Controlled Rheology of Polypropylene: Modeling of Molecular Weight Distributions

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ABSTRACT: A mathematical model for the controlled degradation of polypropylene is presented in this article. A previous model of this process was extended to predict the whole molecular weight distribution of the modified resin. Probability generating functions were applied to transform the infinite set of mass balance equations of both polymer and radicals. The integration of the transformed set of equations yielded the probability generating function transforms. These transforms were then inverted with two different inversion algorithms, recovering the molecular weight distributions of the polymer. The model predictions were compared with our experimental data and other information taken from the literature. Good agreement was obtained. The approach presented here is also useful for other polymerization and postpolymerization processes. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 1676–1685, 2003

Key words: molecular weight distribution/molar mass distribution; poly(propylene) (PP); modeling; modification

INTRODUCTION

The processability of polyolefins and/or the performance of their final products are strongly dependent on molecular parameters such as molecular weight, molecular weight distribution (MWD), and branching. Desired values of these properties can be achieved either by manipulation of the polymerization reactor operating conditions or by a postreactor modification of the resin.

In particular, polypropylene (PP) produced in conventional reactors has excellent mechanical properties, but because of catalyst characteristics, it has a relatively high molecular weight and a broad MWD. These features cause high melt viscosity and elasticity, which result in unsuitable melt flow properties. Better control of the MWD is usually difficult and is not economical to perform during the polymerization process. However, it has been shown that the induction of chain scission in the synthesized resin improves flow characteristics because scission preferentially affects the longer chains and narrows the MWD. At the same time, the mechanical properties remain practically unchanged.[1,2] Chain scission is commercially achieved by means of a process called the *controlled degradation* (or *controlled rheology*) of PP. This is a postreactor

procedure that consists of a reactive extrusion of the polymer with organic peroxides. These peroxides decompose into radicals that attack the tertiary carbon atoms on the polymer backbone to form macroradicals that under usual extrusion conditions, undergo scission reactions. Because each tertiary carbon on the polymer molecule has an equal chance of being attacked, larger molecules are more likely to suffer scission. As a result, the molecular weight is reduced, and the MWD narrows.[3] With this process, the polymerization reactor can run at a set of optimal operating conditions, and the undesirable properties of the virgin resin can then be modified to different extents, resulting in a wide variety of higher priced products.

The use of peroxides implies that a variety of reactions occurs simultaneously. It is common practice to make several trials on the operating conditions before the desired product is obtained. More fundamental studies would help to clarify how these operating conditions affect the molecular properties of modified resins. It would also be helpful in the design of new products and in the optimization strategies before production on a commercial scale.

Several authors have dealt with modeling the controlled degradation of PP;[4–16] about half of them have presented models that calculate complete MWD.[4,10,11,13,15,16] Mead[16] and Triacca et al.[11] used a statistical approach with a single adjustable parameter, the degree of chain scission. Triacca et al.[11] determined this parameter from experimental average molecular weights; Mead did not present experimental information about MWD but showed the evolution of theoretical distributions for different degrees of

chain scission. The statistical approach does not provide information on the time evolution of the MWD. Suwanda et al.[13] and Pabedinskas et al.[10] developed semianalytical solutions based on a kinetic scheme. The kinetic mechanism they considered included only peroxide decomposition, hydrogen abstraction, chain scission, and termination by disproportionation. They used the pseudostationary state hypothesis for the radical species. Iedema et al.[4] and Oliveira et al.[15] based their model on more complete kinetic mechanisms, which included peroxide decomposition, hydrogen abstraction, and chain scission; chain transfer; thermal degradation; and termination by disproportionation. Oliveira's kinetic scheme coincides with the one we present in this article. They used the pseudostationary state hypothesis for radical species. They also simplified by setting the kinetic constant of the thermal degradation reaction equal to zero, which was a reasonable assumption for the experimental data they tried to reproduce. Nevertheless, in the literature, we found that thermal degradation cannot be neglected in many cases.[4,6] With other considerations, Oliveira et al. fit the model to experimental MWD by adjusting only the peroxide decomposition constant. To solve the model, they approximated the chain length as a continuous variable and then solved a system of partial differential equations. They obtained a good approximation of the tail of high molecular weights but large deviations in the shortest chains. Iedema et al.'s model consists of the same kinetic steps as our model and Oliveira's model but differs in the formulation of some of these steps. They solved the model with a discrete Galerkin method. They analyzed the kinetic mechanism and fit the kinetic constant with experimental MWD. They concluded that all the kinetic steps mentioned previously were necessary to reproduce the experimental data. Krell et al.[6] and Berzin et al.[9] also solved a complete set of kinetic reactions, including thermal degradation and chain transfer, but they did not model complete MWD.

In the work by Krell et al.,[6] some of the authors proposed a kinetic model that predicted average molecular weights for the controlled rheology of PP. It was based on a kinetic mechanism proposed in earlier publications but included relevant corrections with respect to some of the terms of the mass balances. What is more, the complete kinetic mechanism had never been solved before. This model resulted in good predictions of the experimental data obtained at different temperatures and screw rotational speeds.

In this work, we extend our previous mathematical model to predict the complete MWD of PP during the modification process given the operating conditions. We focus on the modification taking place in an extruder at isothermal conditions. To this purpose, we make use of our previously established set of mass balances for the reaction species and apply a transform technique. By doing this, the infinite set of differential equations corresponding to the balances of macromolecules of chain length n, with $1 \leq n \leq \infty$, is transformed into a finite set of differential equations for the transforms of the number, weight, and chromatographic MWDs. The chosen transform is the probability generating function (pgf), which we described extensively elsewhere.[17] It has already been used for the prediction of the MWD of polyethylene both in polymerization processes and postreactor modification.[18,19] The pgf transforms are defined for discrete distributions, as the MWD is, so it is not necessary to assume the chain length to be a continuous variable. Besides, they require no previous insight on the shape of the MWD. Other methods, such as the discrete Galerkin method, require some knowledge about the MWD shape to find an appropriate weight function.

Three different pgf's are defined to describe the number, weight, and chromatographic distributions. pgf's are integrated along residence time. Then, they are numerically inverted with two previously tested numerical inversion methods.[20,21] This allows recovery of the MWDs. The moments of the distributions are needed as input for the pgf differential equations, so they are calculated as functions of residence time simultaneously with the pgf's.

