken at random in the polymer is still oriented. The environment survival probability is a conditional probability applied to a segment, which is not relaxed by reptation nor by fluctuations. That implies that all the segments between the center of any molecule k and a fractional distance x_{k_trans}, equivalent (potential-wise) to the test segment x_i, are also not relaxed by fluctuations. Therefore, the general expression of the environment survival probability can be described by the following equation:

$$p_{envir}(x_i, t) = \left(\sum_k \varphi_k \left[\int_0^{x_{k,trans}} p_{rept}(x_k, t) p_{fluc}(x_k, t) dx_k + \int_{x_{k,trans}}^1 p_{rept}(x_k, t) dx_k \right] \right)^{\alpha}. \tag{12}$$

The high-frequency Rouse relaxation is taken into account as described in Likhtman $et~al.$ (2002). Linear chains with a molecular weight shorter than $2~M_e$ are nonentangled and relax according to a full Rouse process [Leonardi $et~al.$ (2000)].

In the model, only three materials parameters are needed: the plateau modulus G_N^0, the Rouse time of a segment, τ_e, and the molecular weight between two entanglements, M_e. Theoretically, G_N^0 and M_e are linked [Larson $et~al.$ (2003)] but in this case, it is necessary to slightly relax this restriction and treat the two parameters as independent (within reasonable bounds). The dilution exponent α can be considered as an additional fitting parameter within strict bounds. Consistent with our last work [van Ruymbeke $et~al.$ (2006)], we have fixed the value of α at 1, which is also consistent with literature for linear polymers [Park $et~al.$ (2004); (2005)].

The model is implemented in MATLAB as described in van Ruymbeke $et~al.$ (2005b).

B. Monte Carlo simulation

In order to approach the branching distribution of the investigated melt-polymerized samples from a theoretical standpoint, we have developed a simulation model based on a random sampling technique, also called Monte Carlo simulation. Three types of polymer building blocks must be considered: bifunctional units, which are the most common, trifunctional units, which represent the branching points, and monofunctional units, representing the terminal groups. Because monomers are redistributed by transesterification during synthesis [Hagenaars $et~al.$ (2002)], bifunctional and trifunctional units are located randomly along the chains, i.e., the probability that any monomeric unit carries a branching point is independent of the status of other units on the same chain or others [Hagenaars $et~al.$ (2001); Shida $et~al.$ (1998); Karayannis $et~al.$ (2003); Lee $et~al.$ (2001)]. Terminal units are by definition located at a chain extremity. The number of linear, branching, and terminal building blocks, respectively called L, B, and X, can be calcu-
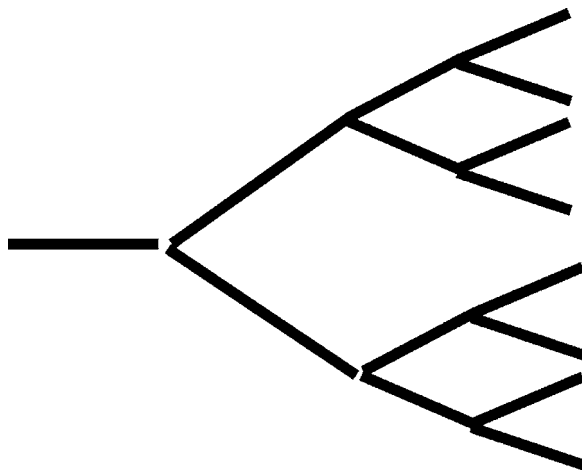
FIG. 1. Construction of the molecules from a terminal group, by considering a three-generation tree architecture.

lated from the number average molar mass M_n, the branching density ρ (the fraction of branching units) determined by nuclear magnetic resonance, and an arbitrary total number M of building blocks used for the simulation,

$$B = \rho \cdot M, \tag{13}$$

$$X = ((2 + \rho)/M_n) \cdot M, \tag{14}$$

$$L = M - B - X. \tag{15}$$

Chains are constructed by picking up building blocks at random from a set containing the numbers B, L, and X of corresponding units according to Eqs. (13)–(15). The starting point for the construction of any molecule has to be a terminal group picked up from the same box. One additional terminal unit is enough for termination a linear chain, but a branched molecule requires additional terminal groups (one per branching point). When a branching monomer is taken from the box, we have to consider the construction of each of the two arms one after the other. A molecule is complete when all arms are terminated. Branching densities for the investigated systems are very small (between 1 and 3 $\times 10^{-3}$; see Sec. III). Therefore, we have only considered branched molecules up to a third-generation tree architecture, as depicted in Fig. 1. The exhaustive information concerning the simulated molecules has been stored in a large matrix, each line of which represents a specific molecule, and each of the 15 columns is associated with a specific arm represented in Fig. 1. So, we know exactly the architecture of each molecule, and different statistical tests can easily be performed. In particular, we are interested to know the volumetric fraction of linear, star or higher branched molecules as a function of their molar mass, i.e., the MMD of certain types of architecture.

