

# Rheological Behavior of Degraded Polypropylene Melts: From MWD to Dynamic Moduli

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## SYNOPSIS

The linear viscoelastic behavior of polydisperse polypropylenes in the melt is predicted using the molecular weight distribution (MWD) as determined from gel permeation chromatography, on the basis of simplified molecular dynamics: single exponential form of the relaxation modulus of narrow fractions, double reptation, tube renewal, and constraint release. Owing to a few approximations, the calculation only requires a few parameters, namely the scaling law for the zero shear viscosity of narrow fractions  $\eta_0 = f(M)$ , the plateau modulus  $G_N^0$ , and the value of the molecular weight between entanglements  $M_e$ . Using this method a relaxation spectrum of Maxwellian contributions with a large number of modes is obtained. This spectrum well predicts the rheological behavior in the terminal zone of samples obtained by controlled peroxydic degradation of polypropylene with polydispersity ranging from 4 to 10. Attention is focused on the zero shear rate viscosity, frequency, and modulus of the crossover of the storage and loss moduli from experiments and calculations, because these parameters are generally thought to be sensitive to both average molecular weight and polydispersity and are relatively easy to get from dynamic experiments. How the initial spectrum can be conveniently reduced to a more simple spectrum with only a few modes, without significant loss of information, is shown. This spectrum may be useful and time saving in calculations, for example, to describe the memory function in nonlinear constitutive equations while keeping its physical meaning in relation to the MWD. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

The problem of the interconversion between rheological data and the molecular weight distribution (MWD) of polymers remains one of the most famous challenges of polymer rheology. Three major methods at three different levels of complexity and empiricism are found in the literature to reach this goal. In 1992, Fleissner<sup>1</sup> had already made some classification of the various methods that can be used for this purpose.

At the basic level, many authors have tried to find correlations between some "easy to handle" rheological parameters and the various moments of the MWD. Many well-known attempts have been made using the zero-shear rate viscosity, equilibrium

compliance, terminal slope of the storage, and loss moduli connected with average molecular weights  $M_n$ ,  $M_w$ ,  $M_z$ , and polydispersity indices  $M_w/M_n$ ,  $M_z/M_w$ , and  $M_z M_{z+1}/M_w^2$ . Because it is also known that accuracy on averages of order greater than  $M_w$  is generally poor among these last parameters, more attention<sup>2</sup> has been paid to relations between zero shear viscosity ( $\eta_0$ ) and first moments and polydispersity index in the form

$$\eta_0 = KM_w^\alpha \{M_w/M_n\}^\beta \quad (1)$$

Zeichner and Patel<sup>2</sup> also showed that the frequency ( $\omega_c$ ) and modulus ( $G_c$ ) values of the crossover of the storage and loss moduli may be connected with polydispersity and average molecular weight. Especially  $1/G_c$  and  $\eta_0 \omega_c$  are related to  $M_w/M_n$ .

On the other hand, the most sophisticated way certainly deals with any method that might enable the recovery of the entire MWD information from

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rheometry data, just as it could be obtained by physicochemical techniques such as gel permeation chromatography without the discrepancies of these methods. Among the techniques in use to reach this ambitious purpose, one may distinguish between methods that keep some empiricism and those that try to take into account the physics and the dynamics of polymer chains in a more rigorous way. Whatever the method, the first step is to check if the forward calculation from a known MWD to rheological functions is valid. From this result, one might assume that the second step should be straightforward. Unfortunately, this is not the case.

Among more or less empirical methods, many authors proposed the use of the non-Newtonian part of flow curves to calculate the MWD. For example, Bersted<sup>3</sup> assumes that the behavior of the material at any shear rate of the flow curve may be associated with a particular mass  $M_x$  that partitions the MWD into two regions. On one hand, if the masses are lower than  $M_x$ , molecules contribute to the viscosity as their weight fraction times their zero shear rate viscosity. On the other hand, if their masses are higher than  $M_x$ , they only contribute to the viscosity as their weight fraction times the zero shear rate viscosity of  $M_x$ . Calculation requires the scaling law relating the mass to the zero shear viscosity and the power law of the flow curves in the non-Newtonian region of monodisperse samples. Expressing these variations in terms of relaxation times, Bersted also obtains a continuous relaxation time distribution that enables the calculation of dynamic moduli.<sup>4,5</sup> At least the inferred relations make the calculation of the MWD from the flow curve possible,<sup>6</sup> although some question arises here concerning the accuracy that might be obtained in the long time range, or equivalently in the high molecular weight tail of the MWD, keeping in mind that this part of the MWD is dramatically important for the rheological properties and processing behavior. Tuminello et al.<sup>7,8</sup> established the limits of accuracy of the method in the case of the complex viscosity obtained from dynamic experiments. Unfortunately, Malkin and Teishev<sup>9</sup> clearly showed that the inverse problem is typically ill-posed (several MWD giving the same flow curve in the experimental uncertainty range), unless a defined shape is assigned to the MWD.

Finally, regarding a clear picture of physical meaning of the interrelation between the MWD and the rheological properties, recent advances in the various concepts of molecular dynamics certainly offer a promising way, at least in the linear viscoelastic domain. From the theoretical equations that enable the calculation of the dynamic moduli in the

terminal zone of linear polymer melts from a given MWD, one might try some minimization procedure to solve the inverse problem. Among the various studies based on this guess, Wu<sup>10</sup> uses the Doi-Edwards theory to get the MWD of polystyrene samples from the storage modulus versus frequency curve  $G'(\omega)$ . A simple correspondence between relaxation time (or frequency) and mass is assumed and the storage modulus variation in the terminal zone is just the cumulative MWD. Tuminello and coworkers<sup>11-13</sup> noticed that, because in concentrated polymer solutions the plateau modulus is proportional to the squared concentration of chains in the solvent, the storage modulus variation might rather reflect the squared MWD in the case of a melt, with unrelaxed molecules playing the role of the diluent. Wasserman and Graessley,<sup>14</sup> using the concept of double reptation of Des Cloiseaux,<sup>15</sup> together with different forms of the relaxation function of the monodisperse species, also presented different examples of calculation of the dynamic moduli from known MWD without carrying any calculation of the inverse problem. Refinements of the theory concerning some changes of relaxation times in a composite surrounding are taken into account in several ways for example by Yu<sup>16</sup> and Eder et al.<sup>17</sup> A one to one correspondence between mass and relaxation times is assumed, and the modification of chain dynamics by the surrounding is taken into account by the use of a shift factor to be applied on the relaxation times. Montfort and colleagues<sup>18,19</sup> showed how the coupling of reptation and tube renewal effects drastically changes the relaxation times of polymer chains in a complex surrounding toward their values in monodisperse fractions. In particular, constraint release and tube renewal alter the dynamic of polymer chains from a reptation process to a Rouse-like process. Cassagnau et al.<sup>20</sup> used this theory to successfully calculate the dynamic moduli in the terminal zone for various linear polymers.