In the following sections, we show a description of our MWD model for the controlled rheology of PP and a validation of the model results with experimental information taken from our previous work and other published data. Different applications of the MWD model are also illustrated.
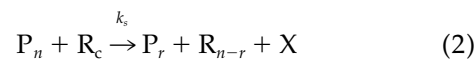
MWD MODEL

The kinetic mechanism considered by Krell et al.[6] for the controlled rheology of PP by peroxides at low concentration is summarized next.
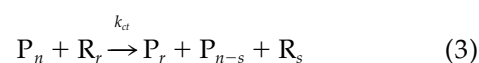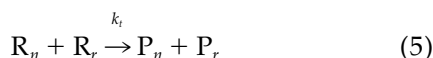
For peroxide decomposition

$$I \xrightarrow{k_d} 2R_c \qquad (1)$$

For scission

$$P_n + R_c \xrightarrow{k_s} P_r + R_{n-r} + X \qquad (2)$$

For chain transfer

$$P_n + R_r \xrightarrow{k_{ct}} P_r + P_{n-s} + R_s \qquad (3)$$

For thermal degradation

$$P_n \xrightarrow{k_{td}} R_r + R_{n-r} \qquad (4)$$

For termination by disproportionation

$$R_n + R_r \xrightarrow{k_t} P_n + P_r \qquad (5)$$

The mechanism includes radical generation by initiator decomposition (eq. (1)), scission (eq. (2)), chain transfer to the polymer [eq. (3)], thermal degradation (eq. (4)) and termination by disproportionation (eq. (5)), with kinetic constants k_d, k_s, k_{ct}, k_{td}, and k_t, respectively. In these equations, I is the initiator, R_c is the initiation radical, P and R are polymer molecules and macroradicals with as many monomer units as their subscripts (n, r, s, . . .) indicate. X is an inert molecule.

The modification process is postulated to occur isothermally. The equations are written in a general manner avoiding the usual assumption of quasi steady state of radicals, although we verified that in this particular case that assumption is valid. Radicals and macroradicals are assumed to contain only one active site, something reasonable for a system expected to remain far from the gel point.

pgf definitions for the number, weight, and chromatographic chain distributions of radicals and the polymer must be applied to the corresponding mass balances. In the following text, we first present these mass balances developed for the modification performed in an extruder where plug flow is assumed. Afterward, we describe the application of the pgf's to this problem.

Mass balances for all the species present during the process are shown in eqs. (6)–(9), where the independent variable t is the residence time.

For the initiator

$$\frac{d[I]}{dt} = -k_d[I] \qquad (6)$$

For the initiation radical

$$\frac{d[R_c]}{dt} = 2k_d f[I] - [R_c]k_s \sum_{i=1}^{\infty} (i-1)[P_i] \qquad (7)$$

where f is the initiator efficiency.

For the polymer molecule P_n ($n = 1, 2, ...$)

$$\frac{d[P_n]}{dt} = k_s[R_c]\left[\sum_{r=n+1}^{\infty}[P_r] - (n-1)[P_n]\right] - k_{ct}(n-1)$$

$$\times [P_n]\sum_{r=1}^{\infty}[R_r] + k_{ct}[R_n]\sum_{r=1}^{\infty}(r-1)[P_r]$$

$$+ k_{ct}\sum_{i=1}^{\infty}[R_i]\sum_{r=n+1}^{\infty}[P_r] + k_t[R_n]\sum_{r=1}^{\infty}[R_r] - k_{td}(n-1)[P_n]$$

$$(8)$$

For the macroradical R_n ($n = 1, 2, ...$)

$$\frac{d[R_n]}{dt} = k_s[R_c]\sum_{r=n+1}^{\infty}[P_r] - k_{ct}[R_n]\sum_{r=1}^{\infty}(r-1)[P_r]$$

$$+ k_{ct}\sum_{i=n+1}^{\infty}[P_i]\sum_{r=1}^{\infty}[R_r] - k_t[R_n]\sum_{r=1}^{\infty}[R_r] + 2k_{td}\sum_{r=n+1}^{\infty}[P_r]$$

$$(9)$$

As the radical and polymer molecules may have any length between 1 and infinity, the mass balance equations are infinite in number. One of the techniques we employ in this work to overcome this difficulty is the well-known moment technique.[22,23] To this purpose, the following moment equations must be defined [eqs (10) and (11)].

For the ath moment of chain-length distribution of polymer molecules (M_a)

$$M_a = \sum_{n=1}^{\infty} n^a P_n \quad a = 0, 1, 2, ... \qquad (10)$$

For the ath moment of chain-length distribution of radicals (Y_a)

$$Y_a = \sum_{n=1}^{\infty} n^a R_n \quad a = 0, 1, 2, ... \qquad (11)$$

Replacing the sum in the second term of the right hand side of eq. (7) by the corresponding moments leads to eq. (12):

$$\frac{d[R_c]}{dt} = 2k_d f[I] - [R_c]k_s(M_1 - M_0) \qquad (12)$$

To obtain the moment balance equations for the polymer and radicals, both sides of eqs. (8) and (9) must be multiplied by n^a and then summed for all possible values of n ($n = 1, 2, . . .$). After some labori-

ous algebraic steps, eqs. (13)–(15) result, as detailed in our previous work.[6]

