

# Mathematical Modeling of the Reactive Modification of High-Density Polyethylene. Effect of Vinyl Content

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Molecular properties of high-density polyethylene resulting after its peroxide modification process depend not only on peroxide concentration and temperature but also on the molecular weight distribution and vinyl content of the virgin resin. A model able to predict average molecular weights and vinyl content changes after treatment with different peroxide concentrations is presented in this work. The model is able to handle virgin resins with or without vinyl content. For that purpose, a kinetic mechanism is proposed that includes the reactions of termination with initiation radicals and polymer double-bond propagation besides other commonly accepted reactions. Average molecular weights and vinyl content were calculated after solving the mass balance equations. These were previously bounded by applying a double moment technique. Molecular weights and vinyl content predictions compare well with experimental data. A deeper insight into the influence of initial vinyl content on the evolution of molecular weights is obtained through model calculations.

## Introduction

Polyethylene (PE) is one of the most widely used thermoplastics in the world because it combines low cost with adequate properties to be used in a great variety of applications. Even though a large offer of different polyethylene grades with distinctive properties is available, the polymers are subjected to reactive processing to modify their molecular structure. Among the sought modifications are changes in the average molecular weight, the polydispersity, or the degree of branching. The introduction of grafts is sometimes the aim of the modification. All these changes are induced in the polymers to satisfy specific property requirements for particular applications.<sup>1–3</sup>

The use of organic peroxides for the modification of PE is a method frequently used in industry to obtain polymers with physical and mechanical properties different than the original materials.<sup>1–3</sup> The method is based on the formation of oxy-radicals due to the thermal decomposition of the peroxide. The oxy-radicals abstract hydrogen atoms from the macromolecules, generating macroradicals which participate mostly in combination reactions producing chain-linking, that is, cross-linking, long-chain branching, and chain extension. The modification of PE by reaction with organic peroxides is studied in many publications in the literature. Many of them analyze the use of large concentrations of peroxide in order to transform part of the material in an insoluble molecular network or gel.<sup>4–9</sup> Other studies use peroxide concentrations below the critical concentration to produce a gel in order to change the viscoelastic response of the molten PE.<sup>10–16</sup> The molecular structure of the PE changes in such a way that the average molecular weights increase and the molecular weight distribution becomes wider, altering its properties in the molten and solid states.

There are many factors to be taken into account in the process of chain-linking when PE is exposed to peroxide attack in the melt. The main one is the molecular structure, which is given by the number- and weight-average molecular weights ( $M_n$  and  $M_w$ ) of the polymer, the molecular weight distribution (MWD), the presence of tertiary carbons (branch points), and vinyl groups (Vi). Other factors are the concentration and type of peroxide,

the treatment temperature and the presence of additives. It was observed that the amount of peroxide needed to reach the gel point decreases as the molecular weight of the treated PE increases. Another observation was that vinyl-containing polyethylenes cross-link faster and produce higher final gel contents than equivalent saturated polymers.<sup>4–16</sup> According to Hulse et al.,<sup>4</sup> the molecular weight and MWD of polyethylenes with low vinyl concentrations have no effect on the cross-link efficiency, calculated as the ratio between the theoretical expectation and the actual amount of peroxide needed to reach the gel point. Polyethylenes with vinyl groups need smaller amounts of peroxide to generate a given amount of gel when compared with a reference material having lower levels of unsaturation.<sup>8,9</sup> Moreover, the increment in  $M_w$  with peroxide concentration in the pregel region is much larger in polyethylenes with concentrations of about one vinyl group per molecule than in equivalent polyethylenes with very low vinyl group concentrations.<sup>15,16</sup>

In spite of the economic interest in the process of modification of polyethylene and the usefulness of a mathematical model for prediction, design, and optimization purposes, few of such models have been developed and published in the open literature. Details on former modeling attempts may be found elsewhere.<sup>17–23</sup> Some of those models are based on a statistical approach.<sup>18–20</sup> Statistical models are appropriate for predictions as a function of conversion, not as a function of time. In order to obtain results as a function of time, one would need a function to relate conversion with time. Typical reported results are predictions of gel points, average molecular weights, and molecular weight distributions of the soluble fractions.

The first model to exploit a kinetic approach to this problem was presented by Suwanda and Balke.<sup>21</sup> This model was meant to predict two pregel quantities as functions of time: molecular weight distributions and concentration of vinyl groups. These authors focused on a process carried out at moderate temperatures in extruders. The quantification of vinyl groups was performed through a rather detailed kinetic model. In brief, molecules were considered to have either zero or one terminal vinyl group. Primary radicals abstract either secondary protons from the main chain of polymer molecules or allyl protons from the carbon atoms near the vinyl groups. Termination may only occur by combination, giving rise to cross-linking, chain extension, and endlinking reactions. Other assumptions include

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negligible degradation and pseudo-steady state for all radicals. The  $M_w$  predictions are fairly good for low density polyethylene (LDPE) and linear low density polyethylene (LLDPE). As for the vinyl content, the model predicts the correct trend—vinyl concentration drops—but the concentrations themselves are overestimated. In the case of high density polyethylene (HDPE), predictions were not good for both  $M_w$  and the vinyl content. A simplified model that ignores terminal vinyl groups, also presented by the authors, was successful at predicting  $M_w$  for HDPE samples of low initial vinyl content.

Pedernera et al.<sup>22</sup> presented a model for the peroxide initiated modification of polyethylene. They proposed a kinetic model that includes combination reactions as well as transfer to polymer and scission. This model is able to predict both average molecular weights and the concentration of vinyl groups as functions of time. The kinetic constants and the initiation efficiency were estimated through a nonlinear regression using experimental data on HDPE with a high vinyl content. This model followed well the observed experimental trends when varying the initial peroxide concentration or temperature and gave good estimates of both average molecular weights and average vinyl content, within experimental error. The predictions of this model compared better with experimental data than those of Suwanda and Balke's model.<sup>21</sup>

Asteasuain et al.<sup>23</sup> predicted the complete MWD using an extension of the previously mentioned kinetic model.<sup>22</sup> Model predictions on molecular weight distributions were in agreement with experimental data corresponding to the peroxide modification of HDPE with high vinyl content.

It is known that model predictions are only reliable in the range of operating variables for which parameters were fitted. This becomes evident for the last two models when they were used for predicting molecular properties of HDPE with no vinyl content. As will be discussed later in the paper, model predictions were poor in this case, not only quantitatively but also qualitatively.