The simulation procedure has been implemented in MATLAB. The simulations have been performed with a total number of units (M) around 10^7.
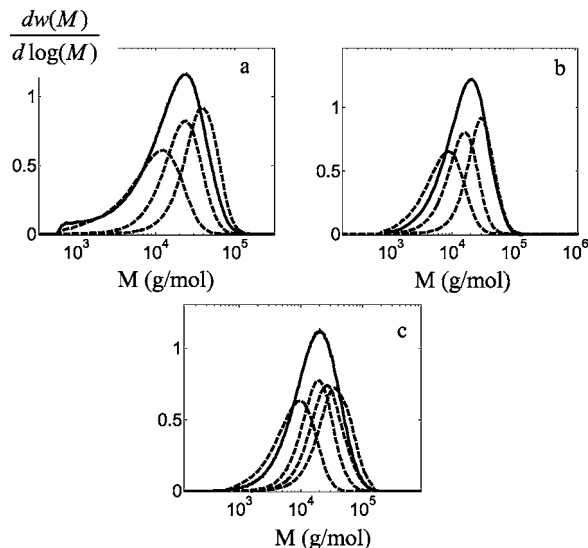
FIG. 2. Molar masses distribution of (a) PCL; (b) PC1; (c) PC2 and their fractions (see Table I).

III. EXPERIMENTAL SECTION

A. Materials

Anionic polystyrene standards have been used in order to construct the polystyrene and universal calibrations. Standards of molar masses ranging from 870 and 460 000 g/mol have been supplied by Tosoh (Japan), Polymer Laboratories (the Netherlands), and Pressure Chemicals (USA).

Branched PC samples, called PC1 and PC2, synthesized by a melt transesterification process and a linear sample, called PCL, synthesized by an interfacial process have been fractionated by the continuous polymer fractionation method as described in Hagenaars *et al.* (2001). The fractions are denoted PC*xFy*, with *x* a reference to the original sample (L, 1, or 2) and *y* a reference to the fraction. Molar mass distributions (MMD) are shown in Fig. 2 and average molar masses are described in Table I. The average number of branching points in PC2 as determined by NMR and used for the Monte Carlo simulation is 0.107 branching points per chain on average, which corresponds to a branching probability or density of 2.955×10^{-3} (that is the probability that a given monomer unit is branched along the chain). For PC1, the average number of branching points per chains is equal to 0.04 and its branching probability is 1.068×10^{-3}. Several blends of PC2F1 and PC2F4 have also been prepared.

B. SEC-IV chromatography

SEC-IV experiments have been performed on a GPCV-2000 instrument from Waters. The solvent is methylene chloride, the flow rate, 1 ml/min, the temperature, 30 °C, and the injection loop volume, 215.5 μl. The columns are three PL gel columns from Polymer Laboratories (pore sizes: 100, 1000, and 10 000 Å). A differential refractometer is used as detector and calibrated for each polymer following a procedure described in a previous paper [Kaivez *et al.* (2002)]. An interdetector delay of 0.057 min has been determined following a procedure described in Kaivez (2004). Data have been acquired with the ALLIANCE GPCV 2000 software from Waters at an acquisition rate of 5 pts/s. The

TABLE I. Average molar masses of PCL, PC1, PC2 and their fractions

	M_w (g/mol)	M_n (g/mol)	$I_p = M_w/M_n$
PCL	22 700	9 600	2.35
PCLF1	11 300	5 500	2.05
PCLF2	23 200	15 300	1.51
PCLF3	39 000	28 100	1.39
PC1	20 500	9 500	2.16
PC1F1	8 700	5 100	1.72
PC1F2	15 900	10 400	1.53
PC1F3	30 900	21 200	1.46
PC2	22 400	9 400	2.37
PC2F1	9 500	5 300	1.8
PC2F2	20 700	13 300	1.55
PC2F3	30 100	18 300	1.65
PC2F4	40 600	24 300	1.67

data have been processed with the help of procedures developed in the laboratory, using the IGOR software from Wavemetrics. In order to determine the MMD of branched PC, the evolution of intrinsic viscosity with retention time is approximated by a third-order polynomial. This approximation has not been used for the determination of viscosity laws and branching parameters, for which only slices with both significant signals are taken into account.

When analyzing PC by SEC viscometry, the applicability of universal calibration can sometimes be questioned. It does not represent any problem for sufficiently high molar masses, but the lower molar mass validity limit is not clearly defined [Balke *et al.* (2002)] as well for universal calibration as for the viscosity law [Bartosiewicz *et al.* (1974)]. Therefore, the best calibrations for PC would be obtained by using some PC oligomers in the low molar mass region [Beigzadeh *et al.* (1999)]. However, it is difficult to appropriately detect oligomers with the viscometer and to include them in the universal calibration. Moreover, long chain branching is scarcely expected to appear in the very low molar mass part of the distribution. Therefore, in this work, oligomer synthesis and fractionation have been avoided, and universal as well as PC specific calibrations have been constructed using polystyrene standards and a broad linear PC (Lexan 130 from GE Plastics). Moreover, we have tried to characterize branching only from the measured intrinsic viscosity at each retention time, without any calibration.

C. Rheological measurements

For rheological measurements, PC samples in powder form have been predried at 120 °C overnight and subsequently pressed into compact circular pellets (10 mm diameter, 2 mm thickness) at room temperature using a hydraulic press. The pellets have been dried again under vacuum at 120 °C overnight, prior to measurements.

Dynamic storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, have been determined with a strain-controlled ARES rheometer from TA Instruments in dynamic mode with a parallel-plate configuration at temperatures ranging from 160 °C to 220 °C. Linearity of the viscoelastic regime has been checked with the help of a strain sweep. In order to conserve quantities of the fractionated samples, plates with a diameter of 8 mm have been used. The angular frequency sweep interval is 10^{-1} to 5×10^2 rad/s, with a strain amplitude of 15%. All measurements have been performed under dry nitrogen atmosphere. Ther-

morheological simplicity has been verified for branched PC with the help of Van Gurp–Palmen plots as described in Trinkle *et al.* (2002). Master curves (reference temperature 200 °C) have been constructed by applying the time-temperature superposition (TTS) principle with both horizontal and vertical shifts [Ferry (1980)].