For the ath moment of the polymer ($a = 0, 1, 2, 3, \ldots$)

$$\frac{dM_a}{dt} = k_s[\mathrm{R}_c]\left[\sum_{i=2}^{\infty}[\mathrm{P}_i]\sum_{r=1}^{i-1}r^a - (M_{a+1} - M_a)\right] - k_{ct}$$

$$\times (M_{a+1} - M_a)Y_0 + k_{ct}Y_a(M_1 - M_0) + k_{ct}Y_0\sum_{i=2}^{\infty}[\mathrm{P}_i]\sum_{r=1}^{i-1}r^a$$

$$+ k_t Y_a Y_0 - k_{td}(M_{a+1} - M_a) \quad (13)$$

For the ath moment of the radical ($a = 0, 1, 2, 3, \ldots$)

$$\frac{dY_a}{dt} = k_s[\mathrm{R}_c]\sum_{i=2}^{\infty}[\mathrm{P}_i]\sum_{r=1}^{i-1}r^a - k_{ct}Y_a(M_1 - M_0)$$

$$+ k_{ct}\sum_{i=2}^{\infty}[\mathrm{P}_i]\sum_{r=1}^{m-1}r^a Y_0 - k_t Y_a Y_0 + 2k_{td}\sum_{i=2}^{\infty}[\mathrm{P}_i]\sum_{r=1}^{i-1}r^a \quad (14)$$

where

$$\sum_{i=2}^{\infty}[\mathrm{P}_i]\sum_{r=1}^{i-1}r^a$$

$$= \begin{cases} M_1 - M_0 & \text{if } a = 0 \\ \dfrac{1}{2}M_2 - \dfrac{1}{2}M_1 & \text{if } a = 1 \\ \dfrac{1}{3}M_3 - \dfrac{1}{2}M_2 + \dfrac{1}{6}M_1 & \text{with } M_3 = \left(\dfrac{M_2}{M_1}\right)^3 M_0 \quad \text{if } a = 2 \end{cases}$$

$$(15)$$

As we explain later, the zeroth, first, and second moments are necessary for the pgf calculations. Equations (6) and (12)–(15) must be solved together with the pgf equations.

pgf transformation

pgf's ($\psi_i(z)$) are defined as

$$\psi_a(z) = \sum_{n=0}^{\infty} p_a(n)z^n \quad a = 0, 1, \text{ and } 2 \quad (16)$$

where z is the pgf dummy variable, n is the macromolecule chain length, and $p_a(n)$ is a probability. We define three different probabilities, indicated with the subscript $a = 0, 1,$ and 2, which are equivalent to the number, weight, and chromatographic fraction of the macromolecules of chain length n, respectively. When each of these probabilities is used, the resulting pgf is the transform of the number, weight, and chromato-

graphic distribution. A detailed explanation is found elsewhere.[17–19] Through appropriate numerical inversion of these transforms, the corresponding entire MWDs can be obtained.

pgf's are defined for both polymer and radical distributions, for which we use the symbols $\psi_a(z)$ and $\phi_a(z)$, respectively.

The pgf balance equations for polymer and radical distributions are obtained by transforming term by term the balances for P_n and R_n, respectively. The pgf transforms of several individual balance terms can be found in a pgf transform table we presented previously[17] or by following the procedure indicated in ref. 17. A reduced version of this table for this system is shown in Table I. In this table, all variables of the balance term that do not depend on the chain length are included in a constant α.

To obtain the transforms of the radical and polymer distributions, eqs. (9) and (8) are transformed, respectively. Finally, the following expressions are obtained.

For the pgf balance of the radical-number distribution [$\phi_0(z)$]

$$\frac{\partial(Y_0\phi_0(z))}{\partial t} = \frac{k_s}{z-1}[\mathrm{R}_c][M_0\psi_0(z) - M_0] - k_{ct}Y_0\phi_0(z)(M_1$$

$$- M_0) + \frac{k_{ct}}{z-1}[M_0\psi_0(z) - M_0]Y_0 - k_t Y_0 Y_0 \phi_0(z)$$

$$+ 2\frac{k_{td}}{z-1}[M_0\psi_0(z) - M_0] \quad (17)$$

For the pgf balance of the polymer-number distribution [$\psi_0(z)$]

$$\frac{\partial[M_0\psi_0(z)]}{\partial t} = k_s[\mathrm{R}_c]\left[\frac{1}{z-1}[M_0\psi_0(z) - M_0]\right.$$

$$\left. - \left(z\frac{\partial[M_0\psi_0(z)]}{\partial z} - M_0\psi_0(z)\right)\right] - k_{ct}Y_0$$

$$\times \left(z\frac{\partial[M_0\psi_0(z)]}{\partial z} - M_0\psi_0(z)\right) + k_{ct}Y_0\phi_0(z)(M_1 - M_0)$$

$$+ k_{ct}Y_0\frac{1}{z-1}[M_0\psi_0(z) - M_0] + k_t Y_0\phi_0(z)$$

$$- k_{td}\left(z\frac{\partial[M_0\psi_0(z)]}{\partial z} - M_0\psi_0(z)\right) \quad (18)$$

For the pgf balance of the radical-weight distribution [$\phi_1(z)$]

$$\frac{\partial[Y_1\phi_1(z)]}{\partial t} = \frac{k_s}{(z-1)^2}[\mathrm{R}_c][M_1\psi_1(z)(z-1) + z[M_0$$

$$- M_0\psi_0(z)]] - k_{ct}Y_1\phi_1(z)(M_1 - M_0) + \frac{k_{ct}}{(z-1)^2}$$

TABLE I
Reduced pgf Transform Table

Balance term, $n \geq 0$	Pgf transform
$\dfrac{d([\mathrm{T}_n])}{dt}$	$\dfrac{d[U_a \Phi_a(z)]}{dt}$
$\alpha[\mathrm{T}_n]$	$\alpha U_a \Phi_a(z)$
$\alpha n[\mathrm{T}_n]$	$\alpha \left[z \dfrac{\partial(U_a \Phi_a(z))}{\partial z} + \left(\dfrac{MW_{T_0}}{MW_M} \right)^{a+1} \right]$
$\alpha \sum_{m=n+1}^{\infty}[\mathrm{T}_m]$	$gst(a) = \begin{cases} \dfrac{\alpha}{1-z}[U_0 - [U_0\Phi_0(z)]] & a = 0 \\[2ex] \dfrac{\alpha}{(1-z)^2}[(z-1)(U_1\Phi_1(z)) + z(U_0 - [U_0\Phi_0(z)])] & a = 1 \\[2ex] \dfrac{\alpha}{(1-z)^3}[-(z-1)^2[U_2\Phi_2(z)] + 2z(z-1)[U_1\Phi_1(z)] - z(z+1)[U_0\Phi_0(z)] + z(z+1)U_0] & a = 2 \end{cases}$