In this work, we propose an extension of the kinetic mechanism proposed by Pedernera et al.<sup>22</sup> for the peroxide initiated modification of polyethylene. This enabled us to expand the prediction capabilities of our model to polyethylenes with negligible or no vinyl content. The physical problem we are modeling is modification of a polymer in a press kept at a constant temperature, under conditions where scission is not measurable. This process is comparable to the peroxide modification under plug flow in an extruder. We develop a set of mass balances for the reacting species, which are transformed by means of the moment technique. A detailed description of the mathematical steps required for obtaining the moment balances is also presented. An experimental set of data covering the modification of HDPE with different molecular structures is used to estimate some of the kinetic parameters. Another set is used for testing the predicting capabilities of the model. Finally, model predictions on peroxide concentrations needed to reach the gel point for resins with different average molecular weights, and vinyl contents are compared with experimental data from the literature.<sup>4</sup>

### Model Development

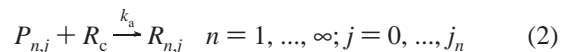
We make the following assumptions: the process is isothermal, each polymer molecule may have any number of vinyl groups, radicals and macroradicals contain only one active site, and termination is by combination only. An additional consideration is that the quasi-steady state approximation for radicals is not used. The model is meant to perform up to the gel point

only. The proposed kinetic mechanism is shown below (eqs 1–8). This mechanism is an extension of the one previously reported.<sup>22</sup>

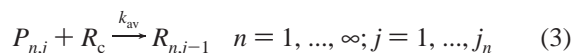
Initiation



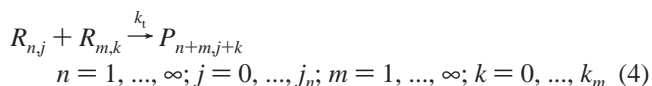
Hydrogen Abstraction on a Site with No Vinyl Group



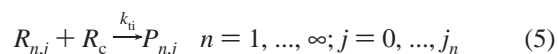
Hydrogen Abstraction on a Site with a Vinyl Group



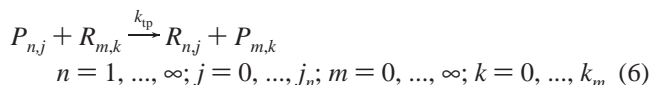
Termination by Combination



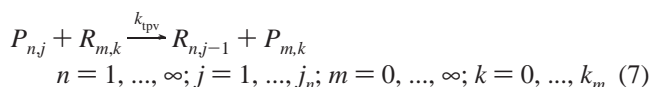
Termination with Initiation Radical



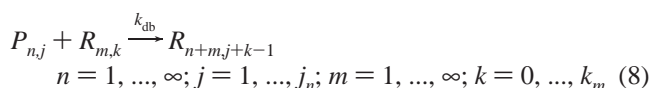
Chain Transfer to a Polymer on a Site with No Vinyl Group



Chain Transfer to a Polymer on a Site with a Vinyl Group



Double-Bond Propagation



In the above equations,  $I$  is the peroxide initiator, which may thermally decompose into  $\gamma$  initiation radicals ( $R_c$ ) (eq 1), and  $P$  and  $R$  account for polymer molecules and macroradicals, respectively. Those species have two subscripts or indexes, which represent the number of monomeric units and the number of vinyl groups, in that order. The values that the first and second subscripts can take are shown beside each reaction.

It is assumed that the peroxide decomposes through a first-order reaction into  $\gamma$  radicals (eq 1). The type of peroxide used determines the particular value of  $\gamma$ ; the usual values are two or four. When a hydrogen atom is abstracted from the chain backbone (eq 2), the attacked polymer molecule converts into a macroradical maintaining the number of monomeric units as well as the number of vinyl groups. If a hydrogen atom is abstracted from a vinyl group (eq 3), the attacked polymer molecule turns into a macroradical that contains the same number of monomeric units and one fewer vinyl group. The fact that the kinetic constants for these reactions are given per unit of reactive site must be kept in mind when performing mass balances, since they must be multiplied by the number of reactive sites involved. For instance, if the molecule  $P_{n,j}$  is

considered, when the attack takes place in the backbone, there are  $(\alpha n - \beta j)$  sites involved, and there are  $\beta j$  sites affected when the attack involves the vinyl site. For the particular case studied in this work, the factors  $\alpha$  and  $\beta$  have been taken as 2 and 3, respectively.<sup>22</sup>

The result of the termination by combination reaction (eq 4) is a polymer molecule that contains all the repeat units and vinyl groups of both reacting macroradicals. This reaction includes those of chain extension, endlinking, and cross-linking reported by Suwanda and Balke<sup>21</sup> because our model makes no distinction between macroradicals whose active sites are in different positions.

If an initiation radical reacts with a macroradical, a dead polymer molecule of the same size and vinyl content results (eq 5). When the reaction is between a macroradical and any hydrogen atom on a polymer molecule, the consequence may be a chain transfer to polymer (eqs 6 and 7). The results vary depending on whether the attacked hydrogen was part of a vinyl group or not.

According to the above mechanism, the transfer to polymer reactions cannot have a significant influence on the molecular weight prediction. This might appear to be odd, especially if one considers that in the case of the polymerization of ethylene that is precisely the reaction that is responsible for the long chain branching and broadening of the MWD. The difference between the polymerization process and the polymer modification considered in this work stands in the large availability of monomer present in the polymerization case. Here, the monomer readily propagates from a new formed active site increasing the molecular weight. By contrast, in the modification process, the transfer reactions only exchange active sites among macromolecules with a negligible effect on molecular weight. However, in the modification process that we are studying in this work, changes in molecular weight may be produced by other reactions, such as hydrogen abstraction followed by termination by combination. For this reason, it is possible to predict molecular weights reasonably well whether the transfer to the polymer reaction is included or not.<sup>22</sup> Even though this reaction has negligible influence on molecular weight predictions, we found in a previous work that it was very important to be able to predict the large drop in vinyl group content observed in experimental data.<sup>22</sup> This drop could not be predicted through hydrogen abstraction alone. It must be also kept in mind that the transfer to polymer shown in eq 7 consumes vinyl groups that otherwise would be available for new macro-radical generation through the hydrogen abstraction reaction, thus limiting the increase in molecular weight.

Double-bond propagation is also allowed (eq 8), where the polymer molecule reacts with a macroradical to produce a larger macroradical. In this reaction, the polymer plays the same role the monomer does in the propagation reaction of a free radical polymerization process. This type of mechanism was proposed by Smedberg et al.,<sup>8</sup> who studied the effect of the vinyl concentration on the cross-linking process of low density polyethylene with peroxide. They proposed that two cross-linking reactions take place simultaneously in the process, which are equivalent to the termination by combination and double-bond propagation reactions shown in eqs 4 and 8, respectively.

Since the experimental data that we used for comparison were obtained under operating conditions at which scission was negligible, this reaction is not included in the proposed mechanism.