Among the various works found in the literature, it is worth mentioning that of Rahalkar<sup>21,22</sup> that combines the interests of the various points of view previously discussed. Indeed, the author used the Doi-Edwards theory in the case of a monodisperse sample to calculate terminal parameters but also showed that in the case of a polydisperse sample, the effect of polydispersity must be taken into account. Short chains are assumed to behave as being fully entangled, thus relaxing according to Doi-Edwards' predictions; long chains are assumed to be less entangled and to have a Rouse movement. This defines an arbitrary molecular weight cutoff for one process or the other, giving physical sense to the ideas of authors such as Bersted.<sup>3-6</sup>

In the present article it is shown how the MWD of different widely polydisperse polypropylene samples (polydispersity ranging from nearly 4 to 10) can be used to calculate a relaxation spectrum and in turn dynamic moduli in the terminal zone. Reptation and Rouse theories are used for this purpose together with constraint release and tube renewal ideas. The calculation only requires a limited number of experimentally obtainable parameters, namely the plateau modulus, the molecular weight between entanglement, and the scaling law for zero shear rate viscosity versus molecular weight. The calculation shows the good agreement between calculated and measured parameters such as zero shear rate viscosity or crossover frequency. At the least it is shown that the complex spectrum can be transformed into a reduced spectrum with a minimum loss of information.

## THEORY

The starting point of the calculation is the MWD that is supposed to be constituted of  $N$  types of different species having different species having different molecular weights  $M_i$  and corresponding weight fractions  $W_i$ .

### Relaxation Modulus

The relaxation modulus  $G(t)$  is assumed to be a sum of three major contributions. The most important one is attributed to entanglements between chains giving rise to a time dependent network corresponding to a modulus  $G_N(t)$ . Entanglements between two chains are assumed to be possible provided that both their molecular weights are higher than the critical value  $M_c \approx 2M_e$ , where  $M_e$  is the molecular weight between entanglements. The relaxation modulus of such a network can be written using the double reptation concept of Des Cloiseaux<sup>15,23,24</sup> in the form

$$G_N(t) = G_N^0 \left\{ \sum_i W_i F^{1/2}(t, \lambda_i) \right\}^2 \quad \text{if } M_i > M_c \quad (2)$$

where  $F$  is such that at short times  $G_N(t)$  tends to the plateau modulus  $G_N^0$ , which means that the material behaves as a physically crosslinked rubber. One can get an idea of the significance of  $F$  considering that for a monodisperse sample of mass  $M_i$  greater than  $M_c$

$$\begin{aligned} G_N(t) &= G_N^0 \left\{ \sum_i F^{1/2}(t, \lambda_{ei}) \right\}^2 \\ &= G_N^0 \sum_i F(t, \lambda_{ei}) \quad (3) \end{aligned}$$

So in this case  $F$  can be considered as the normalized relaxation function of a monodisperse sample. Because this function is generally known to be a series of exponential terms containing one dominant term, it may be written as

$$F(t, \lambda_{ei}) = \exp(-t/\lambda_{ei}) \quad (4)$$

with  $\lambda_{ei}$  being the relaxation time of a junction between similar chains of mass  $M_i$  or the observed relaxation time of such a monodisperse sample.  $F$  can also be considered as the probability of survival of an  $i$ - $i$  entanglement, or equivalently as the product of two probability functions, each of the following form:

$$F^{1/2}(t, \lambda_{ei}) = F(t, 2\lambda_{ei}) \quad (5)$$

which means that the  $i$ - $i$  entanglement between two  $i$  chains remains only if none of them has relaxed, each chain having its own relaxation function in the form of eq. (5). Going back to the case of entanglements between chains of different length, similar considerations lead to eq. (2) that states that the modulus is the sum of contributions of  $i$ - $j$  junctions for which none of the two chains, either of  $i$  or  $j$  type, has relaxed. This is of course weighted according to the frequency of such  $i$ - $j$  contacts in the blends that depends on the volume fraction of each species (assumed to be equal to the weight fraction if variation of melt density with chain length is neglected).

It is now worth noticing that the characteristic relaxation time  $\lambda_i$  of each type of chain is also different from its value  $\lambda_{ei}$  in a monodisperse sample of same mass, because the surrounding effects may be prominent in this case. At least, eq. (2) can also be written as

$$\begin{aligned} G_N(t) &= G_N^0 \sum_i \sum_j W_i W_j F^{1/2}(t, \lambda_i) F^{1/2}(t, \lambda_j) \\ &\quad \text{if } M_i \text{ and } M_j > M_c \quad (6) \end{aligned}$$

Finally, if  $N_H \leq N$  is the number of fractions of the MWD such as  $M_i > M_c$ , this gives a relaxation spectrum containing:

1.  $N_H$  modes with relaxation times  $\lambda_k = \lambda_i$  and  $g_k = G_N^0 W_i^2$  and

2.  $N_H(N_H - 1)/2$  modes with relaxation times  $\lambda_k = 2\lambda_i\lambda_j/(\lambda_i + \lambda_j)$  and  $g_k = 2G_N^0 W_i W_j$ .

As far as molecular weights smaller than  $M_c$  are concerned, they are assumed to contribute to the relaxation modulus in the form of a single time Rouse spectrum such as

$$G_R(t) = \frac{\pi^2}{6} M_c G_N^0 \left\{ \sum_i \frac{W_i}{M_i} F(t, \lambda_i) \right\} \quad \text{if } M_i < M_c \quad (7)$$

It should be noticed that in this case, the relaxation time remains unchanged whatever the surrounding is and is equal to that observed in a monodisperse sample of the same mass, so that  $\lambda_i = \lambda_{ei}$ . So, the total spectrum contains  $N_L = N - N_H$  additional modes with relaxation times  $\lambda_k = \lambda_i$  and  $g_k = (\pi^2/6) M_e G_N^0 (W_i/M_i)$ .