IV. RESULTS

A. Solution characterisation

1. Global characterization

The best method to obtain a global index for long chain branching is to determine the branching parameter g'. To this end, a mean intrinsic viscosity must be obtained for each sample. Several possibilities exist for calculating these average values,

$$[\eta]_w = \frac{\sum c_i[\eta]_i}{\sum c_i}, \tag{16}$$

$$[\eta]_g = \frac{\sum \eta_{spec,i}}{\sum c_i}, \tag{17}$$

$$g'_w = \frac{\sum c_i g'_i}{\sum c_i}, \tag{18}$$

$$g'_g = \frac{\sum \eta_{spec,i}}{\sum c_i K M_i^\alpha}, \tag{19}$$

where c_i is the concentration of the ith slice, directly obtained from the refractometer chromatogram, $\eta_{spec,i}$ is the specific viscosity of the ith slice, directly obtained from the viscometer chromatogram, $[\eta]_i = \eta_{spec,i}/c_i$ is the intrinsic viscosity of the ith slice, M_i is the real molar mass of the ith slice, obtained from $[\eta]_i$ and the universal calibration, K and α are the Mark-Houwink coefficients [Netopilik *et al.* (2003)] for linear polycarbonate, and

$$g'_i = \frac{[\eta]_i}{K M_i^\alpha} = \left(\frac{[\eta]_{br,i}}{[\eta]_{lin,i}}\right)_M \tag{20}$$

is the branching coefficient of the ith slice. It should be noted that $[\eta]_w$ and $[\eta]_g$ represent the same macromolecular property: the intrinsic viscosity of the sample that could be measured with an "off line" viscometer. However, $[\eta]_g$ is only based on the two chromatograms, whereas $[\eta]_w$ requires their slice-per-slice division. The same kind of nuance appears in the calculations of g'_w and g'_g.

The potential problem of all these global characteristics, except $[\eta]_g$, is that the molar mass of each slice must be calculated by universal calibration. Therefore, a polynomial fit of the intrinsic viscosity is necessary before applying this calibration, to eliminate meaningless values of $[\eta]$ at the peak feet. Low molar masses values obtained by this procedure can lack reproducibility. In order to get around this problem, another mean branching factor g'_{HV} has been calculated, based on the measured intrinsic viscosity of the branched polymer and of the intrinsic viscosity of linear PC,

TABLE II. Intrinsic viscosity and branching parameters of the PC samples and their fractions.

	$[\eta]_\omega$ (dl/g)	$[\eta]_g$ (dl/g)	g'_g	g'_ω	$g'_{HV,\omega}$ (no fit)	$g'_{HV,\omega}$ (fit) log $[\eta]$ (RT)
PC1	1.13	1.18	0.89	0.88	0.92	0.92
PC1F1	0.66	0.65	0.87	0.87	0.80	0.91
PC1F2	0.99	0.97	0.89	0.89	0.88	0.93
PC1F3	1.59	1.60	0.95	0.94	0.97	0.96
PC2	1.18	1.19	0.91	0.91	1.01	0.94
PC2F1	0.71	0.71	0.91	0.90	0.93	0.94
PC2F2	1.14	1.13	0.86	0.87	0.91	0.92
PC2F3	1.42	1.43	0.90	0.90	0.94	0.94
PC2F4	1.75	1.74	0.85	0.90	0.92	0.93

$$g'_{HV,w} = \sum \frac{c_i g'_{HV,i}}{c_i}, \tag{21}$$

with

$$g'_{HV,i} = \left(\frac{[\eta]_{br,i}}{[\eta]_{lin,i}} \right)_{HV}. \tag{22}$$

The subscript HV is used to indicate that the intrinsic viscosity of each slice has been divided by the intrinsic viscosity of a linear polymer having the same hydrodynamic volume (thus retention time) as the branched polymers, and not the same molar mass, as in the usual g'. For determining $g'_{HV,w}$, the measured $[\eta]_i$ or their polynomial approximation can be used. A representative selection of the different results is shown in Table II. Expectedly, the reproducibility for the low molar mass fractions is low, as illustrated by the difference between $g'_{HV,w}$ of PC1F1 with or without polynomial approximation of log$[\eta]$.

2. Local branching characterization of the fractions

As the branching parameters differ only slightly from one fraction to another, it is difficult to classify these fractions according to their branching content and thus to locate the branched fractions into the complete samples PC1 or PC2. A more local branching characterization is thus necessary. First, we have analyzed the fractions. Their main advantage is that both low and high molar mass parts of the distribution can be analysed at a much higher concentration than in the original polymer [van Ruymbeke *et al.* (2005a)]. In a next step, several blends of fractions have been analyzed before finally going to the unfractionated samples.