There are substantial differences between the reaction mechanism proposed in this work and those reported before by Suwanda and Balke<sup>21</sup> and Pedernera et al.<sup>22</sup> With respect to the former, the differences are that molecules may have more than one vinyl group and that the chain transfer to polymer reaction is included. Both issues were already included in the model by Pedernera et al.<sup>22</sup> With respect to the latter model, we have added two reactions to the kinetic mechanism: termination by initiation radicals (eq 5) and the double-bond propagation presented in eq 8. The first one accounts for a decrease of the cross-linking efficiency.<sup>18</sup> The second one provides a path for the production of higher molecular weights for those resins with vinyl groups and remains inactive for resins with no vinyl content.

The mass balances for the isothermal batch process, where  $t$  is the reaction time, are presented in eqs 9–12. Mass balance equations may be written for all the species involved in the mechanism. The same set of equations can be employed for the extrusion process when considering the independent variable to be the residence time. The terms in brackets represent molar concentrations.

Peroxide Initiator

$$\frac{d[I]}{dt} = -k_i[I] \quad (9)$$

Initiation Radical

$$\frac{d[R_c]}{dt} = \gamma k_f[I] - k_a[R_c] \sum_{n=1}^{\infty} \sum_{j=0}^{j_n} [P_{n,j}] (\alpha n - \beta j) - k_{av}[R_c] \sum_{n=1}^{\infty} \sum_{j=0}^{j_n} \beta j [P_{n,j}] - k_{ti}[R_c] \sum_{n=1}^{\infty} \sum_{j=0}^{j_n} [R_{n,j}] \quad (10)$$

Polymer Molecules with  $n$  Monomer Units and  $j$  Vinyl Groups ( $n = 1, \dots, \infty; j = 0, \dots, j_n$ )

$$\begin{aligned} \frac{d[P_{n,j}]}{dt} = & -k_a[R_c] (\alpha n - \beta j) [P_{n,j}] - k_{av}[R_c] \beta j [P_{n,j}] (1 - \delta_{j,0}) + \\ & \frac{1}{2} k_t \sum_{m=1}^{n-1} \sum_{k=0}^j [R_{n-m,j-k}] [R_{m,k}] (1 - \delta_{n,1}) + k_{ti}[R_c] [R_{n,j}] - \\ & k_{ip} (\alpha n - \beta j) [P_{n,j}] \sum_{m=1}^{\infty} \sum_{k=0}^{k_m} [R_{m,k}] + \\ & k_{ip}[R_{n,j}] \sum_{m=1}^{\infty} \sum_{k=0}^{k_m} (\alpha m - \beta k) [P_{m,k}] - \\ & \beta j k_{ipv} [P_{n,j}] \sum_{m=1}^{\infty} \sum_{k=0}^{k_m} [R_{m,k}] (1 - \delta_{j,0}) + \\ & \beta k_{ipv}[R_{n,j}] \sum_{m=1}^{\infty} \sum_{k=0}^{k_m} k [P_{m,k}] (1 - \delta_{k,0}) - \\ & \beta j k_{db} [P_{n,j}] \sum_{m=1}^{\infty} \sum_{k=0}^{k_m} [R_{m,k}] (1 - \delta_{j,0}) \quad (11) \end{aligned}$$

Radical Molecules with  $n$  Monomer Units and  $j$  Vinyl Groups ( $n = 1, \dots, \infty; j = 0, \dots, j_n$ )

$$\begin{aligned} \frac{d[R_{n,j}]}{dt} = & k_a[R_c](\alpha n - \beta j)[P_{n,j}] + k_{av}[R_c]\beta(j+1)[P_{n,j+1}] - \\ & k_{ti}[R_c][R_{n,j}] - k_t[R_{n,j}]\sum_{m=1}^{\infty}\sum_{k=0}^{k_m}[R_{m,k}] - \\ & k_{tp}[R_{n,j}]\sum_{m=1}^{\infty}\sum_{k=0}^{k_m}(\alpha m - \beta k)[P_{m,k}] + \\ & k_{tp}(\alpha n - \beta j)[P_{n,j}]\sum_{m=1}^{\infty}\sum_{k=0}^{k_m}[R_{m,k}] - \\ & \beta k_{tpv}[R_{n,j}]\sum_{m=1}^{\infty}\sum_{k=0}^{k_m}k[P_{m,k}](1 - \delta_{k,0}) + \\ & \beta k_{tpv}(j+1)[P_{n,j+1}]\sum_{m=1}^{\infty}\sum_{k=0}^{k_m}[R_{m,k}] - \\ & \beta k_{db}[R_{n,j}]\sum_{m=1}^{\infty}\sum_{k=0}^{k_m}k[P_{m,k}](1 - \delta_{k,0}) + \\ & \beta k_{db}\sum_{m=1}^{n-1}\sum_{k=0}^j(j-k+1)[R_{m,k}][P_{n-m,j-k+1}](1 - \delta_{n,1}) \quad (12) \end{aligned}$$

The set of mass balance equations represented by eqs 9–12 is infinitely large. The method of moments is one of the most commonly used techniques to deal with this type of problem in order to calculate average molecular properties. In this study, we are interested in calculating average molecular weights and vinyl content. For that purpose, the moment definitions must be applied to the polymer length and number of vinyl groups, leading to double moments. The corresponding moments for both radical and polymer length distributions are defined in eqs 13 and 14.

$a$ th,  $b$ th Order Moment for Polymer with  $j$  Vinyls

$$M_{a,b} = \sum_{n=1}^{\infty}\sum_{j=0}^{j_n} n^a j^b [P_{n,j}] \quad a = 0, 1, 2, \dots; b = 0, 1, \dots \quad (13)$$

$a$ th,  $b$ th Order Moment for Radicals with  $j$  Vinyls

$$Y_{a,b} = \sum_{n=1}^{\infty}\sum_{j=0}^{j_n} n^a j^b [R_{n,j}] \quad a = 0, 1, 2, \dots; b = 0, 1, \dots \quad (14)$$

In order to transform mass balances, eqs 11 and 12 must be multiplied by  $n^a j^b$  and then added up for all polymer lengths and numbers of vinyl groups. Equation 10 can also be rearranged as a function of those moments, since their expressions appear directly in this balance. Basic moment terms as well as the deductions of other terms for which the moment expressions cannot be easily detected are presented in the Appendix. After the transformation, the resulting initiation radical balance and the moment balances are those shown in eqs 15–17.