The third contribution to the relaxation modulus is that of parts of the chains between entanglements for which a Rouse spectrum equivalent to that of a chain of mass  $M_e$  is supposed.

$$G_E(t) = \frac{\pi^2}{6} G_N^0 \left\{ \sum_i W_i F(t, \lambda_{ee}) \right\} \quad \text{if } M_i > M_c \quad (8)$$

where  $\lambda_{ee}$  is the theoretical relaxation time of a chain of length  $M_e$ . So, one more mode with relaxation time  $\lambda_k = \lambda_{ee}$  and  $g_k = (\pi^2/6) G_N^0 \sum_i W_i$  is added to the final spectrum.

At least the three contributions are summed to get the total relaxation modulus

$$G(t) = G_N(t) + G_E(t) + G_R(t) \quad (9)$$

### Experimental Relaxation Time of Monodisperse Sample $\lambda_{ei}$

The basis of the calculation of the relaxation time of any species  $M_i$  in a complex surrounding remains the experimental relaxation time of a monodisperse polymer  $\lambda_{ei}$  with the same mass, that is, in its own surrounding. This is calculated using the scaling law for zero shear rate viscosity  $\eta_0$  as a function of molecular weight

$$\eta_0(M_i) = K_E M_i^\alpha \quad (10)$$

with  $\alpha$  generally known to be close to 3.4 for molecular weight greater than  $M_c$ . The viscosity may also

be related to the characteristic time of the monodisperse sample through

$$\eta_0(M_i) = G_N^0 \lambda_{ei} \quad (11)$$

Thus

$$\lambda_{ei} = K_{tE} M_i^\alpha \quad (12)$$

with

$$K_{tE} = \frac{K_E}{G_N^0} \quad (13)$$

These expressions are valid for molecular weight  $M_i > M_c$ , whereas in the opposite case, it is assumed that the zero shear viscosity is proportional to  $M_i$  and can be calculated from the Rouse theory

$$\eta_0(M_i) = K_R M_i = \frac{\pi^2}{6} G_N^0 \frac{M_e}{M_i} \lambda_{ei} \quad (14)$$

and

$$\lambda_{ei} = K_{tR} M_i^2 \quad (15)$$

with

$$K_{tR} = \frac{6}{\pi^2} \frac{K_R}{G_N^0 M_e} \quad (16)$$

Because at  $M_c = 2M_e$  the Rouse behavior crosses the entanglement domain for the zero shear rate viscosity versus molecular weight curve

$$\eta_0(M_c) = K_R M_c = K_E M_c^\alpha \quad (17)$$

thus

$$K_{tR} = \frac{6}{\pi^2} \frac{(2M_e)^{\alpha-1}}{G_N^0 M_e} K_E \quad (18)$$

### Relaxation Time of an $i$ Chain in Polydisperse Surrounding: Tube Renewal

The relaxation time of any species such as  $M_i > M_c$  changes with the surrounding and the observed relaxation time of a polymer chain of mass  $M_i$  in a composite surrounding can be very different from that in a monodisperse environment.

Even in the case of a monodisperse sample, the relaxation time of an  $i$  chain can be assumed to be a combination of two mechanisms because either the chain has reptated out of the tube formed by

surrounding molecules with a characteristic time  $\lambda_{di}$  (wherein fluctuation of path length might also be included), or the initial surrounding has vanished through motion of other chains and the molecule under scope can renew its configuration by a Rouse motion with characteristic time  $\lambda_{Rii}$  (renewal time of the  $i$  chain in its own surrounding).

The two phenomena are assumed to act independently to give the observed experimental relaxation time of the monodisperse sample that following Graessley,<sup>25</sup> leads to

$$1/\lambda_{ei} = 1/\lambda_{di} + 1/\lambda_{Rii} \quad (19)$$

The same considerations can be taken into account for an  $i$  chain in a composite surrounding, but the renewal time in this surrounding is now  $\lambda_{Rbi}$  and the relaxation time  $\lambda_i$  of the chain is now

$$1/\lambda_i = 1/\lambda_{di} + 1/\lambda_{Rbi} \quad (20)$$

Combining (19) and (20) enables us to write

$$\lambda_i = \lambda_{ei} \{1 + \lambda_{ei}(1/\lambda_{Rbi} - 1/\lambda_{Rii})\}^{-1} \quad (21)$$

#### Tube Renewal Times $\lambda_{Rii}$ and $\lambda_{Rbi}$

Experimentally, there is some evidence that, in the monodisperse case, the renewal time is proportional to  $M_i^{4.4}$ .<sup>18,19</sup> Moreover, according to Klein,<sup>26</sup> Montfort et al.,<sup>18,19</sup> and Cassagnau et al.<sup>20</sup> the renewal time of an  $i$  chain in a  $j$  surrounding, which is the case of binary blends, is proportional to  $M_j^{2.4}M_i^2$ . According to Graessley,<sup>25</sup> these renewal times are the expression of the probability that portions of surrounding chains involved in any entanglement, playing the role of obstacles, have experienced a local "jump" to free the  $i$  chain by a constraint release process and that this chain can consequently relax according to a Rouse motion. The segment of the equivalent Rouse chain has a length of  $M_e$ . These two processes are dependent and in the monodisperse case,

$$\lambda_{Rii} = \lambda_{oi} \left( \frac{M_i}{M_e} \right)^2 \quad (22)$$

In the polydisperse case,

$$\lambda_{Rbi} = \langle \lambda_o \rangle \left( \frac{M_i}{M_e} \right)^2 \quad (23)$$

where  $\lambda_{oi}$  is the survival time of the obstacles in the monodisperse one, which all are of  $i$  nature. How-

ever, in the polydisperse case, because of the complexity of the surrounding, an average jump time of obstacles  $\langle \lambda_o \rangle$  has to be defined.