T = polymer (P) or radical (R) molecule macroradicals with as many monomer units as its subscript indicates; U_a = polymer or radical moment of order a ($a = 0, 1, 2$) (M_a or Y_a); MW_M = monomer molecular weight; MW_{T_0} = molecular weight of a macromolecule of chain length 0 (in this case, $MW_{T_0} = 0$); $\Phi_a(z)$ = polymer or radical pgf (with $a = 0, 1,$ or 2) ($\psi_a(z)$ or $\phi_a(z)$).

$$\times [M_1\psi_1(z)(z-1) + z[M_0 - M_0\psi_0(z)]]Y_0 - k_t Y_1\phi_1(z)Y_0$$

$$+ 2\frac{k_{td}}{(z-1)^2}[M_1\psi_1(z)(z-1) + z[M_0 - M_0\psi_0(z)]] \quad (19)$$

For the pgf balance of the polymer-weight distribution $[\psi_1(z)]$

$$\frac{\partial[M_1\psi_1(z)]}{\partial t} = k_s[\mathrm{R_c}]\left[\frac{1}{(z-1)^2}[M_1\psi_1(z)(z-1) \right.$$

$$\left. + z[M_0 - M_0\psi_0(z)]] - \left(z\frac{\partial[M_1\psi_1(z)]}{\partial z} - M_1\psi_1(z) \right) \right]$$

$$- k_{ct}Y_0\left(z\frac{\partial[M_1\psi_1(z)]}{\partial z} - M_1\psi_1(z) \right) + k_{ct}Y_1\phi_1(z)(M_1 - M_0)$$

$$+ k_{ct}Y_0\frac{1}{(z-1)^2}[M_1\psi_1(z)(z-1) + z[M_0 - M_0\psi_0(z)]]$$

$$+ k_t Y_1\phi_1(z)Y_0 - k_{td}\left(z\frac{\partial[M_1\psi_1(z)]}{\partial z} - M_1\psi_1(z) \right) \quad (20)$$

For the pgf balance of the radical chromatographic distribution $[\phi_2(z)]$

$$\frac{\partial[Y_2\phi_2(z)]}{\partial t} = \frac{k_s}{(z-1)^3}[\mathrm{R_c}][(z-z^2)2M_1\psi_1(z)$$

$$+ (z^2 + z)M_0\psi_0(z) + (z^2 - 2z + 1)M_2\psi_2(z) - (z^2 + z)M_0]$$

$$- k_{ct}Y_2\phi_2(z)(M_1 - M_0) + \frac{k_{ct}}{(z-1)^3}[(z-z^2)2M_1\psi_1(z)$$

$$+ (z^2 + z)M_0\psi_0(z) + (z^2 - 2z + 1)M_2\psi_2(z)$$

$$- (z^2 + z)M_0]Y_0 - k_t Y_2\phi_2(z)Y_0 + 2\frac{k_{td}}{(z-1)^3}$$

$$\times [(z-z^2)2M_1\psi_1(z) + (z^2 + z)M_0\psi_0(z)$$

$$+ (z^2 - 2z + 1)M_2\psi_2(z) - (z^2 + z)M_0] \quad (21)$$

For the balance of the pgf of the polymer chromatographic distribution $[\psi_2(z)]$

$$\frac{\partial[M_2\psi_2(z)]}{\partial t} = k_s[\mathrm{R_c}]\left[\frac{1}{(z-1)^3}[(z-z^2)2M_1\psi_1(z) \right.$$

$$+ (z^2 + z)M_0\psi_0(z) + (z^2 - 2z + 1)M_2\psi_2(z) - (z^2 + z)M_0]$$

$$\left. - \left(z\frac{\partial[M_2\psi_2(z)]}{\partial z} - M_2\psi_2(z) \right) \right] - k_{ct}Y_0$$

$$\times \left(z\frac{\partial[M_2\psi_2(z)]}{\partial z} - M_2\psi_2(z) \right) + k_{ct}Y_2\phi_2(z)(M_1 - M_0)$$

$$+ k_{ct}Y_0\frac{1}{(z-1)^3}[(z-z^2)2M_1\psi_1(z) + (z^2 + z)M_0\psi_0(z)$$

$$+ (z^2 - 2z + 1)M_2\psi_2(z) - (z^2 + z)M_0] + k_t Y_2\phi_2(z)Y_0$$

$$- k_{td}\left(z\frac{\partial[M_2\psi_2(z)]}{\partial z} - M_2\psi_2(z) \right) \quad (22)$$

As shown in the pgf balance equations, the integration variable is the product of the pgf by a moment. This is done for convenience in the numerical resolution. After integration, the pgf values are calculated with these integration variables and the moments, whose balances are integrated together with the pgf ones.

TABLE II
Kinetic Parameters

Kinetic constant	A (L mol s)	E (cal mol)
Efficiency, $f = 0.68$	—	—
k_d	1.98×10^{12}	29,700
k_s	1×10^9	20,000
k_{ct}	5.49×10^3	10,658
k_{td}	0.12	18,646
k_t	3.5×10^8	19.87

A = pre-exponential factor; E = activation energy.