$$\begin{aligned} \frac{d[R_c]}{dt} = & \gamma k_f [I] - k_a[R_c](\alpha M_{1,0} - \beta M_{0,1}) - \\ & k_{av}[R_c]\beta M_{0,1} - k_{ti}[R_c]Y_{0,0} \quad (15) \end{aligned}$$

$$\begin{aligned} \frac{dM_{a,b}}{dt} = & -k_a[R_c](\alpha M_{a+1,b} - \beta M_{a,b+1}) - k_{av}[R_c]\beta M_{a,b+1} + \\ & \frac{1}{2}k_t\sum_{r=0}^a\sum_{s=0}^b\binom{a}{r}\binom{b}{s}Y_{a-r,b-s}Y_{r,s} + k_{ti}[R_c]Y_{a,b} - \\ & k_{tp}[(\alpha M_{a+1,b} - \beta M_{a,b+1})Y_{0,0} - Y_{a,b}\sum_{k=0}^{\infty}(\alpha M_{1,0} - \beta M_{0,1})] + \\ & k_{tpv}\beta Y_{a,b}M_{0,1} - k_{tpv}\beta M_{a,b+1}Y_{0,0} - k_{db}\beta M_{a,b+1}Y_{0,0} \quad (16) \end{aligned}$$

$$\begin{aligned} \frac{dY_{a,b}}{dt} = & k_a[R_c](\alpha M_{a+1,b} - \beta M_{a,b+1}) + \\ & k_{av}\beta[R_c]\sum_{r=0}^b(-1)^{b-r}M_{a,r+1} - k_t Y_{a,b}Y_{0,0} - k_{ti}[R_c]Y_{a,b} + \\ & k_{tp}(\alpha M_{a+1,b} - \beta M_{a,b+1})Y_{0,0} - k_{tp}Y_{a,b}(\alpha M_{1,0} - \beta M_{0,1}) - \\ & \beta k_{tpv}Y_{a,b}M_{0,1} + k_{tpv}\beta M_{a,b+1}Y_{0,0} - \beta k_{db}Y_{a,b}M_{0,1} + \\ & \beta k_{db}\sum_{r=0}^a\sum_{s=0}^b\sum_{q=0}^s\binom{a}{r}\binom{b}{s}\binom{s}{q}Y_{a-r,b-s}M_{r,q+1} \quad (17) \end{aligned}$$

Since the resulting expressions depend on moments of orders that are higher than those included in the balances, we used a closure technique<sup>24,25</sup> that requires finding expressions for the higher order moments as functions of the known lower order moments. The procedure is exact if the type of distribution is known (geometric, binomial, log-normal, etc.). If that is not the case, one assumes a distribution type and uses the resulting expressions for the higher order moments, which renders the procedure approximate. In this work, the closure technique was an approximation, where we assumed a log-normal distribution for the length of the molecule and a binomial one for the vinyl groups. These assumptions were successfully employed for this system previously.<sup>22</sup> The expressions used in the estimation of the third moment in length and the third moment in vinyl content are shown in eqs 18 and 19. The log-normal distribution was selected based on the inspection of the shape of experimental MWD of the virgin resins.<sup>15</sup> Since almost all the molecules have one vinyl group in the virgin and most of the molecules of the modified resins have either none or one vinyl group, the binomial approximation for the vinyl groups was suitable. The validity of our assumptions was also checked by performing simulations including the third-order moment balance equations in the mathematical model and using the corresponding closure equations for the fourth order moments. This strategy reduced the influence of the closure approximation on the number and average molecular weight calculations. The predictions were equivalent to those obtained when the third moments were approximated indicating that the above assumptions were appropriate.

$$M_{3,b} = \frac{M_{2,b}}{M_{1,b}} M_{0,b} \quad b = 0, 1, 2 \quad (18)$$

$$M_{a,3} = \frac{M_{a,2}^2}{(M_{a,1} + M_{a,2})} \quad a = 0, 1, 2 \quad (19)$$

Once the various moments are calculated, the following measurable quantities may be calculated:

Number-Average Molecular Weight

$$M_n = 28 \frac{M_{1,0} + Y_{1,0}}{M_{0,0} + Y_{0,0}} \quad (20)$$

## Weight-Average Molecular Weight

$$M_w = 28 \frac{M_{2,0} + Y_{2,0}}{M_{1,0} + Y_{1,0}} \quad (21)$$

## Vinyl Group Content

$$V_i = 28 \frac{M_{0,1} + Y_{0,1}}{M_{0,0} + Y_{0,0}} \quad (22)$$

Equations 9 and 15–22 constitute a stiff algebraic–differential system which is solved numerically in the gPROMS environment (Process System Enterprise, Ltd.). For this particular system, the DASSL solver was employed.<sup>26</sup>

The model requires some input data, namely, the mass of the unmodified polymer, the molecular weight of the repeat unit in the polymer chain, the average molecular weights ( $M_n$  and  $M_w$ ) and the vinyl content of the virgin resin, the concentration and molecular weight of the peroxide, the operating temperature, and the residence time. The model also requires the values of the kinetic parameters. They were estimated by fitting the model to experimental information as described in the following sections. Other model parameters that remained unchanged for all simulations were the following:  $\alpha = 2$ ;  $\beta = 3$ ;  $\gamma$  was 4 for diperoxides and 2 for single peroxides.

## Experimental Data

We used four high-density polyethylenes. Two resins were Alathon 7050 (PE1) and 7030 (PE3) from DuPont de Nemours. For PE1, the average molecular weight was  $M_w = 53\,200$  and  $M_w/M_n = 2.4$ . For PE3, these quantities were  $M_w = 83\,000$  and  $M_w/M_n = 2.3$ . We also used two resins from Petropol S.A.: PE2 with  $M_w = 55\,000$  and  $M_w/M_n = 4.5$  and PE4 with  $M_w = 79\,000$  and  $M_w/M_n = 3.6$ . The resins from the different providers have different vinyl contents: PE1 and PE3 have about one vinyl per molecule, while PE2 and PE4 have a very low vinyl content, less than one vinyl for every 20 molecules.

The initiator for the modification process was 2,5-dimethyl-2,5-di(tert-butylperoxy)-hexane. The resins were dissolved in xylene at boiling temperature and afterward precipitated in cool methanol to obtain a fine powder. Fractions of these powders were then impregnated with different amounts of a peroxide–hexane solution to obtain the desired final peroxide concentrations once the solvent was removed.

The impregnated polyethylenes were placed between 3 mm thick steel plates held apart by a 0.5 mm thick brass frame. The samples were then compression moulded between the hot plates of a hydraulic press during 5 min at 170 °C and 10 bar. Then, the pressure was relieved and the samples were kept at that temperature between the plates for another 15 min.

The average molecular weights of the polymers were estimated by analyzing chromatograms obtained by size exclusion chromatography (SEC) using a Waters 150-C ALP/GPC equipped with a set of 10 mm PLGel columns from Polymer Labs having nominal porous sizes of 10<sup>6</sup>, 10<sup>3</sup>, and 500 Å. The solvent used was 1,2,4-trichlorobenzene (TCB) at 140 °C. The molecular weights of the polymers were estimated following the standard calibration procedure using monodisperse polystyrene samples and the corresponding Mark–Houwink coefficients for polystyrene and linear polyethylene in TCB.<sup>27</sup>

The concentration of vinyl groups of each polymer was determined from infrared spectroscopic measurements (FTIR, Nicolet 520) performed on thin films. The vinyl concentration

Table 1. Experimental Information on HDPE Peroxide Modification

$[I]_0$	$M_n$	$M_w$	$V_i/V_{i0}$	$[I]_0$	$M_n$	$M_w$
PE1			PE2			
250	24500	71000	0.76	250	16700	70000
500	28900	78000	0.61	500	15600	71800
750	26000	98700	0.38	750	13600	76000
1000	31700	130000	0.27	2500	12400	87000
2000	30600	159000	0.12	3500	12500	96000
PE3			PE4			
65	35000	98000	0.77	250	18100	85000
130	32700	108000	0.71	500	19200	94000
250	37700	117000	0.54	750	19800	95000
500	44300	155000	0.46			

was calculated from the intensity of the 908 cm<sup>-1</sup> band using a molar extinction coefficient of 153 L/(mol cm).<sup>28</sup>

The experimental information used for modeling fitting and testing is summarized in Table 1.