#### Obstacle Time in Monodisperse Case $\lambda_{oi}$

Considering the previous remarks, one can write

$$\lambda_{oi} = K_o M_e^2 M_i^{2.4} \quad (24)$$

It is worth mentioning that there is some doubt about the physical meaning of the 2.4 exponent in eq. (24). For Klein<sup>26</sup> the obstacle time is related to the reptation time of the surrounding chains (proportional to the third power of the molecular weight), but the constraints may not be independent because they may belong to the same chain, so that

$$\lambda_{oi} \approx M_e^2 \frac{\lambda_{di}}{M_i^{0.5}} \quad (25)$$

For Montfort<sup>18,19</sup> the obstacle time is related to the experimental relaxation time, thus scaling nearly as  $M^{3.4}$ , and obstacles vanish in a much faster way.

$$\lambda_{oi} \approx M_e^2 \frac{\lambda_{ei}}{M_i} \quad (26)$$

Equation (26) enables us to write eq. (24) in a more general form, using the  $\alpha$  exponent of the scaling law (10) of the Newtonian viscosity as a function of the molecular weight:

$$\lambda_{oi} = K_o M_e^2 M_i^{\alpha-1} \quad (27)$$

$\lambda_{oi}$  is taken to be zero for short chains ( $M_i < M_e$ ). The constant  $K_o$  is determined assuming that in the vicinity of the critical molecular weight ( $M_c$ ), contributions of the reptation and renewal processes are of the same order of magnitude in eq. (19). Thus, in this case, the renewal time is twice the experimental time and

$$K_o = \frac{K_E}{G_N^0 M_e} \quad (28)$$

#### Constraint Release: Average Obstacle Time in Polydisperse Case $\langle \lambda_o \rangle$

Graessley<sup>25</sup> and Montfort and colleagues<sup>18</sup> consider that  $\lambda_{oi}$  is the lifetime of  $i$  obstacles and that their relaxation is obtained by the release of one over  $z$  constraints, forming a surrounding cell, each relaxing according to a Rouse function, such as

$$\lambda_{oi} = \int_0^\infty \left[ \exp\left(\frac{-t}{z\lambda_{oi}}\right) \right]^z dt \quad (29)$$

In the composite surrounding, the previous authors proposed that

$$\langle \lambda_o \rangle = \int_0^\infty \left[ \sum_i W_i \exp\left(\frac{-t}{z\lambda_{oi}}\right) \right]^z dt \quad (30)$$

Assuming  $z = 3$ ,  $\langle \lambda_o \rangle$  can be calculated:

$$\langle \lambda_o \rangle = 3 \sum_i \sum_j \sum_k W_i W_j W_k \frac{\lambda_{oi}\lambda_{oj}\lambda_{ok}}{\lambda_{oi}\lambda_{oj} + \lambda_{oi}\lambda_{ok} + \lambda_{oj}\lambda_{ok}} \quad (31)$$

for  $M_i > M_c$ ,  $M_j > M_c$ , and  $M_k > M_c$ .

## EXPERIMENTAL

### Basic and Modified Materials: Peroxidation Process

Four basic polypropylenes were used in this study and they are referenced in Table I (A1, B1, C1, D1). To get samples with different types of MWD, peroxidations were performed on these resins in a 50-mL cell batch mixer (Rheocord Haake) at a temperature of 190°C and a rotational speed of 16 rpm. The temperature of the melt and the torque resulting from the viscous friction of the polymer on the counterrotating paddles were controlled. For degradation, resins were introduced in the temperature regulated cell where they experienced thermal and shear effects. A homogeneous melt was obtained in 11 min; 0.1% of 2,5 dimethyl-2,5-di(*t*-butylperoxy) hexane from Akzo Chemicals peroxide was then introduced and samples were removed either at the

end or during the reaction, after addition of an antioxidant that inhibits the reaction of degradation. The most effective antioxidant was found to be the Irgafos P-EPQ from Ciba Geigy (combined primary and secondary antioxidants) at 4% weight. Nine samples were finally obtained for this study. Their references and origins are summarized in Table I.

### Characterization: MWD and Rheological Behavior

The MWD characterization was performed by gel permeation chromatography at 145°C in ODCB (o-dichlorobenzene) after filtration of the solutions before injection [Fig. 1(a-d)].

Rheological measurements were obtained in dynamic oscillatory mode with a Rheometrics Dynamic Analyser RDA 700, using parallel plates geometry; 25- or 40-mm diameter plates were used depending on the material under study. The tests were performed at 185, 170, and 200°C with frequencies ranging, when possible, between 0.01 and 500 rad/s and master curves at 185°C were built. All experiments were carried out in the linear viscoelastic domain. This was systematically checked for each material and temperature at various frequencies. Maximum strain amplitude was chosen to avoid any strain dependence of the moduli and to insure acceptable values of the measured torque whenever possible.

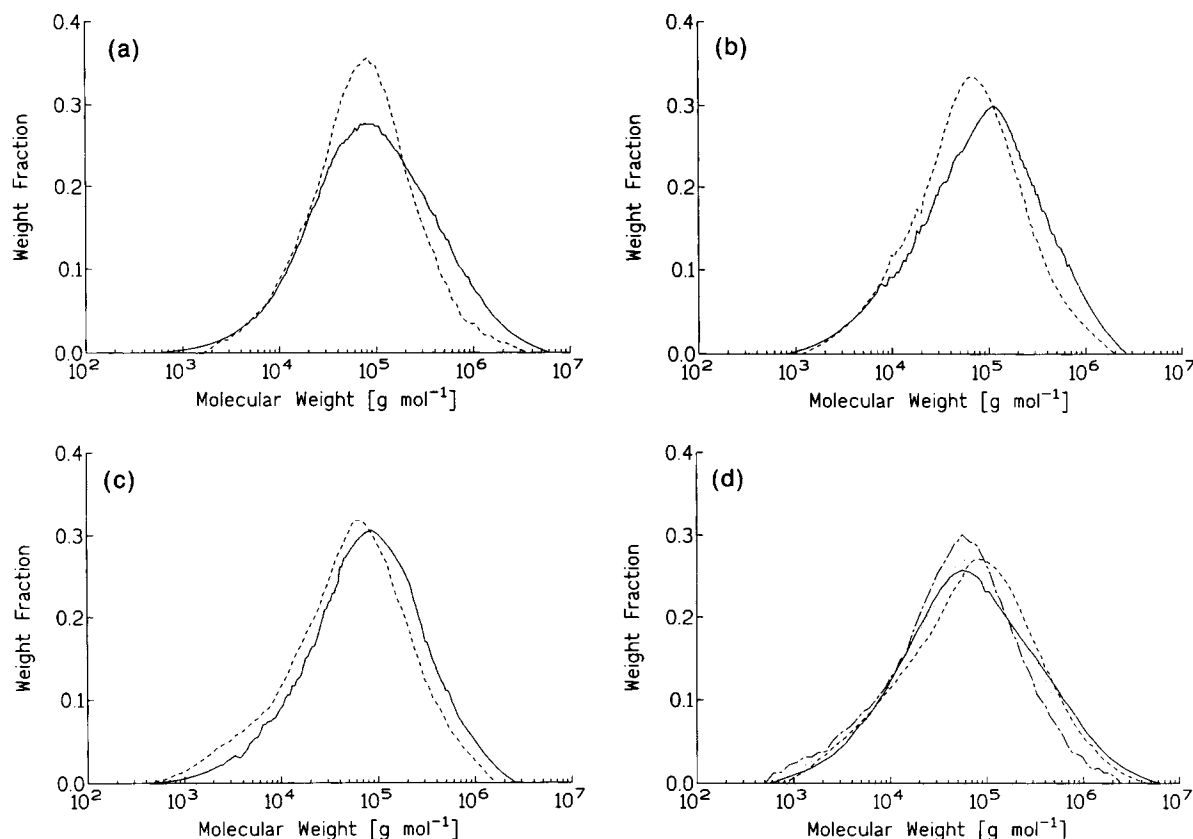
## RESULTS AND DISCUSSION

### Data for Calculation

The calculation only requires the knowledge of a few data, namely the molecular weight between entanglements, the plateau modulus, and the scaling