pgf model resolution

The system of equations formed by eqs. (6), (12)–(15), and (17)–(22) was solved by means of Gear's method[24] for stiff systems. Partial derivatives with respect to z that appear in pgf balances were discretized by backward finite differences. The kinetic parameters involved in these equations were obtained as a fine tuning of those reported in our previous model.[6] These parameters were adjusted to fit experimental average molecular weights. It is important to mention
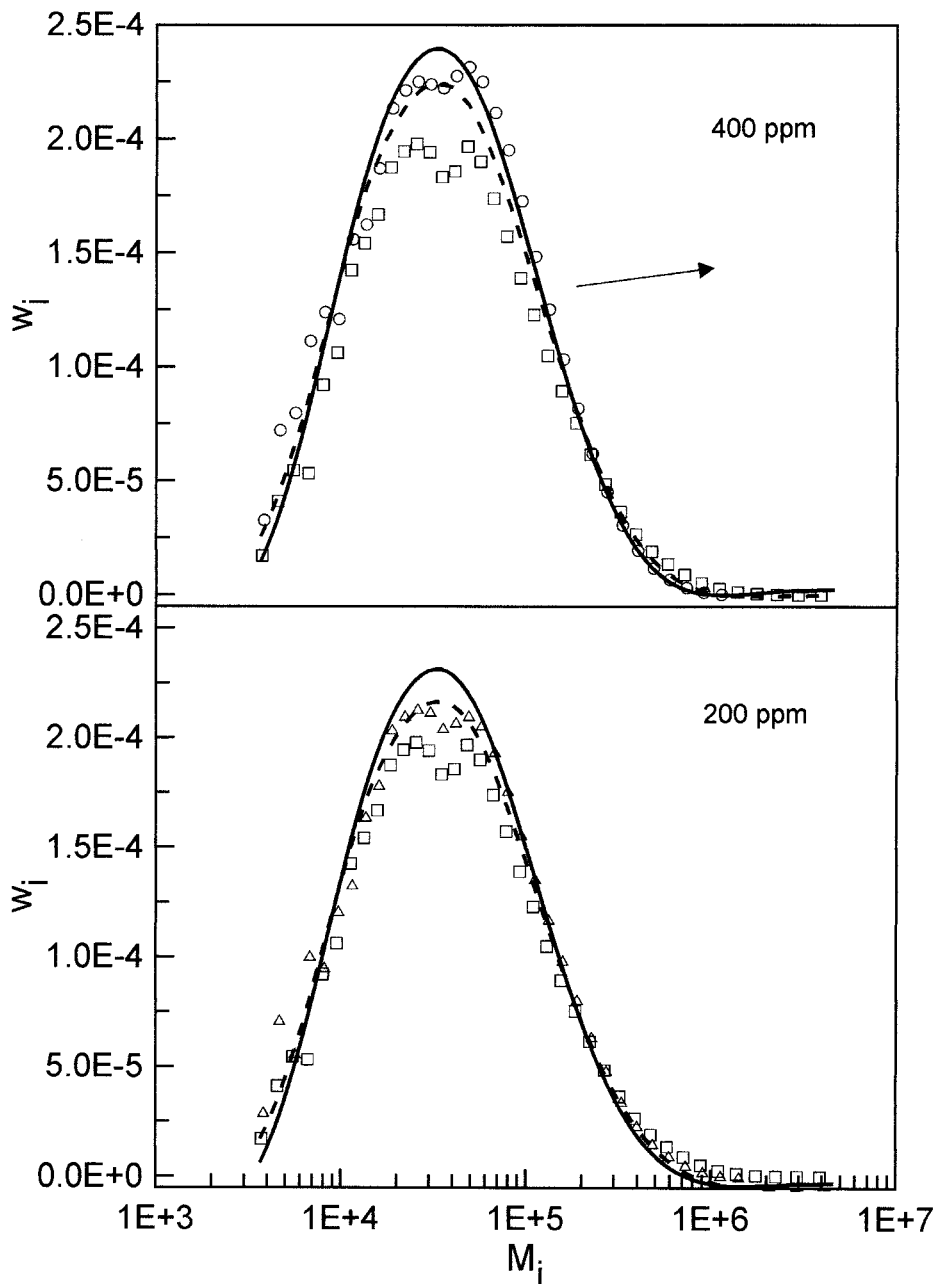

Figure 1 Experimental and calculated weight MWDs of the modified resin for different peroxide concentrations with both inversion methods: (□) virgin resin, (△) 200 ppm, (○) 400 ppm, (- - -) Stehfest inversion method, and (—) Papoulis inversion method.
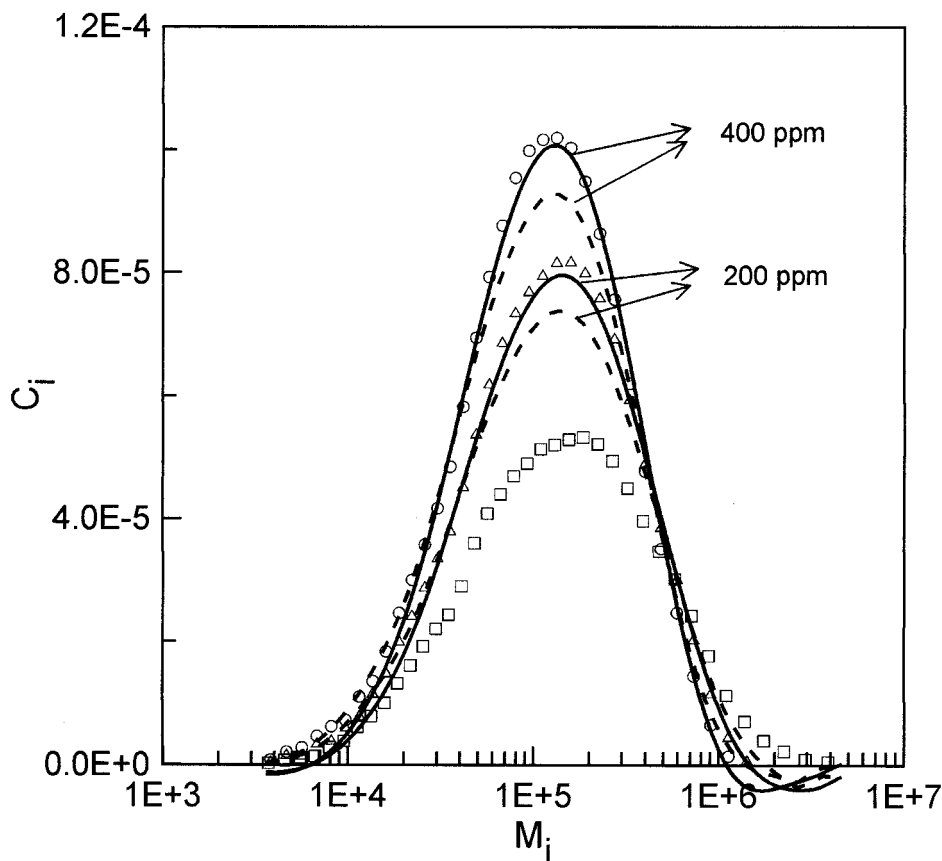
Figure 2 Experimental and calculated chromatographic MWDs of the modified resin for different peroxide concentrations with both inversion methods: (□) virgin resin, (△) 200 ppm, (○) 400 ppm, (- - -) Stehfest inversion method, and (——) Papoulis inversion method.

that no further adjustment was made to improve the fitting to experimental MWDs. The kinetic parameters are presented in Table II. With these values, we verified that the quasi steady state approximation for radicals is valid for this system. To maintain generality, we decided to continue with the more rigorous set of equations where the approximation is not used.