The first polymer characteristic that can indicate the presence of long chain branching is the evolution of intrinsic viscosity with retention time. It is presented in Fig. 3 for all PC2 fractions (i.e., the sample containing the highest level of branching units) together with a fitted log$[\eta]$ vs RT plot for linear PC. The figure shows a growing gap between the analyzed fractions and linear PC for short retention times, thus mainly for PC2F3 and PC2F4. This seems to indicate the presence of long chain branching on high molar mass chains and is confirmed by Fig. 4, which compares the viscosity laws of the fractions and of linear PC. The disconnection between branched and linear PC starts around a molar
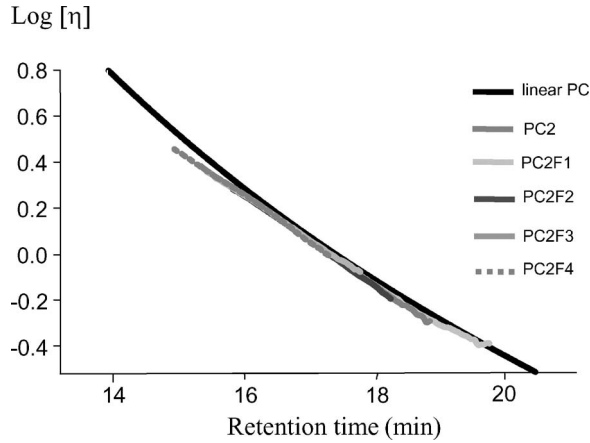
Log [η]

FIG. 3. Evolution of intrinsic viscosity with retention time of PC2 and its fractions.

mass of 40 000 g/mol. In order to quantify this observation, slice-by-slice branching factors have been calculated. They have been determined by two different ways as $g'_{HV,i}$ and g'_i.

The former is the more easy to determine. It just needs a preliminary injection of a linear polymer in the same retention time range in order to know $[\eta]_{lin,i}$ at each retention time. No calibration is needed. Evolution of $g'_{HV,i}$ with retention time is presented in Fig. 5 for PC2 fractions.

Figure 6 presents the evolution of g'_i [Eq. (20)] vs molar mass for all PC fractions. This parameter is more complicated to determine and less accurate than $g'_{HV,i}$ since g'_i will be sensitive to calibration errors for the branched polymer, which is not the case for g'_{HVi} as readily understood from a comparison of Eqs. (20) and (22). However, it is necessary to calculate g'_i if we want to obtain the corresponding geometric structure factor g_i in order to determine a number of branches, for example by using a Zimm and Stockmayer formula [Zimm et al. (1949)].

Comparing Figs. 5 and 6, we observe that $g'_{HV,i}$ is always higher than g'_i. This is expected as long chain branching decreases hydrodynamic volume, and thus increases
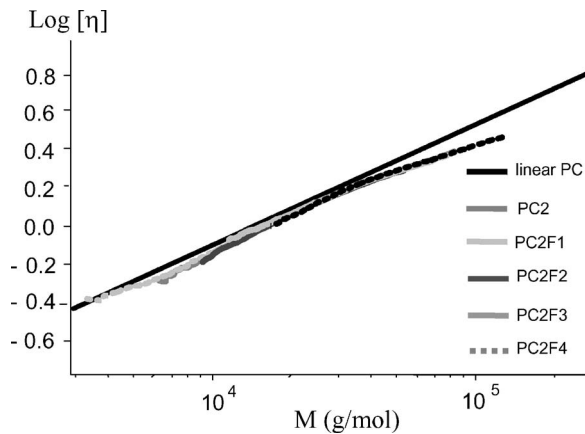
Log [η]

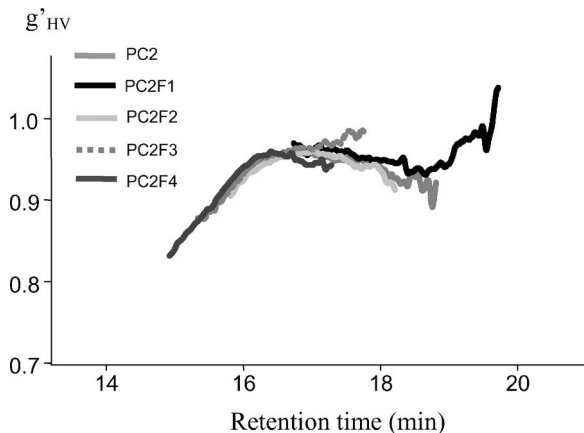FIG. 4. Viscosity law of PC2 and its fractions.

FIG. 5. Evolution of g'_{HV} vs the retention time of PC2 and its fractions.

retention time compared to a linear polymer of the same molar mass. The reproducibility at low molar mass is very poor and it is impossible to obtain branching information about these fractions by SEC-IV. However, for molar masses higher than 30 000 g/mol, (retention times of 16.5 min or less), the data spread is small. The decrease of the branching index is observed at 40 000 g/mol for g'_i and 16 min for $g'_{HV,i}$. The value of g' at this molar mass is 0.92. This corresponds to the transition from quasilinear polymer to slightly branched polymer in the classification established for polystyrene blends [Kaivez (2004)].

The same procedure has been followed to analyze PC1 fractions. The evolution of $g'_{HV,i}$, together with the chromatograms of the different fractions, is presented in Fig. 7. Even if a small decrease is observed at 16.5 min, it is difficult to assess if this decrease is significant enough to be attributed to branching. Obviously, the branching level of PC1 is below the detection limit of the solution characterization method.
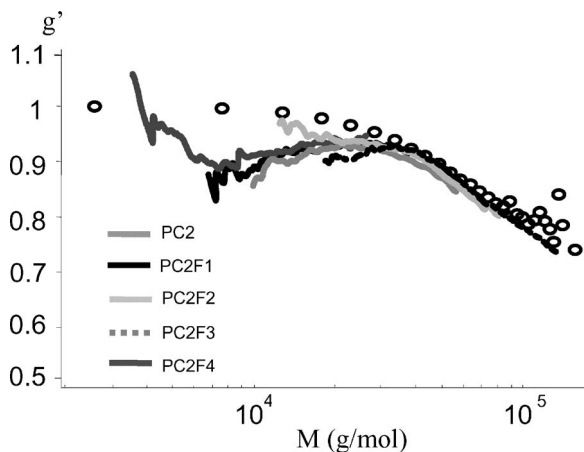