**Table I** Molecular Characteristics of Different Polypropylene Resins

Material	Sampling	$M_n$ (g mol <sup>-1</sup> )	$M_w$ (g mol <sup>-1</sup> )	$M_z$ (g mol <sup>-1</sup> )	$M_w/M_n$
A1	Basic Resin	30,800	225,000	1,190,000	7.3
A2	End of reaction ( $\approx$ 240 s)	33,700	150,000	581,000	4.4
B1	Basic resin	27,100	189,000	605,000	7.0
B2	End of reaction ( $\approx$ 240 s)	26,200	128,000	415,000	4.9
C1	Basic resin	25,100	165,000	540,000	6.6
C2	End of reaction ( $\approx$ 240 s)	16,100	113,000	359,000	7.0
D1	Basic resin	19,400	212,000	1,110,000	10.6
D2	Reaction stopped 45 s	20,100	186,000	795,000	9.3
D3	Reaction stopped 105 s	17,300	149,000	534,000	8.7
D4	End of reaction ( $\approx$ 240 s)	14,000	119,000	496,000	8.5



**Figure 1** (a) Molecular weight distribution of samples (—) A1 and (---) A2. (b) Molecular weight distribution of samples (—) B1 and (---) B2. (c) Molecular weight distribution of samples (—) C1 and (---) C2. (d) Molecular weight distribution of samples (—) D1, (---) D2, (···) D3, (-·-·) D4.

law for the zero shear viscosity at the temperature of the study. The plateau modulus  $G_N^0$  was taken to be  $8 \cdot 10^5$  Pa according to the results of Baumgaertel and Winter.<sup>27</sup> The molecular weight between entanglements  $M_e$  can be calculated from this value, assuming a melt density of polypropylene<sup>28</sup>  $\rho = 0.750$  g/mL according to the classical definition

$$G_N^0 = \frac{\rho RT}{M_e} \quad (32)$$

The value was found to be  $M_e = 3570$  g mol<sup>-1</sup> in agreement with Van Krevelen.<sup>28</sup> The following theoretical scaling law of the zero shear rate viscosity was used at 185°C:

$$\eta_0 = 4.10 \cdot 10^{-17} M^{3.7} \quad (33)$$

where  $\eta_0$  is in Pa s and  $M$  is in g mol<sup>-1</sup>.

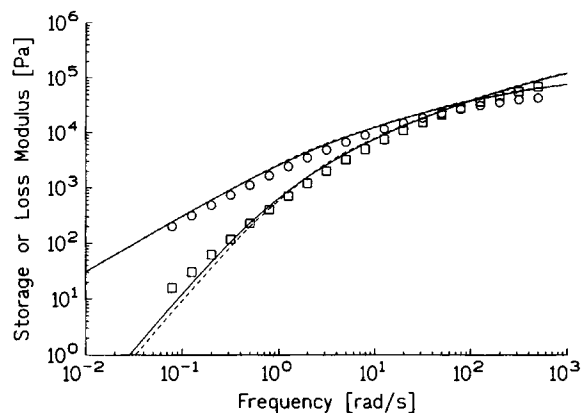
#### Discrete Spectrum with a Large Number of Modes

Calculation of the relaxation spectra were performed using a fine discretization (20 fractions) of the MWD

of the various samples. This resulted in spectra containing a large number of modes, generally on the order of 100, as shown in Table II. However, these spectra contained too many modes to be easily handled in subsequent calculations, for example, flow modelization. To get more simple and more useful

**Table II** Time Limits and Mode Number of Complete Spectrum

Material	Mode Number	Minimum Time (s)	Maximum Time (s)
A1	126	$2.67 \cdot 10^{-10}$	47.54
A2	141	$1.85 \cdot 10^{-9}$	5.09
B1	126	$4.94 \cdot 10^{-10}$	5.14
B2	126	$9.00 \cdot 10^{-10}$	1.13
C1	99	$1.17 \cdot 10^{-10}$	3.25
C2	99	$1.20 \cdot 10^{-10}$	0.49
D1	112	$2.18 \cdot 10^{-10}$	26.68
D2	126	$4.50 \cdot 10^{-10}$	15.45
D3	112	$2.05 \cdot 10^{-10}$	2.17
D4	112	$1.89 \cdot 10^{-10}$	1.16



**Figure 2** Dynamic moduli of sample C1 at 185°C from experiments (□) storage modulus, (○) loss modulus, and calculation (—) full spectrum, (---) reduced spectrum.

spectra, an “economic” spectrum with only a few modes was defined.

### Economic Spectrum with a Small Number of Modes

This spectrum with  $N_E$  modes  $(\lambda_i, g_i)$  was calculated from the previous one according to the following procedure. At first, the longest relaxation time  $\lambda_{\max}$  of the complete spectrum, which is generally known to be very important for the rheological behavior, is always taken into account in the new spectrum

$$\lambda_1 = \lambda_{\max} \quad \text{and} \quad g_1 = g_{\max} \quad (34)$$

Other relaxation times ( $i = 2$  to  $N_E$ ) are calculated starting from this longest time, considering about 1.5 times per decade and thus setting first

$$\lambda_i = 0.469^{(i-1)} \lambda_{\max} \quad (35)$$

Modulus  $g_i$  and viscosity  $\eta_i$  contributions of the new spectrum (for  $i \neq 1$ ) are calculated by summation of the corresponding contributions in the initial spectrum<sup>27</sup> between