The first three moments of the polymer MWD and the three pgf's of the virgin resin are required as initial conditions for the set of equations to be solved. The moments are calculated from the average molecular weights and the mass of the polymer to be modified, and the pgf's are calculated from the virgin resin MWD, as detailed elsewhere.[19] We consider that no radicals are present in the virgin resin; therefore, the corresponding pgf's are equal to zero at the start of the reaction. Other information needed to solve the model includes the initial peroxide concentration, temperature, and residence time.

The integration of the pgf balance equation yields the number, weight, and chromatographic transforms of both polymer and radicals [$\psi_0(z)$, $\psi_1(z)$, and $\psi_2(z)$ and $\phi_0(z)$, $\phi_1(z)$, and $\phi_2(z)$] as functions of the residence time and z. These quantities serve as data for the inversion algorithms, in our case Papoulis's and Steh-

fest's algorithms.[25–27] These are Laplace transform inversion methods that we adapted for the inversion of the pgf of MWD.[20,21] When $\psi_0(z)$ or $\phi_0(z)$ is inverted, the corresponding number MWD is obtained directly. Inversion of $\psi_1(z)$ or $\phi_1(z)$ and $\psi_2(z)$ or $\phi_2(z)$ results in weight and chromatographic MWDs of the polymer or radicals, respectively. In this way, the three distributions are obtained independently of each other, attenuating the noise propagation typical of the high-molecular-weight tail, when the weight MWD is obtained from the calculated number distribution or when the chromatographic distribution is obtained from the calculated weight MWD.

RESULTS AND DISCUSSION

Model results were validated with experimental data obtained in our labs[6] and with other experimental information taken from the literature.[7,8,28] Our data corresponds to the degradation of PP impregnated with the peroxide initiator 2,5-dimethyl-2,5-bis(*t*-butyl peroxy)hexane in a single-screw extruder at isothermal conditions. Experimental data corresponding to runs at a rotational speed of 40 rpm, 207°C, and initial
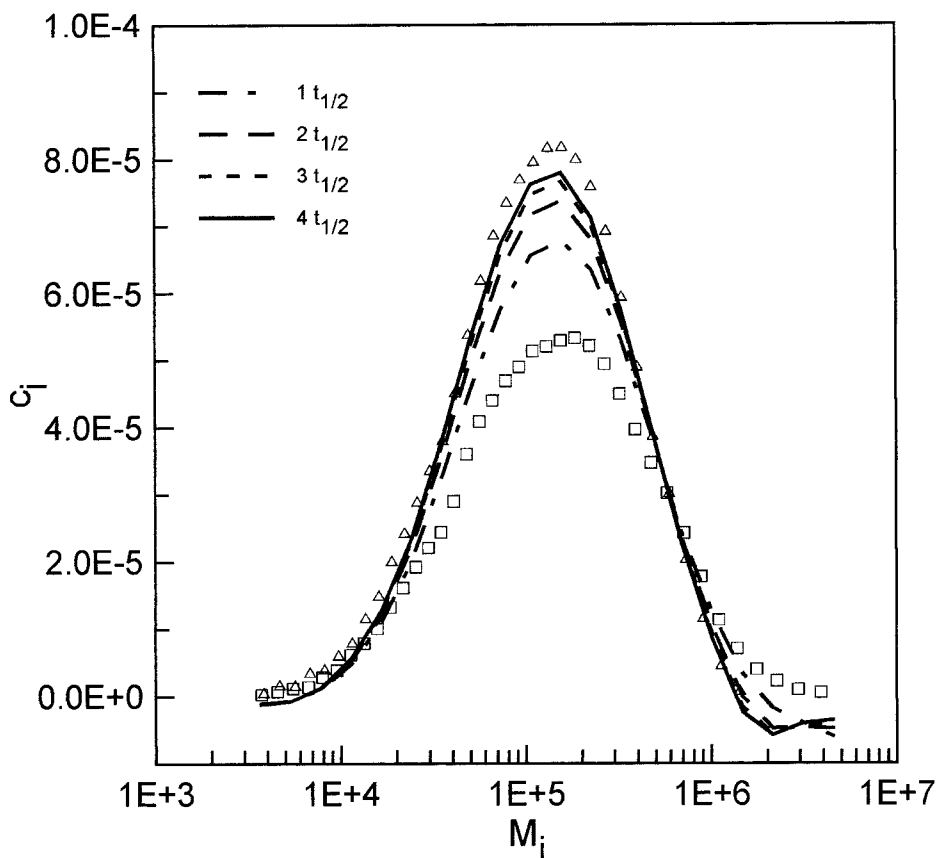
Figure 3 Predicted time evolution of the chromatographic MWD for a peroxide concentration of 200 ppm with the Papoulis inversion method: ($\square$) virgin resin and ($\triangle$) experimental at a reaction time of 70 s, or six half-lives ($t_{1/2}$).

peroxide concentrations of 0, 200, and 400 ppm were used.

Figures 1 and 2 show the weight and chromatographic MWDs of the product samples for 200- and 400-ppm initial peroxide concentrations. The rotational speed of 40 rpm corresponds to a residence time of 70 s. Symbols correspond to experimental data, and curves correspond to theoretical predictions. The ordinate labels W_i and C_i in the figures stand for the weight and chromatographic fractions, respectively. An increment in peroxide concentration produces a shift in the peak to the left and removes the high-molecular-weight tails, whereas the low-molecular-weight region remains practically unaffected, resulting in a narrower MWD. These changes are more evident in the chromatographic distribution (Fig. 2), where the higher molecular weights are stressed. The calculated distributions show that the model is able to predict the experimental trends. We remark again (see pgf model resolution section) that no parameter adjustment was performed to fit the calculated distributions to the experimental ones.

We present in Figures 1 and 2 the MWDs calculated with the two inversion methods. Stehfest's method slightly underestimates the height of the curve peaks, but the results are in general equivalent with both inversion methods. As advised elsewhere,[29] it is better to perform the transform inversion with more than one method to improve the chances that anomalous behavior of one method with a particular numerical problem can be identified as such.