FIG. 6. Evolution of g'_i with molar mass for PC2 and its fractions. (−): measured by SEC-viscometry coupling; (ooo): g predicted from the Monte Carlo simulations.
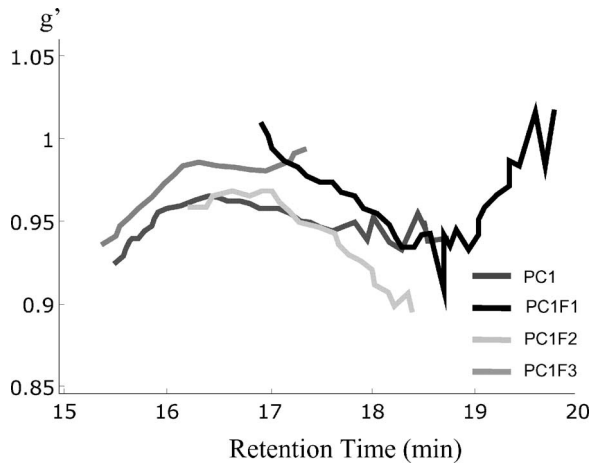
FIG. 7. Evolution of g' vs the retention time of PC1 and its fractions.

3. Fractions blends and unfractionated samples

In order to analyze the detection limit of the branching index method, several blends of the two extreme PC2 fractions PC2F1 and PC2F4 have been produced with weight ratios ranging from approximately 25 F1/75 F4 to 75 F1/25 F4 and analyzed in the same way as above. For all the blends, the intrinsic viscosity at low retention superimposes with the one observed for PC2F4 alone. The conclusion about branching detection thus remains unchanged: even when the high molar mass fraction is only present as 25% of the total, the decrease of g'_{HV} at retention times shorter than 16 min and of g' at molar masses higher than 40 000 g/mol is still observable.

The evolution of intrinsic viscosity vs retention time, the viscosity law, and the evolution of the branching parameters g'_{HV} and g' for unfractionated PC2 are presented with those of the fractions in Figs. 5–7. As indicated above, results for PC1 are below detection limit. In all the figures, data located near the peak foot have been removed because of excessive noise. The results obtained for unfractionated PC2 are in good agreement with those of the fractions. In Figs. 5 and 6, the reduction of g'_{HV} and g' can be observed, exactly as for PC2F4. However, the number of significant slices which show this decrease is quite small, and the presence of long chain branching would have been uncertain without the results obtained for the fractions.

B. Rheological results

We have first calibrated our model on the broad linear polydisperse sample PCL, and tested the calibration on its three fractions. Molecular characteristics of the samples are described in Table I. Next, we have predicted the linear viscoelastic properties of the two sparsely branched samples PC1 and PC2. The model of course assumes that they are linear. The MMD of the samples obtained by universal calibration is used as input of the model. We have finally compared predictions and experimental data: if rheology is sensitive enough to detect low levels of LCB, a discrepancy should appear. In Fig. 8, predicted and experimental data for the linear PC are compared. Only the terminal region is relevant for testing molecular architecture. The parameters we have used to fit PCL and to predict its fractions are 1.5×10^{-5} s for τ_e, 1.8 MPa for G_N^0, and 1350 g/mol for M_e [Fetters *et al.* (1994); Liu *et al.* (2004)]. The value of M_e is consistent with values
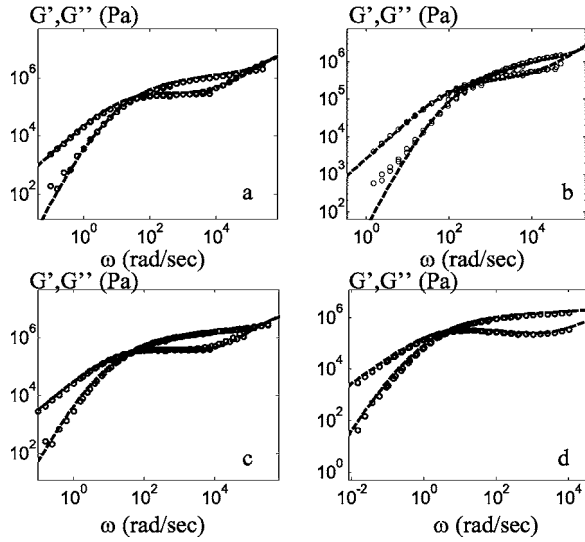
FIG. 8. Comparison between experimental (ooo) and theoretical (---) storage and loss moduli for (a) PCL; (b) PCLF1; (c) PCLF2; (d) PCLF3.

proposed by Fetters *et al.* (between 1200 and 1600 g/mol). The value of G_N^0 is slightly on the low side. However, there is no consensus in literature about the plateau modulus of polycarbonate (reported values between 2.1 and 9 MPa). The results are in very good agreement for the four tested samples. The apparent slight discrepancy observed for the lowest fraction [Fig. 8(b)] is in fact due to a partial overlap of the terminal and the Rouse relaxations in the terminal zone.