$$\lambda_i^- = \sqrt{\lambda_i \lambda_{i-1}} \quad (36a)$$

and

$$\lambda_i^+ = \sqrt{\lambda_i \lambda_{i+1}} \quad (36b)$$

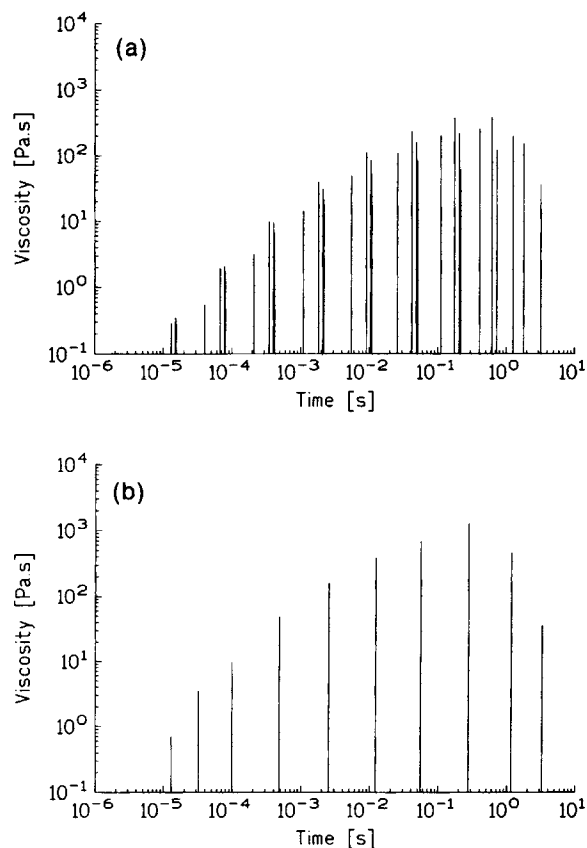
Finally, these relaxation times are renormalized according to

$$\lambda_i = \eta_i / g_i \quad (37)$$

Because short times are generally less important for calculation of the rheological behavior, the time spectrum can be more or less rapidly cut off in the short time range, depending on the operator’s will through the number of modes  $N_E$ . Figure 2 shows a comparison between values of dynamic moduli calculated either with the complete [Fig. 3(a)] or an economic spectrum using only 10 modes for sample C1 [Fig. 3(b)]. Note that, in this particular case, the spectrum was cut off in the short time range at nearly  $10^{-5}$  s.

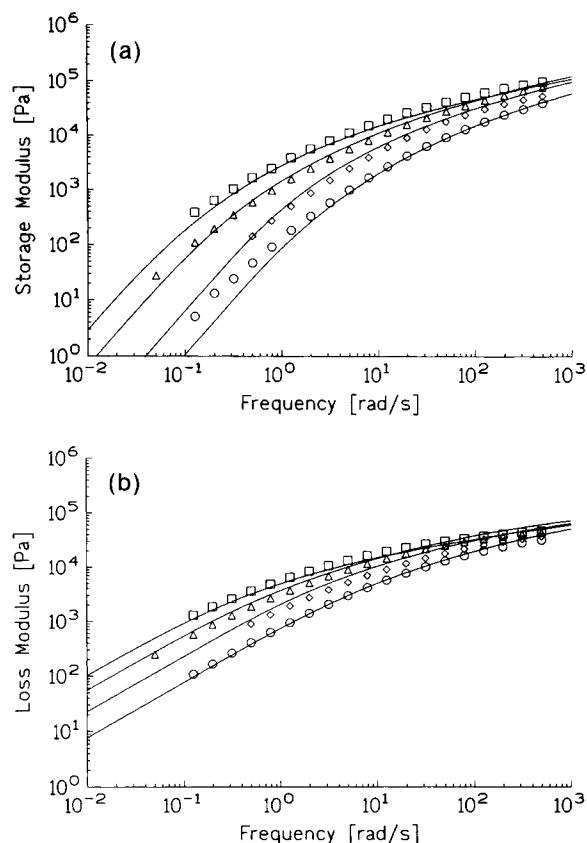
### Dynamic Moduli

Owing to the complete spectra, the storage and loss moduli of the various samples were calculated and Figure 4(a,b) shows the experimental and calculated moduli in the case of samples D1–D4 that were obtained at various times during the peroxidation of polypropylene D1. Successful depiction of the data can be obtained in these cases with physically meaningful spectra, the situation being at its best for the loss modulus and slightly worse in the case of the storage modulus. Because elasticity is known



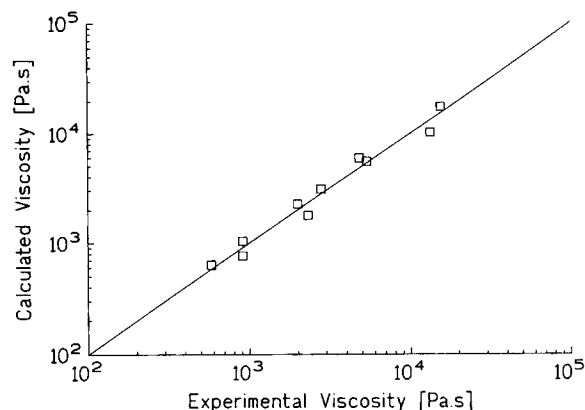
**Figure 3** (a) Complete calculated relaxation spectrum of sample C1. (b) Reduced calculated relaxation spectrum of sample C1.





**Figure 4** (a) Storage modulus of samples D at 185°C from experiments ( $\square$ ) D1, ( $\triangle$ ) D2, ( $\diamond$ ) D3, ( $\circ$ ) D4, and (—) calculation. (b) Loss modulus of samples D at 185°C from experiments ( $\square$ ) D1, ( $\triangle$ ) D2, ( $\diamond$ ) D3, ( $\circ$ ) D4, and (—) calculation.

to be very susceptible to the shape of the MWD, this might be attributed to imperfections in the description of the effect of the surrounding or tube renewal, certainly due to the strong simplifying assumptions of the calculation. It could also be shown



**Figure 5** Experimental and calculated zero shear rate viscosities.

that reduced spectra with fewer modes are also efficient to describe the dynamic moduli.

### Terminal Parameters

Table III shows the values of terminal parameters, namely the zero shear rate viscosity  $\eta_0$  and the elastic compliance  $J_e^0$ , for all samples as calculated from the complete spectrum, a 10-mode spectrum, or experiments. Figure 5 shows the perfect agreement with the later values and the calculated ones for the zero shear rate viscosity. Unfortunately, experimental values of the elastic compliance are not available because the experimental window does not extend far enough in the low frequency range to enable an accurate estimate of this parameter.