## Kinetic Parameter Estimation

The initiator decomposition rate constants and the initiation efficiencies were kept equal to the values already reported.<sup>22</sup> The remaining rate constants were estimated with gPROMS so that the model predictions would fit experimental average molecular weights for the modified polyethylenes (PE1, PE2, PE3, and PE4) and experimental vinyl content for PE1 and PE3.

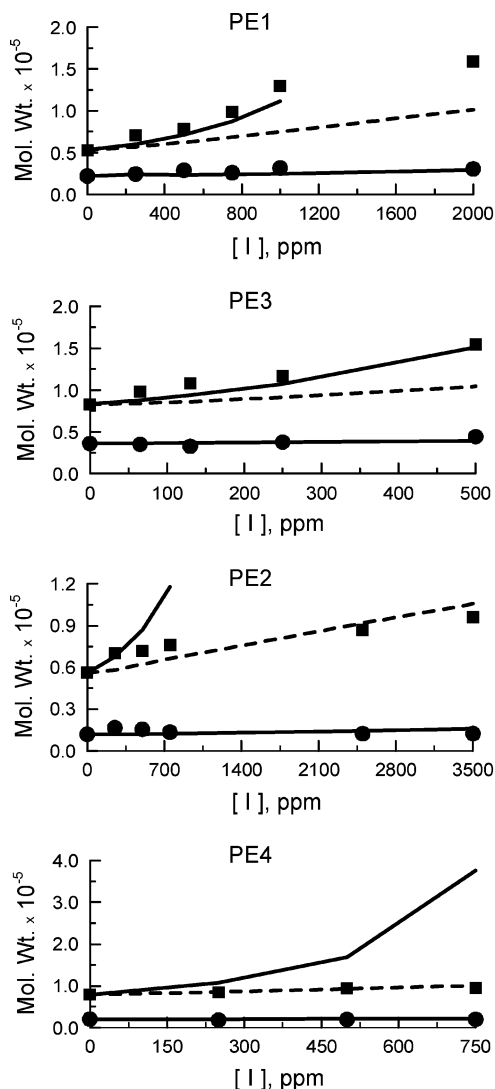
The parameter estimator built in gPROMS uses the following objective function:

$$\text{ObjF} = \frac{N}{2} \ln(2\pi) + \frac{1}{2} \min_{\theta} \sum_{i=1}^{N_{\text{exp}}} \sum_{j=1}^{N_{\text{var},i}} \sum_{k=1}^{N_{\text{meas},ij}} \left[ \ln(\sigma_{ijk}^2) + \frac{(z_{ijk}^{\text{meas}} - z_{ijk}^{\text{calc}})^2}{\sigma_{ijk}^2} \right] \quad (23)$$

In the above equation,  $N$  is the total number of measurements;  $\theta$  represents the set of model parameters to be estimated, which are bounded;  $N_{\text{exp}}$  is the number of experiments;  $N_{\text{var},i}$  is the number of variables measured in the  $i$ th experiment;  $N_{\text{meas},ij}$  is the number of measurements of the  $j$ th variable in the  $i$ th experiment;  $\sigma_{ijk}^2$  is the variance of the  $k$ th measurement of variable  $j$  in experiment  $i$ ;  $z_{ijk}^{\text{meas}}$  is the  $k$ th measured value of variable  $j$  in experiment  $i$ ; and  $z_{ijk}^{\text{calc}}$  is the  $k$ th calculated value of variable  $j$  in experiment  $i$ . The variances are described as  $\sigma^2 = \omega^2(z^{\text{meas}} + \epsilon)^\gamma$ , where  $\omega$  and  $\gamma$  are adjustable parameters and  $\epsilon$  is a very small number related to the computer accuracy.

Initial rate parameter values were chosen from Pedernera et al.,<sup>22</sup> except the ones for the new reactions (eqs 5 and 8) which were taken from a preliminary parametric analysis. That analysis allowed us to detect the range of parameter values for which these reactions become relevant. Then, we constructed various sets of initial parameters, by changing the values of those related to the new reactions while keeping the others in their previously reported values. The statistical information reported by gPROMS after performing the parameter estimations, allows the selection of the best set of kinetic parameters for the model.

In a first stage, parameter estimation was performed taking into account the former kinetic model composed by eqs 1–4, 6, and 7 and using the entire set of 21 experimental modification conditions. By these means, we aimed to evaluate whether such a mechanism was capable of describing the experimental data under study. As expected, this was not the case. In consequence, the complete set of reactions proposed in this work was included in the parameter estimation. In this case, only 14 of the



**Figure 1.** Average molecular weights calculated with the complete model of Pedernera et al.:<sup>22</sup> (—) original kinetic parameters, (---) fitted kinetic parameters; experimental values (■)  $M_w$ , (●)  $M_n$ .

**Table 2. Kinetic Parameters**

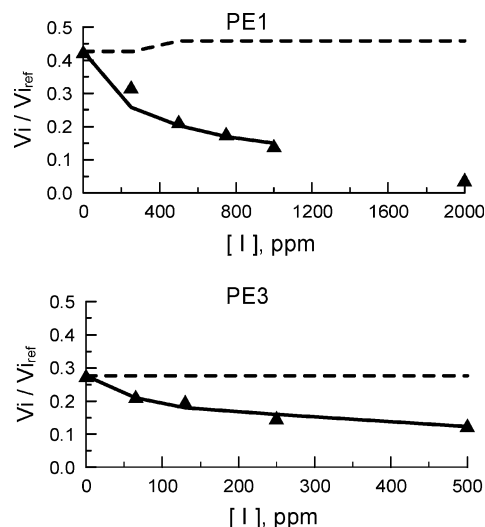
kinetic constant	$k_{170^\circ\text{C}}$ (L mol s)
initiator decomposition, $k_i$ , and efficiency <sup>22</sup>	$5.598 \times 10^{-3}$ ( $f = 0.98$ )
hydrogen abstraction, $k_a^a$	2.013
hydrogen abstraction on vinyl site, $k_{av}^a$	$2.365 \times 10^6$
chain transfer to polymer, $k_{tp}^a$	$3.254 \times 10^{-1}$
chain transfer to polymer, $k_{tpv}^a$	$5.666 \times 10^1$
double-bond propagation, $k_{db}^a$	$5.119 \times 10^{10}$
termination by combination, $k_t^a$	$4.033 \times 10^5$
termination by initiation radical, $k_{it}^a$	$1.693 \times 10^7$

<sup>a</sup> Obtained by parameter estimation.

experimental modification conditions were used in the estimation stage. The remaining 7 conditions were used for testing model predicting capabilities. The resulting kinetic constants for the new model are shown in Table 2.