In the next step, we have used the same parameters to predict the linear viscoelasticity of the branched sample PC2 and its fractions, as shown in Fig. 9. The storage and the loss
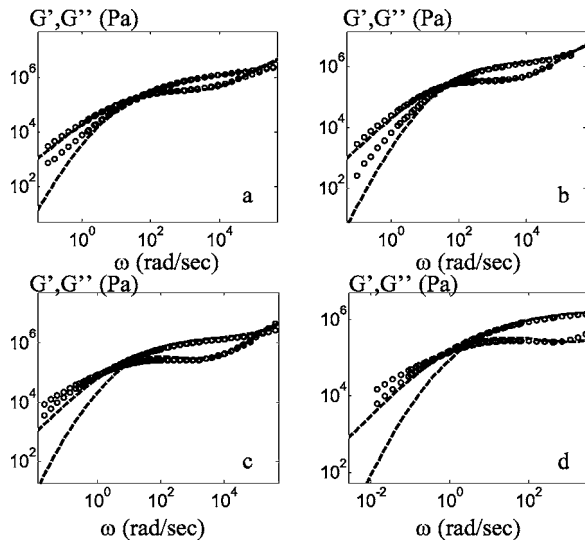

FIG. 9. Comparison between experimental (ooo) and theoretical (---) storage and loss moduli for (a) PC2; (b) PC2F2; (c) PC2F3; (d) PC2F4.
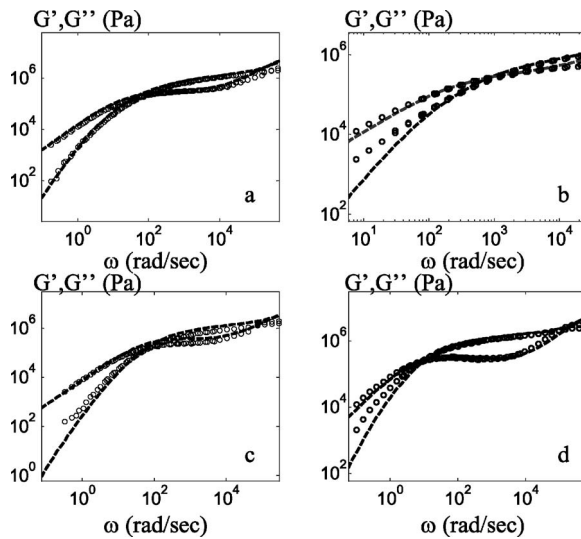
FIG. 10. Comparison between experimental (ooo) and theoretical (---) storage and loss moduli for (a) PC1; (b) PC1F1; (c) PC1F2; (d) PC1F3.

moduli predictions for PC2 and its fractions do not show quantitative agreement with the experimental data in the relevant terminal region. The discrepancy increases for the highest fractions, which means that these fractions seem more branched than the lowest molar mass fraction or the total sample. These results confirm that the rheological response of an entangled polymer is very sensitive to the presence of long chain branching when the obscuring influence of the MMD can be removed, in this case through the use of a quantitative model. The rheology-based method is clearly more sensitive than the solution method since LCB was only unambiguously detected for the highest fraction PC2F4 while it is clearly observed here on all fractions and the unfractionated sample.

In the same way, we have analyzed the very low LCB sample PC1 and its fractions. The results are presented in Fig. 10. In this case, the branching level is too low to observe any divergence between predictions and experiments for the total sample and the lower fractions. On the other hand, the highest fraction PC1F3 clearly shows a discrepancy, which is indicative of LCB. In this case, fractionation has been a good way to enhance detection, since LCB for this sample is concentrated in the highest fraction [Gabriel *et al.* (2002); Hagenaars *et al.* (2001)]. Rheology is far more sensitive than solution characterization, which fails to detect any LCB.

C. Monte Carlo simulations

1. Validation of the simulation by comparison with the Flory method

In order to validate our Monte Carlo method, we have compared the simulation results for PC1 and PC2 with the same characteristics obtained by the Flory method [Flory (1946)]. This statistical method, which is useful for the analysis of gelation, generates the MMD of a nonlinear polymeric sample and calculates the volumetric fraction of molecules containing a defined number of branching, bifunctional, and terminal units from knowledge of branching density and number average molar mass. However, a large array of isomeric structures can be derived from these numbers and the method is unable to distinguish between "long chain" and "short chain" branches. In Fig. 11, we compare the
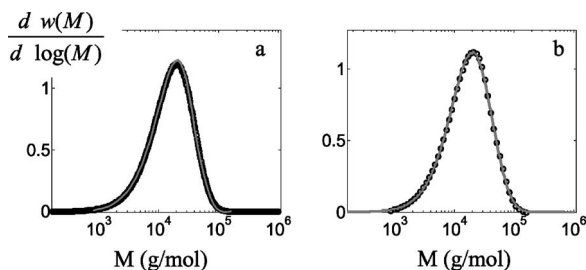
FIG. 11. Comparison between SEC data (−) and molar masses distribution obtained with the Flory method (ooo), for (a) PC1; (b) PC2.

molar mass distributions of PC1 and PC2 measured by SEC with those calculated by the Flory and Monte Carlo methods. Both methods use the same inputs (the values of M_n and branching density ρ refer to Sec. II). The results obtained with both statistical methods are in perfect agreement with the distributions determined by SEC, a clear confirmation of the random nature of the PC samples. In Fig. 12, the total MMD of PC1 and PC2 obtained with the Flory and Monte Carlo methods are compared and split in three sub-distributions: the proportion of linear chains, the fraction of star molecules (first generation tree), and the fraction of more complex molecules. Again, agreement between the two methods is very good. These results validate our simulation method, which will now essentially be used to distinguish between long and short chain branching.