### Crossover Parameters

Because it is known<sup>2</sup> that the crossover characteristics (frequency and modulus of the crossing point

**Table III** Parameters of Terminal Zone

Material	Experimental	Complete Spectrum		Reduced Spectrum	
	$\eta_0$ (Pa s)	$\eta_0$ (Pa s)	$J_e^0$ (Pa <sup>-1</sup> )	$\eta_0$ (Pa s)	$J_e^0$ (Pa <sup>-1</sup> )
A1	$1.54 \cdot 10^4$	$1.77 \cdot 10^4$	$2.70 \cdot 10^{-4}$	$1.76 \cdot 10^4$	$2.23 \cdot 10^{-4}$
A2	$2.32 \cdot 10^3$	$1.78 \cdot 10^3$	$2.49 \cdot 10^{-4}$	$1.77 \cdot 10^3$	$2.06 \cdot 10^{-4}$
B1	$4.82 \cdot 10^3$	$5.94 \cdot 10^3$	$1.17 \cdot 10^{-4}$	$5.87 \cdot 10^3$	$9.55 \cdot 10^{-5}$
B2	$9.12 \cdot 10^2$	$1.04 \cdot 10^3$	$1.27 \cdot 10^{-4}$	$1.03 \cdot 10^3$	$1.05 \cdot 10^{-4}$
C1	$2.79 \cdot 10^3$	$3.09 \cdot 10^3$	$1.30 \cdot 10^{-4}$	$3.05 \cdot 10^3$	$1.00 \cdot 10^{-4}$
C2	$5.80 \cdot 10^2$	$6.34 \cdot 10^2$	$1.02 \cdot 10^{-4}$	$6.27 \cdot 10^2$	$8.39 \cdot 10^{-5}$
D1	$1.33 \cdot 10^4$	$1.02 \cdot 10^4$	$2.84 \cdot 10^{-4}$	$1.01 \cdot 10^4$	$2.27 \cdot 10^{-4}$
D2	$5.36 \cdot 10^3$	$5.52 \cdot 10^3$	$2.20 \cdot 10^{-4}$	$5.51 \cdot 10^3$	$1.94 \cdot 10^{-4}$
D3	$2.00 \cdot 10^3$	$2.26 \cdot 10^3$	$1.28 \cdot 10^{-4}$	$2.24 \cdot 10^3$	$1.07 \cdot 10^{-4}$
D4	$9.11 \cdot 10^2$	$7.64 \cdot 10^2$	$1.84 \cdot 10^{-4}$	$7.52 \cdot 10^2$	$1.44 \cdot 10^{-4}$

Table IV Crossover Values

Material	Experimental		Complete Spectrum		Reduced Spectrum	
	$\omega_c$ (rad s <sup>-1</sup> )	$G_c$ (Pa)	$\omega_c$ (rad s <sup>-1</sup> )	$G_c$ (Pa)	$\omega_c$ (rad s <sup>-1</sup> )	$G_c$ (Pa)
A1	13	2.99 10 <sup>4</sup>	9	1.97 10 <sup>4</sup>	8	1.94 10 <sup>4</sup>
A2	87	3.16 10 <sup>4</sup>	294	5.10 10 <sup>4</sup>	294	5.13 10 <sup>4</sup>
B1	44	3.16 10 <sup>4</sup>	36	3.11 10 <sup>4</sup>	36	3.14 10 <sup>4</sup>
B2	270	3.63 10 <sup>4</sup>	346	4.52 10 <sup>4</sup>	304	4.31 10 <sup>4</sup>
C1	64	2.44 10 <sup>4</sup>	95	3.80 10 <sup>4</sup>	92	3.83 10 <sup>4</sup>
C2	339	2.73 10 <sup>4</sup>	478	4.24 10 <sup>4</sup>	470	4.25 10 <sup>4</sup>
D1	11	1.82 10 <sup>4</sup>	9	1.43 10 <sup>4</sup>	9	1.40 10 <sup>4</sup>
D2	30	2.01 10 <sup>4</sup>	36	2.49 10 <sup>4</sup>	43	2.96 10 <sup>4</sup>
D3	79	2.12 10 <sup>4</sup>	82	2.78 10 <sup>4</sup>	82	2.80 10 <sup>4</sup>
D4	177	2.24 10 <sup>4</sup>	346	3.29 10 <sup>4</sup>	263	3.02 10 <sup>4</sup>

of the storage modulus and loss modulus versus frequency curves) are very susceptible to the MWD, we paid some attention to these values. As can be seen in Table IV and Figure 6, there is a fair agreement between the experimental and theoretical values for the frequency. The result is rather unsatisfying as far as the modulus is concerned, although the variation of the calculated values is consistent with that of the experimental data. Because the crossover modulus is generally assumed to be related to the polydispersity,<sup>2</sup> this discrepancy may be attributed to an improper or at least incomplete description of the surrounding effect on the relaxation of a given chain as already mentioned earlier.

### Terminal Parameters in Relation to Average Molecular Weights

Figure 7 shows the variation of the calculated zero shear viscosity versus the weight average molecular weight of the various samples. The calculated scaling

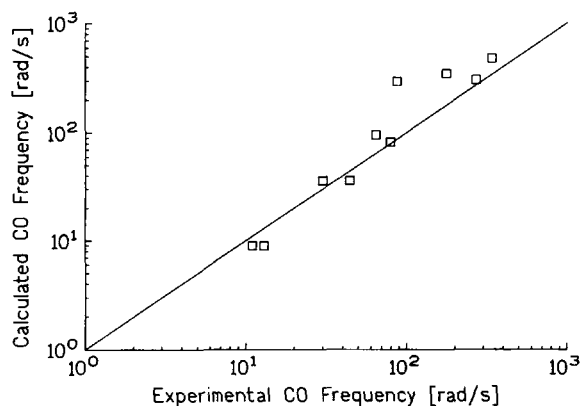


Figure 6 Experimental and calculated crossover frequencies.

law for polydisperse polypropylene samples at 185°C is

$$\eta_0 = 1.89 \cdot 10^{-21} M_w^{4.65} \quad (38)$$

where  $\eta_0$  is in Pa s and  $M_w$  is in g mol<sup>-1</sup>.