Although the predicted MWDs are very similar to the experimental ones, for the chromatographic distribution negative values are predicted for the highest molecular weights. This is due to the fact that the inversion methods have difficulties in following sudden changes in curve slopes, as happens in this case. Nevertheless, these wrong values can be easily identified and disregarded.

Figures 3 and 4 show the evolution in time of the chromatographic MWDs for the resin modified with 200- and 400-ppm initial peroxide concentration, respectively. A rapid decrease in the higher molecular weights was observed during about one or two half-lives of the peroxide. In this period, 50–75% of the peroxide decomposed into primary radicals that preferentially caused scissions of the longer polymer chains.[7] The MWDs underwent practically no further change after about four times the half-life of the peroxide. This is in good agreement with reported experimental results.[7] In our system, the peroxide half-life at the operating temperature was 11.55 s.
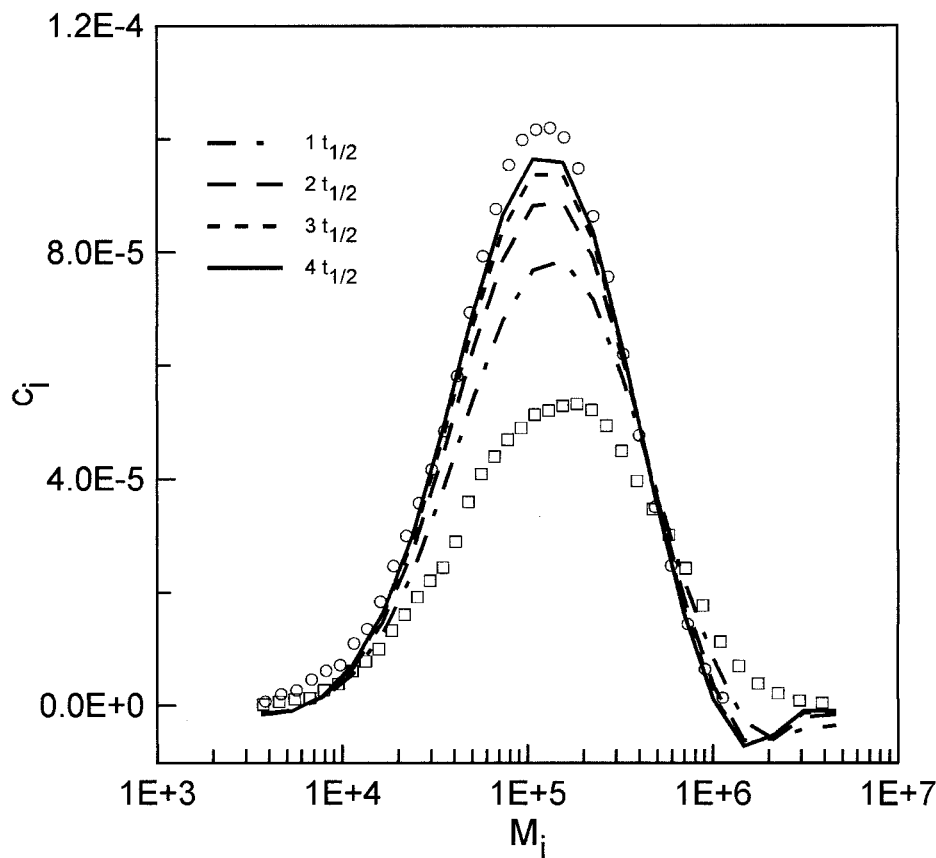
Figure 4   Predicted time evolution of the chromatographic MWD for a peroxide concentration of 400 ppm with the Papoulis inversion method at a temperature = 207°C: ($\square$) virgin resin and ($\triangle$) experimental at a reaction time of 70 s, or six half-lives.

In Figure 5, we show another application of the model, the study of the effect of the reaction temperature. All calculated distributions corresponded to 11 half-life periods of the initiator. In every case, the predicted curve was the same. This means that the degree of modification was independent of temperature, provided that the amount of decomposed initiator was always the same. This agrees with most reported results.[7,28] Few authors have reported that temperature influences the degree of degradation. Ryu et al.[7] found no differences in reactions taking place at temperatures between 190 and 210°C, which also agrees with our model predictions, but when the modification took place at a higher temperature (about 220°C), they obtained a distribution richer in the intermediate molecular weights. They attributed this to a larger segregation effect of the peroxide initiator. Our model is not valid when this effect is present. Cheung et al.[8] found an increase in degradations at two temperatures for the same peroxide concentration but with two different peroxides. They concluded that it is the different reactivities of the radicals produced by the peroxide decomposition and not the different temperatures that are responsible for the larger degradation. Therefore, Cheung's results do not contradict our model calculations.

The fact that the modification depends on the amount of decomposed initiator, according to our reaction model, was also verified by performance of the simulations with different temperature profiles and the recycling of the modified polymer, with the total amount of initiator kept constant. If all the initiator was allowed to react, the curves obtained were identical to the ones already shown for the final product.

CONCLUSIONS

In this article, we proposed a model for the calculation of MWD in the controlled degradation of PP. We applied pgf's to the mass balance equations that describe the peroxide modification of PP in an extruder. In this way, we were able to describe the number, weight, and chromatographic MWD of the modified polymers.