2. Confrontation between simulations and solution characterization results

Solution characterization has indicated a transition from essentially linear to slightly branched structures around 40 000 g/mol for PC2 (see Sec. IV A 2). In order to extract useful information from the exhaustive architecture data resulting from the Monte Carlo simulation, it is essential to organise the dataset by dividing the molecules into a limited number of relevant classes. In this case, we are interested in quantifying "long chain branching" as a function of molar mass. Therefore, we have divided the branched architectures into four categories: the linear molecules, the long chain branched star molecules, which contain three long arms, the "quasilinear" star molecules, which contain only one short chain branching, and the long chain branched molecules containing more than two branching points. We here use the definition of long chain branching proposed for polymer melts [Doi and Edwards (1986)]: an arm is considered long if it is longer than twice the molar mass between two entanglements, M_e.
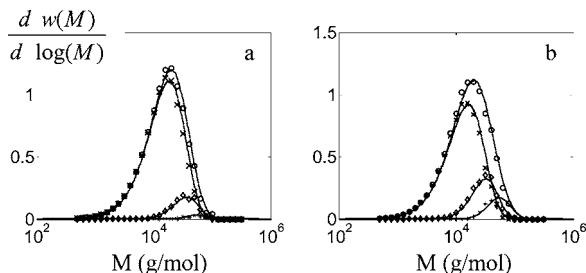

FIG. 12. Comparison between the molar masses distribution obtained with the Flory method (−) and the MMD obtained with the Monte Carlo algorithm for (a) PC1 and (b) PC2. The total distribution (ooo) is split in three subdistributions: linear molecules (xxx), star molecules ($\diamond \diamond \diamond$), and more complex molecules (∗∗∗).
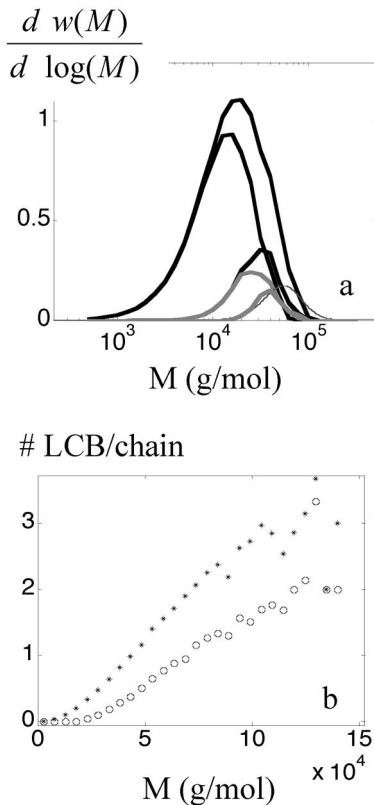
$$\frac{d\ w(M)}{d\ \log(M)}$$

LCB/chain

FIG. 13. (a) MMD obtained with the Monte Carlo algorithm for PC2. (—): total distribution; (---): linear molecules; (-·-·): star molecules; (gray·····): quasilinear molecules; (gray—): star molecules with three long arms; (thin—): more complex molecules. (b) Number of total (∗∗∗) and long (ooo) chain branches per chain as a function of molar mass for PC2.

The distribution of these different structures calculated from our simulation program is presented in Fig. 13(a) for sample PC2, while Fig. 13(b) presents the number of total and long chain branches per chain as a function of molar mass for the same sample. As shown in Fig. 13(a) by the dashed-dotted curve, star molecules appear in PC2 at a molar mass higher than 9000 g/mol. However, these branched chains are not long arm stars, which are represented by the gray continuous curve. It seems that the short branches are not detected by SEC viscometry. The long arm stars start appearing at 20 000 g/mol, but in very small quantity. A 40 000 g/mol molar mass corresponds to approximately 0.3–0.5 long branch per chain, as shown in Fig. 13(b). This minimum value for detection of branching is in agreement with the transition from quasilinear chains to slightly branched polymers in the classification made for polystyrene blends [Kaivez (2004)]. The results obtained by our Monte Carlo simulation are therefore in very good agreement with the observations in solution. This indicates also that the rheological definition of a long chain branch (larger than 2 times M_e) seems to be convenient for solution characterization, although the origin of this coincidence is admittedly unclear. The classification of molecules for sample PC1 is represented in Fig. 14(a). The number of branches per chain is described in Fig. 14(b) for the same sample. The concentration of molecules containing long chain branching is really small, below the minimum detection level, except for the highest fraction PC1F3.
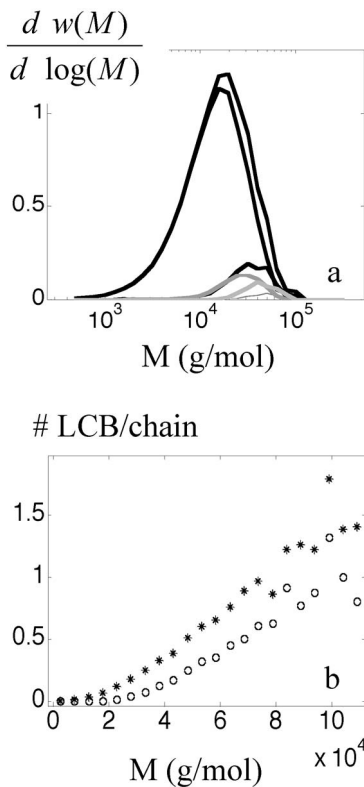
$$\frac{d\ w(M)}{d\ \log(M)}$$

M (g/mol)

LCB/chain

M (g/mol)

FIG. 14. (a) MMD obtained with the Monte Carlo algorithm for PC1. (—): total distribution; (---) linear molecules; (-·--·): star molecules; (gray·····): quasilinear molecules; (gray—): star molecules with three long arms; (thin—): more complex molecules. (b) Number of total (∗∗∗) and long (ooo) chain branches per chain as a function of molar mass for PC1.