This has to be compared with the scaling law (33) for monodisperse fractions. The exponent of scaling law (38) is much larger for polydisperse materials as already mentioned by other authors.<sup>18</sup>

As shown in Figure 8, the calculated equilibrium elastic compliance is found to be related to a polydispersity index defined as  $M_z/M_w$  rather than the classical  $I_p = M_w/M_n$ , according to the linear relation

$$J_e^0 = 10^{-4}(0.79M_z/M_w - 1.40) \quad (39)$$

where  $J_e^0$  is in Pa<sup>-1</sup>. (The former relation was obtained without taking sample A2 into account that shows a large deviation from the set of data.) This

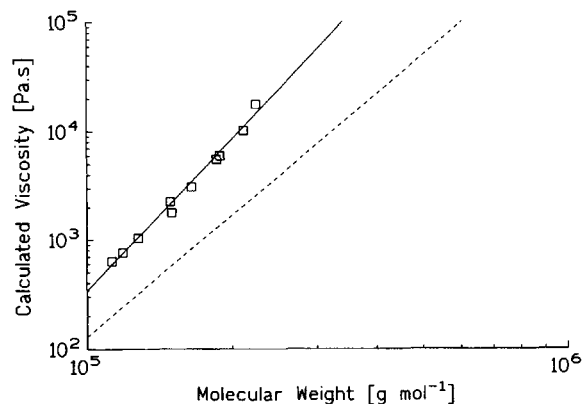
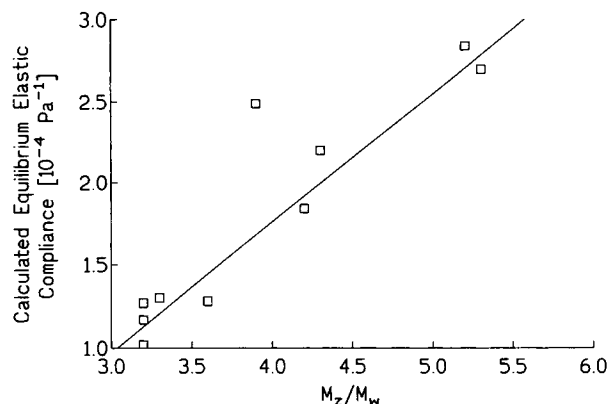


Figure 7 Scaling law of the Newtonian viscosity of polypropylene samples at 185°C: (□) and (—) polydisperse, (---) monodisperse.



**Figure 8** Equilibrium elastic compliance of polypropylene samples at 185°C in relation to polydispersity index, (—) relation (39) without taking into account sample A2.

is consistent with the drastic influence of a small amount of large molecules mentioned in the literature.<sup>29</sup>

## CONCLUSION

Owing to a few assumptions, simplified molecular dynamics enables the calculation of a discrete relaxation spectrum from known MWD of various samples of polypropylene. These samples with different MWD (weight average molecular weight ranging from 110,000 to 225,000 g mol<sup>-1</sup> and polydispersity from 4 to 10) were obtained by melt peroxidation in an internal mixer. Dynamic moduli, Newtonian viscosity, and crossover frequency were fairly well recovered in the experimental range, but some discrepancies were observed for the crossover modulus. These were attributed to the simplified way by which the effect of the surrounding is taken into account. Nevertheless, the predicted variations of the Newtonian viscosity and of the equilibrium elastic compliance toward the averages of the MWD were in agreement with experimental relations already noted in the literature. Because of the complexity of the original spectrum, it has been shown that this spectrum can be reduced to a more simple one, with about 10 modes, without significant loss of information. This could be of great interest for calculation of complex flows using nonlinear constitutive equations and temporary network models. Indeed, time and memory saving can therefore be achieved because the memory function is described with a limited number of parameters while retaining some physical significance of the relaxation times.

## REFERENCES

1. M. Fleissner, *Makromol. Chem., Macromol. Symp.*, **61**, 324 (1992).
2. G. R. Zeichner and P. D. Patel, 2nd World Congress of Chem. Eng., Montréal, 1981.
3. B. H. Bersted, *J. Appl. Polym. Sci.*, **19**, 2167 (1975).
4. B. H. Bersted, *J. Appl. Polym. Sci.*, **20**, 2705 (1976).
5. B. H. Bersted, *J. Appl. Polym. Sci.*, **23**, 1279 (1979).
6. B. H. Bersted and J. D. Slee, *J. Appl. Polym. Sci.*, **21**, 2631 (1977).
7. W. H. Tuminello and N. Cudre-Mauroux, *Polym. Eng. Sci.*, **31**, 1496 (1991).
8. M. T. Shaw and W. H. Tuminello, *Polym. Eng. Sci.*, **34**, 159 (1994).
9. A. Y. Malkin and A. E. Teishev, *Polym. Eng. Sci.*, **31**, 1590 (1991).
10. S. Wu, *Polym. Eng. Sci.*, **25**, 122 (1985).
11. W. H. Tuminello, *Polym. Eng. Sci.*, **26**, 1339 (1986).
12. W. H. Tuminello, *Polym. Eng. Sci.*, **29**, 645 (1989).
13. W. J. McGrory and W. H. Tuminello, *J. Rheol.*, **34**, 867 (1990).
14. S. H. Wasserman and W. W. Graessley, *J. Rheol.*, **36**, 543 (1992).
15. J. Des Cloiseaux, *J. Europhys. Lett.*, **5**, 437 (1988) and **6**, 475 (1988).
16. T. L. Yu, *J. Polym. Eng.*, **12**, 331 (1993).
17. G. Eder, H. Janeschitz-Kriegl, S. Liedauer, A. Schausberger, W. Stadlbauer, and G. Schindlauer, *J. Rheol.*, **33**, 805 (1989).
18. J. P. Montfort, G. Marin, and P. Monge, *Macromolecules*, **19**, 1979 (1986).
19. J. P. Montfort, G. Marin, and P. Monge, *Macromolecules*, **17**, 1551 (1984).
20. P. Cassagnau, J. P. Montfort, G. Marin, and P. Monge, *Rheol. Acta*, **32**, 156 (1993).
21. R. R. Rahalkar and H. Tang, *Rubber Chem. Technol.*, **61**, 812 (1988).
22. R. R. Rahalkar, *Rheol. Acta*, **28**, 166 (1989).
23. J. Des Cloiseaux, *Macromolecules*, **23**, 4678 (1990).
24. J. Des Cloiseaux, *Macromolecules*, **25**, 835 (1992).
25. W. W. Graessley, *Advances in Polymer Science*, Vol. 47, Springer-Verlag, New York, 1982.
26. J. Klein, *Macromolecules*, **19**, 105 (1986).
27. M. Baumgaertel and H. H. Winter, *J. Non-Newton. Fluid Mech.*, **44**, 15 (1992).
28. D. W. Van Krevelen, *Properties of Polymers, Their Estimation and Correlation with Chemical Structure*, 2nd ed., Elsevier, New York, 1976.
29. J. P. Montfort, G. Marin, J. Arman, and P. Monge, *Polymer*, **19**, 277 (1978).

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