## Results and Discussion

Figures 1 and 2 show a comparison between calculations performed with the model by Pedernera et al.<sup>22</sup> and experimental results for PE1, PE2, PE3, and PE4 treated at all the operating conditions shown in Table 1. The kinetic parameters used were the ones reported in Pedernera et al.<sup>22</sup> for their complete model

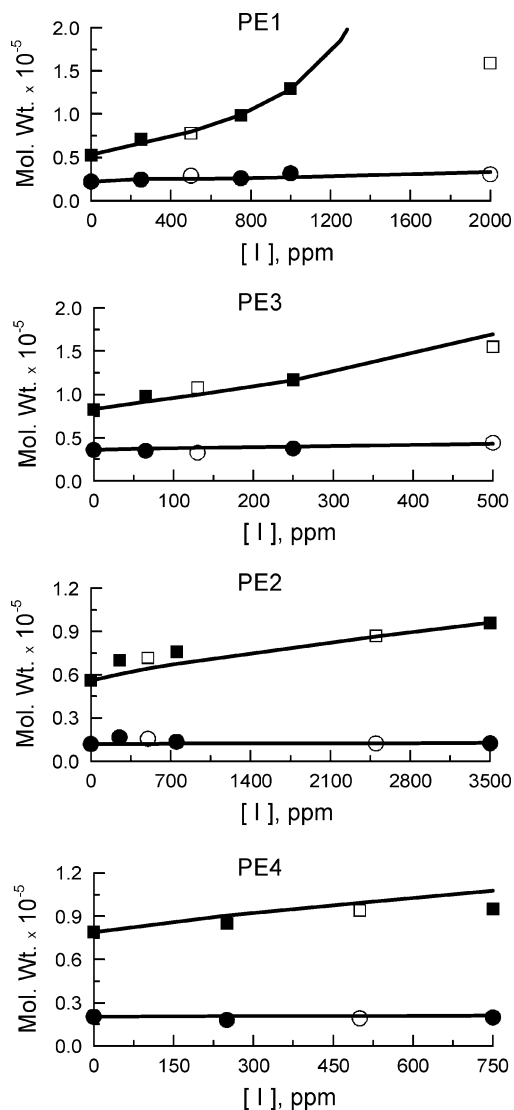


**Figure 2.** Vinyl content calculated with the complete model of Pedernera et al.:<sup>22</sup> (—) original kinetic parameters, (---) fitted kinetic parameters; (▲) experimental values.  $V_{i,ref} = 0.1$  mol/L.

(CM). Each calculated line is obtained by connecting the average molecular weights and vinyl content calculated at the final reaction time for each of the initiator concentrations considered. Symbols indicate experimental values. It must be kept in mind that the kinetic parameters were originally obtained by fitting only some of the experimental data for PE1 for peroxide concentrations ranging from 250 to 1000 ppm, as well as others from the literature.

For all cases, it may be observed that the experimental  $M_w$  of the modified resin increases with peroxide concentration. Experimental  $M_n$  shows a slight increase with the initial peroxide concentration. The vinyl content decreases with peroxide concentration for both PE1 and PE3, as shown in Figure 2. The CM model appropriately follows the experimental trends both qualitatively and quantitatively for PE1 and PE3. These two virgin resins contain vinyl groups at a level of around one per molecule. The particular synthesis process used for producing PE1 and PE3 makes it reasonable to assume that molecules in those two virgin resins contain at most one vinyl group each. Molecules with more than one vinyl group are a result of cross-linking reactions during the modification process. Since vinyl groups are consumed during the peroxide treatment, molecules with no vinyl are also produced. Nevertheless, it must be mentioned that the model was unable to handle 2000 ppm as the initial initiator concentration for polyethylene PE1, since it produces a numeric overflow, indicating that the gel region has been reached. This result is not surprising because there was experimental evidence of microgels under these conditions.<sup>15</sup>

In the case of PE2 and PE4, resins for which the vinyl content is insignificant, the CM model overpredicted molecular weights. This model performed reasonably well for initial initiator concentrations up to 500 ppm, but gave poor predictions for peroxide concentrations of over 1000 ppm. As another measure of the validity of the model, we tried to simulate the behavior of polymers that differed only by their initial vinyl content. The experimental observation is that for the same initial peroxide content, virgin resins with vinyl groups increase their molecular weight more than those with insignificant vinyl content. The model was tested by performing simulations where all parameters were identical except for the vinyl content: in half the simulations, the chains had one vinyl group each, and in the remaining half, they had none. Surprisingly, model results indicated the opposite of the experimental observations, predict-

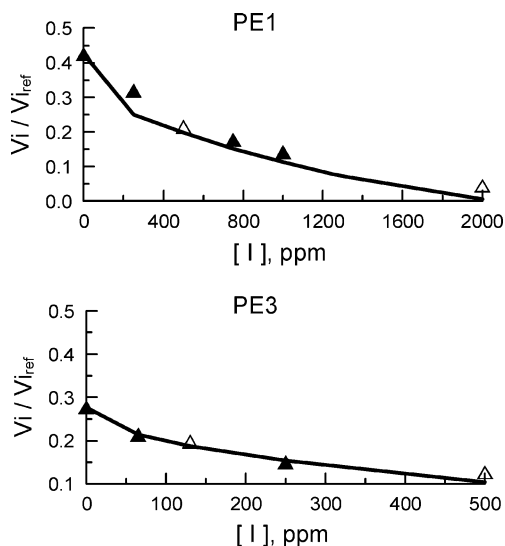


**Figure 3.** (—) Average molecular weights calculated with the new model; experimental values (■, □)  $M_w$ , (●, ○)  $M_n$ .

ing that the weight average molecular weights at the end of the treatment should be higher for the resins with no vinyl content.

In view of these results, a new parameter estimation was done on the CM model using all the available experimental information. Calculated results are presented as broken lines in Figures 1 and 2. The results for weight average molecular weights for PE2 and PE4 improve, at the expense of worsening those for PE1 and PE3. Since the reactions that account for vinyl group consumption were practically disabled, because their kinetic constants were very low, the prediction of vinyl content in PE1 and PE3 worsened severely. The CM model may not produce good predictions of  $M_n$ ,  $M_w$ , and vinyl content for the four resins we are interested in.