The geometric branching factor g is defined as the ratio of the radii of gyration of branched and linear molecules with the same molar mass. The Zimm-Stockmayer formula [Zimm *et al.* (1949)] links g to the number m of branches per chain for randomly branched polymers,

$$g(m) = \left[\sqrt{\left(1 + \frac{m}{7}\right)} + \frac{4m}{9\pi} \right]^{-1/2}. \tag{23}$$

Since the Monte Carlo simulation explicitly provides the number of branches for each molecule, we can use Eq. (23) to obtain g as a function of molar mass. Figure 6 shows the result for PC2 and the comparison with the experimental g'_i determined by SEC-viscometry coupling. Interestingly, g and g' collapse on each other over quite a wide range of molar masses. In general, a relationship $g' = g^\varepsilon$ holds. Various values have been proposed for the exponent ε, ranging from 0.5 [Zimm *et al.* (1959)] to 1.5 [Stockmayer *et al.* (1953)], while values found experimentally go from 0.58 to 1 [Douglas *et al.* (1990); Hadjichristidis *et al.* (2000); Podzimek *et al.* (2001); Roovers *et al.* (1989); Jackson *et al.* (1995)]. In our case, $\varepsilon = 1$. The discrepancy observed at lower masses comes from the inaccuracy of the experimental results in this region. The overlap between the experimental g' curve and the theoretical g curve is an important result. Indeed, by using the Zimm-Stockmayer relation, it allows us to directly translate the

measured g_i' into the average number of branching units at any given molar mass.

3. Confrontation between simulations and rheology results

For PC2, the discrepancy between rheology predictions and experiments, which can be seen as proof of LCB, is important, in particular for the high molar mass fractions. These results are very consistent with the Monte Carlo simulation results: PC2 and its fractions all have a significant proportion of molecules with a molar mass higher than about 20 000 g/mol, above which LCB appears. On the other hand, the proportion of LCB in PC1 and its fractions is very small, going from nearly zero for the lowest molar mass fraction PC1F1, to a significant proportion for the third fraction PC1F3. This last sample is also the only one for which we can see a discrepancy between measured and predicted moduli at low frequencies.

V. CONCLUSIONS

We have investigated two sparsely and randomly branched polycarbonate samples (PC1 and PC2) and their fractions in order to obtain sensitive and unambiguous information about long chain branching by using a combination of solution, rheology, and simulation methods.

Global branching indices can be obtained from solution characterization by comparing apparent and universal calibration-based real average molar masses. However, the results are not really discriminating for sparsely branched samples such as the ones studied. More appropriately, a molar-mass dependent branching index g' can be obtained by on-line SEC-viscosity coupling. This method has been applied to preparative fractions, blends of fractions, and unfractionated samples. The lower detection limit for significant branching (defined as g' departing from horizontal) is about 40 000 g/mol for PC2 (branching probability approximately 3×10^{-3}). On the other hand, no conclusion can be drawn for PC1 (branching probability approx. 1×10^{-3}), even after fractionation.

Next, we have compared the experimental dynamic moduli of fractionated and unfractionated samples to the predictions of a recent tube-based rheological model published by some of the authors [van Ruymbeke *et al.* (2005b)]. The model, which is suited for linear polydisperse polymers, first requires calibration on a linear PC reference. Keeping the same values for the material parameters, we have used the model to predict the viscoelastic behavior of the two branched samples and their fractions, using the MMD obtained by SEC as input for the model. Discrepancies between predictions and experimental data give us a very sensitive, albeit qualitative, long chain branching detection method. Indeed, for PC2, even the lowest fraction PC2F1 shows a significant deviation from linear behavior. Since MW for this fraction is below 10 000 g/mol and the MMD contains virtually no chains with molar mass higher than 40 000 /mol, it has to be concluded that the rheological method is significantly more sensitive than the solution method. For PC1, the highest molar mass fraction shows a departure from the linear PC behavior while solution characterization remains insensitive. Overall, the rheology method has significantly higher sensitivity than the solution method, in particular when combined with fractionation.

Additional information can be gathered by examination of the reconstructed MMD predicted by a Monte Carlo simulation. The method, as opposed to the well-known Flory approach [Flory (1946)], provides exhaustive information on the architecture and size of molecules across the MMD. This detailed picture can be organized by defining "classes of molecules" with significant molecular architectural features. For each class there is a corresponding MMD, and this information can in turn be correlated with the solution and

melt characterization results. Surprisingly, the solution detection limit for PC2 branching (40 000 g/mol) better correlates with the appearance of long arms stars (in the rheological sense of melt entangled) in the distribution, than with all stars. Long arm stars appear from 20 000 g/mol and upward in the distribution of PC2, which again confirms the relative lack of sensitivity of the solution method vs the rheological method. The simulation also shows that the solution detection limit corresponds to about 0.3–0.5 branching point per chain on average. This level is only marginally reached for PC1, which explains the solution method insensitivity for this sample. Finally, we can obtain the geometric branching factor g vs molar mass from the simulations and compare the results with experimental g' measured by SEC-IV. Perfect overlap is found over quite a wide range of molar masses, without the use of any fitting exponent.

ACKNOWLEDGMENTS

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