Numerical inversion of the transformed variables allowed a very good recovery of the entire MWDs, as compared with the experimental distributions measured by size exclusion chromatography. The two numerical inversion methods we used gave results of comparable quality, indicating that no bias was introduced by the inversion method.
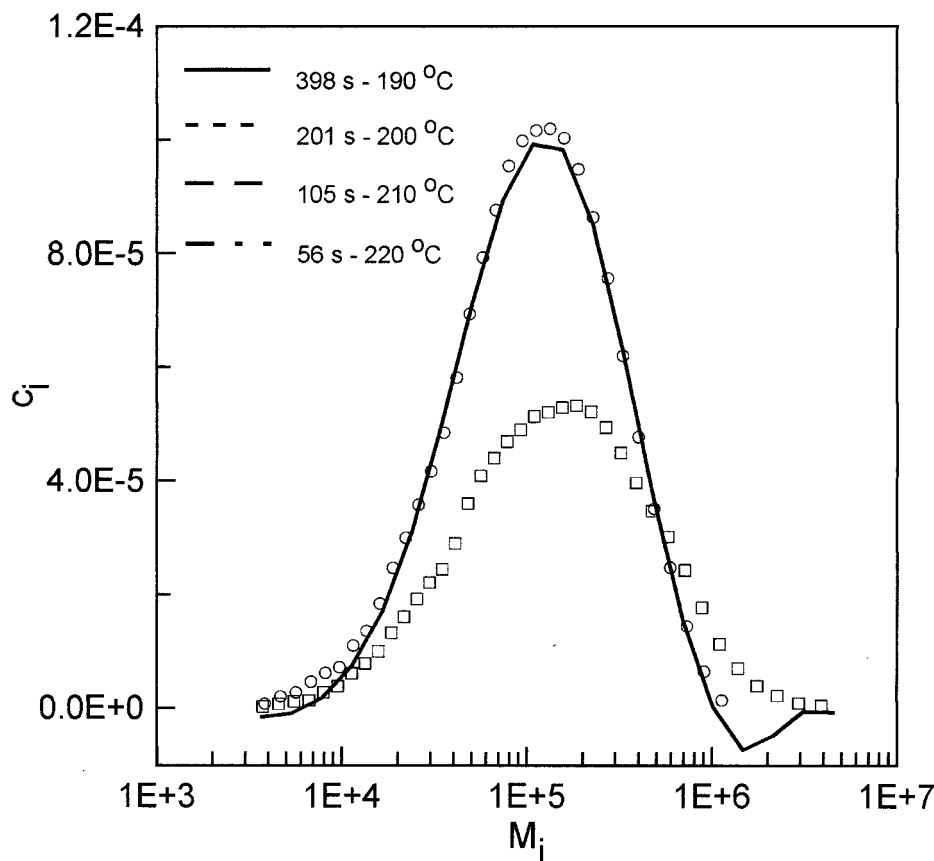
Figure 5 Predicted effect of the reaction temperature for a peroxide concentration of 400 ppm with the Papoulis inversion method: (□) virgin resin, (○) experimental at a temperature of 207°C and a reaction time of 70 s.

Therefore, the use of pgf transform is an attractive alternative to other numerical methods because no previous knowledge of the distribution and no parameter adjustment is required at that stage of calculation.

The model predicts a dependence of the MWD of the modified resin on time and temperature that is consistent with literature data.

References

1. Tzoganakis, C.; Vlachopoulos, J.; Hamielec, A. E. Polym Eng Sci 1988, 28, 170.
2. Tzoganakis, C.; Vlachopoulos, J.; Hamielec, A. E. Polym Eng Sci 1989, 29, 390.
3. Moore, E. P., Jr. Polypropylene Handbook; Hanser: Vienna, Austria, 1996.
4. Iedema, P. D.; Willems, C.; van Vliet, G.; Bunge, W.; Mutsers, S. M. P.; Hoefsloot, H. C. J. Chem Eng Sci 2001, 56, 3659.
5. Dickson, S. B.; Tzoganakis, C.; Budman, H. Ind Eng Chem Res 1997, 36, 1067.
6. Krell, M. J.; Brandolin, A.; Vallés, E. M. Polym React Eng 1994, 2, 389.
7. Ryu, S. H.; Gogos, C. G.; Xanthos, M. Adv Polym Technol 1992, 11, 121.
8. Cheung, P. C.; Balke, S. T. Ind Eng Chem Res 1997, 36, 1191.
9. Berzin, F.; Vergnes, B.; Dufòssé, P.; Delamare, L. Polym Eng Sci 2000, 40, 344.
10. Pabedinskas, A.; Cluett, W. R.; Balke, S. T. Polym Eng Sci 1994, 34, 598.
11. Triacca, V. J.; Gloor, P. E.; Zhu, S.; Hrymak, A. N.; Hamielec, A. E. Polym Eng Sci 1993, 33, 445.
12. Huang, C.; Duever, T. A.; Tzoganakis, C. Polym React Eng 1997, 5, 1.
13. Suwanda, D.; Lew, R.; Balke, S. T. J Appl Polym Sci 1988, 35, 1033.
14. Kim, B.; White, J. L. Polym Eng Sci 1997, 37, 576.
15. Oliveira, J. A.; Biscaia, E. C., Jr.; Pinto, J. C. In Proceedings of the 1st Mercosur Congress on Chemical Engineering (ENPROMER 2001); Universidad Nacional del Litoral, Santa Fe, Argentina, 2001; Vol. II, p 925.
16. Mead, D. W. J Appl Polym Sci 1995, 57, 151.
17. Asteasuain, M.; Sarmoria, C.; Brandolin, A. Polymer 2002, 43, 2513.
18. Sarmoria, C.; Brandolin, A.; López-Rodríguez, A.; Whiteley, K. S.; del Amo Fernández, B. Polym Eng Sci 2000, 40, 1480.
19. Asteasuain, M.; Sarmoria, C.; Brandolin, A. Polymer 2002, 43, 2363.
20. Brandolin, A.; Asteasuain, M.; Sarmoria, C.; López-Rodríguez, A.; Whiteley, K. S.; del Amo Fernández, B. Polym Eng Sci 2001, 41, 1156.
21. Asteasuain, M.; Brandolin, A.; Sarmoria, C. Polymer 2002, 43, 2529.
22. Hulburt, H. M.; Katz, S. Chem Eng Sci 1964, 19, 555.
23. Biesenberger, J. A.; Sebastian, D. H. Principles of Polymerization Engineering; New York: Wiley, 1983; pp 691–695.
24. Gear, C. W. Numerical Initial Value Problems in Ordinary Differential Equations; Prentice Hall: Englewood Cliffs, NJ, 1971.
25. Papoulis, A. Quat Appl Math 1956, 14, 405.
26. Stehfest, H. Commun ACM 1970, 13, 47.
27. Stehfest, H. Commun ACM 1970, 13, 624.
28. Suwanda, D.; Lew, R.; Balke, S. T. J Appl Polym Sci 1988, 35, 1019.
29. Davies, B.; Martin, B. J Comp Phys 1979, 33, 1.