When considering the new kinetic mechanism (NM) presented in this work, model calculations for all the cases are presented in Figures 3 and 4. Experimental data used for parameter adjustment are indicated by filled symbols. Hollow symbols indicate experimental data used only for validation. Excellent agreement was obtained for all the experimental data considered. By including the reaction of termination by an initiation radical (eq 4), it was possible to attenuate the peroxide efficiency as the initial peroxide concentration increases, allowing us to



**Figure 4.** (—) Vinyl content calculated with the new model; (▲, △) experimental values.  $V_{i,ref} = 0.1$  mol/L.

**Table 3.** Mean Relative Absolute Error of Predicted Average Properties of Modified Resins at Different Initial Peroxide Concentrations

resin	[I] (ppm)	CM	fitted CM	NM
$M_n$ (absolute relative error, %)				
PE1	250–1000	12.75	13.40	8.20
PE1	2000	N/A	3.90	9.70
PE2	250–750	17.75	19.00	0.03
PE2	2500–3500	gel region	23.20	0.00
PE3	65–500	6.80	7.00	8.30
PE4	250–750	15.70	11.60	9.50
$M_w$ (absolute relative error, %)				
PE1	250–1000	12.40	28.30	2.50
PE1	2000	gel region		gel region
PE2	250–750	29.00	14.40	11.90
PE2	2500–3500	gel region	7.80	0.40
PE3	65–500	8.57	22.20	6.00
PE4	250–750	134.0	2.60	8.50
$V_i$ (absolute relative error, %)				
PE1	250–1000	8.90	131	16.50
PE1	2000	N/A	1045	85.00
PE3	65–500	5.00	68	6.40

predict lower molecular weights at higher initiator concentrations. Moreover, the double-bond propagation reaction (eq 8) considers in a direct manner the effect of vinyl groups on the increase of molecular weights. We considered the possibility of adding only one of the new reactions (eq 5 or eq 8), but the resulting fit was poor in both cases. We also considered eliminating eq 7, where chain transfer to polymer consumes a vinyl group. Again, poor results were obtained. It was impossible to give a good prediction of vinyl content if this reaction was not considered. In view of these results, the three reactions were considered in the NM model.

As shown in Table 3 and Figures 3 and 4, the differences between model predictions and experimental data are of the same order of magnitude of the inherent measurement error. The only exception is  $M_w$  for PE1 at 2000 ppm. The model overpredicts this molecular weight, which is consistent with the experimentally observed presence of microgels that indicate the onset of the gel region. When gel is present, the measured molecular weight characterizes only a fraction of the sample, that is, the soluble fraction. For the same sample, the prediction of vinyl content is good. This is probably a reflection of the

**Table 4. Initial Peroxide Concentration Needed to Reach the Gel Point: Comparison between Experimental Data<sup>a</sup> and Values Predicted by the NM Model**

polymer	$M_n$	$M_w$	$I_{0,exp}$ (ppm)	$I_{0,NM,model}$ (ppm)
1	8700	79000	11354	11624
2	7000	70000	13517	14868
4	12200	61000	17031	17571
7	7250	58000	18382	20545
9	31700	95000	8921	7569
C <sup>a</sup>	17100	60000	5947	4055
H	8700	52000	21897	24870

<sup>a</sup> Polymer C is the only one with an appreciable amount of vinyl groups.

fact that the vinyl content measurement is reliable even for cross-linked polymers.

In order to test model capabilities near the gel point, the NM model results were compared with the experimental data reported by Hulse et al.<sup>4</sup> We performed the simulations for the polyethylene resins shown in Table 4 at 170 °C, since the kinetic parameters of the NM model were adjusted only for that temperature. Hulse et al.<sup>4</sup> employed dicumyl peroxide as initiator, for 2 h and at 150 °C. This initiator decomposes into two radicals ( $\gamma = 2$ ). Its kinetic parameters and efficiency were taken from the literature.<sup>22</sup> Experimental data indicates that the initiator concentration needed to attain the gel point depends mainly on the weight-average molecular weight and vinyl content. For polymers 1, 2, 4, 7, and 9, with negligible vinyl content, and polymer H (hydrogenated), the NM model follows appropriately the decrease in initiator concentration with  $M_w$ . The model again shows its sensitiveness to detect different resin behavior depending on its vinyl content. For example, polymers 4 and C have a similar  $M_w$  but only polymer C contains molecules with vinyl groups (approximately 48% of the molecules have a vinyl group). Polymer C required a much lower initiator concentration to reach the gel point than polymer 4 did. This behavior is predicted by our model appropriately.

## Conclusions

A generalized model for the reactive modification of high-density polyethylenes of different chemical structure has been proposed. A double moment technique was applied to solve the mass balance equations for the modification performed in a press. Those mass balances account for the number of monomeric units and the number of vinyl groups of all the molecules present in the reacting system. The model is able to simulate appropriately the very different behaviors shown by resins with high and low vinyl content. This fact was confirmed by

comparing model predictions with experimental data on vinyl content,  $M_n$ , and  $M_w$  of the resulting modified resins. A comparison between the predicted peroxide concentration needed to produce a gel at the end of the treatment and experimental data from the literature produced good agreement, both for resins with negligible and non-negligible vinyl content.

We tested partial versions of the new model presented in this work, with fewer chemical reactions in the mechanism, and obtained poor results. The mechanism presented in this work is the simplest one that may produce good predictions of all the parameters for all the polymers in our study.

We think that the model presented in this work is a valuable tool that could replace or at least minimize trial and error experiments in the development of new polymer grades or products. It also has potential to be used in optimization studies of reactors.

Finally, it must be mentioned that the assumptions employed in the present model are suitable for predicting molecular structure evolution in commercial processes where moderate concentrations of peroxides are employed, so as to produce an increase of molecular weight as well as a broadening of the MWD without reaching the gel point. In the future, model capabilities could be extended in order to predict crosslinking and endlinking as well as the properties related to the gel region. In that case, the inclusion of the multiple-radical assumption will be evaluated to determine if it is able to improve model results near the gel point.

## Acknowledgment

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## Appendix

In what follows, the moment technique and its application to mass balance transformation are detailed.

The first column in Table A1 contains the basic terms, where the double summation  $\sum_{n=1}^{\infty} n^a \sum_{j=0}^{j_n} j^b$  appears in eqs 10–12, when taking  $a = 0$  and  $b = 0$  (in eqs A1–A3), regardless of the name given to the indexes. Table A1 also contains the terms which result after applying the double summation  $\sum_{n=1}^{\infty} n^a \sum_{j=0}^{j_n} j^b$  to both members of eqs 11 and 12. Equations 15 and 16 can be constructed by combining the basic terms appropriately.

The procedure followed to obtain each moment expression shown in Table A1 is shown below.

**Table A1. Moment Transformations**

double summation term	moment expression
$\sum_{n=1}^{\infty} \sum_{j=0}^{j_n} n^a j^b n [P_{n,j}]$	$M_{a+1,b}$ (A1)
$\sum_{n=1}^{\infty} \sum_{j=0}^{j_n} n^a j^b j [P_{n,j}] (1 - \delta_{j,0})$	$M_{a,b+1}$ (A2)
$\sum_{n=1}^{\infty} \sum_{j=0}^{j_n} n^a j^b [R_{n,j}]$	$Y_{a,b}$ (A3)
$\sum_{n=1}^{\infty} n^a \sum_{j=0}^{j_n} j^b (j+1) [P_{n,j+1}]$	$\sum_{r=0}^b \binom{b}{r} (-1)^{b-r} M_{a,r+1}$ (A4)
$\sum_{n=1}^{\infty} n^a \sum_{j=0}^{j_n} j^b \sum_{m=1}^{n-1} \sum_{k=0}^j [R_{n-m,j-k}] [R_{m,k}] (1 - \delta_{n,1})$	$\sum_{r=0}^a \sum_{s=0}^b \binom{a}{r} \binom{b}{s} Y_{a-r,b-s} Y_{r,s}$ (A5)
$\sum_{n=1}^{\infty} n^a \sum_{j=0}^{j_n} j^b \sum_{m=1}^{n-1} \sum_{k=0}^j (j-k+1) [R_{m,k}] [P_{n-m,j-k+1}] (1 - \delta_{n,1})$	$\sum_{r=0}^a \sum_{s=0}^b \sum_{q=0}^s \binom{a}{r} \binom{b}{s} \binom{s}{q} (-1)^{s-q} Y_{a-r,b-s} M_{r,q+1}$ (A6)



For eqs A1–A3, simple rearrangements lead to the moment expressions

$$\sum_{n=1}^{\infty} \sum_{j=0}^{j_n} n^a j^b n [P_{n,j}] = \sum_{n=1}^{\infty} \sum_{j=0}^{j_n} n^{a+1} j^b [P_{n,j}] = M_{a+1,b} \quad (\text{A7})$$

$$\begin{aligned} \sum_{n=1}^{\infty} \sum_{j=0}^{j_n} n^a j^b [P_{n,j}] (1 - \delta_{j,0}) &= \sum_{n=1}^{\infty} \sum_{j=0}^{j_n} n^a j^{b+1} [P_{n,j}] - \\ \sum_{n=1}^{\infty} n^a 0^{b+1} [P_{n,0}] &= M_{a,b+1} - 0 = M_{a,b+1} \end{aligned} \quad (\text{A8})$$

$$\sum_{n=1}^{\infty} \sum_{j=0}^{j_n} n^a j^b [R_{n,j}] = Y_{a,b} \quad (\text{A9})$$

In order to obtain eq A4, the variable change  $t = j + 1$  was performed and the binomial theorem expansion

$$(x + y)^c = \sum_{r=0}^c \binom{c}{r} x^r y^{(c-r)} \quad (\text{A10})$$

was employed. In this case,  $x = t$ ,  $y = (-1)$ , and  $c = r$ . Then, we find the following:

$$\begin{aligned} \sum_{n=1}^{\infty} n^a \sum_{j=0}^{j_n} j^b (j + 1) [P_{n,j+1}] &= \\ \sum_{n=1}^{\infty} n^a \sum_{t=1}^{t_n} (t - 1)^b t [P_{n,t}] &= \sum_{n=1}^{\infty} n^a \sum_{t=0}^{t_n} (t - 1)^b t [P_{n,t}] (1 - \delta_{t,0}) = \\ \sum_{n=1}^{\infty} n^a \sum_{t=0}^{t_n} \sum_{r=0}^b \binom{b}{r} (-1)^{b-r} t^r [P_{n,t}] (1 - \delta_{t,0}) &= \\ \sum_{r=0}^b \binom{b}{r} (-1)^{b-r} \sum_{n=1}^{\infty} n^a \sum_{t=0}^{t_n} t^{r+1} [P_{n,t}] (1 - \delta_{t,0}) &= \\ \sum_{r=0}^b \binom{b}{r} (-1)^{b-r} (M_{a,r+1} - 0) &= \\ \sum_{r=0}^b \binom{b}{r} (-1)^{b-r} M_{a,r+1} \end{aligned} \quad (\text{A11})$$

For eq A5, which appears in the termination by combination reaction, the following equivalences for the summations must be considered  $\sum_{n=2}^{\infty} \sum_{m=0}^{n-1} = \sum_{m=1}^{\infty} \sum_{n=m+1}^{\infty}$  and  $\sum_{j=0}^{j_n} \sum_{k=0}^j = \sum_{k=0}^{k_n} \sum_{j=k}^{j_n}$ . A few variable changes must also be made: if  $u = n - m$  and  $t = j - k$ , then  $u = 1$  when  $n = m + 1$  and  $t = 0$  when  $j = k$ . The binomial theorem expression

$$(x + y)^c = \sum_{r=0}^c \binom{c}{r} x^r y^{(c-r)} \quad (\text{A12})$$

must be used again. The resulting expression is derived as follows:

$$\begin{aligned} \sum_{n=1}^{\infty} n^a \sum_{j=0}^{j_n} \sum_{m=1}^{n-1} \sum_{k=0}^j [R_{n-m,j-k}] [R_{m,k}] (1 - \delta_{n,1}) &= \\ \sum_{n=2}^{\infty} (u + m)^a \sum_{j=0}^{j_n} (t + k)^b \sum_{m=1}^{n-1} \sum_{k=0}^j [R_{u,t}] [R_{m,k}] &= \\ \sum_{m=1}^{\infty} \sum_{k=0}^{k_m} \sum_{n=m+1}^{\infty} \sum_{j=k}^{j_n} (u + m)^a (t + k)^b [R_{u,t}] [R_{m,k}] &= \\ \sum_{m=1}^{\infty} \sum_{k=0}^{k_m} \sum_{n=m+1}^{\infty} \sum_{j=k}^a u^r m^{a-r} t^s k^{b-s} [R_{u,t}] [R_{m,k}] &= \\ \sum_{r=0}^a \binom{a}{r} \sum_{s=0}^b \binom{b}{s} \sum_{m=1}^{\infty} \sum_{k=0}^{k_m} m^{a-r} k^{b-s} [R_{m,k}] \sum_{u=1}^{\infty} \sum_{j=k}^{j_u} u^r t^s [R_{u,t}] &= \\ \sum_{r=0}^a \sum_{s=0}^b \binom{a}{r} \binom{b}{s} Y_{a-r,b-s} Y_{r,s} \end{aligned} \quad (\text{A13})$$

For the double bond propagation term shown in eq A6, it is necessary to apply the same considerations for the summations as in the previous term. The changes of variables to be made are:  $j - k + 1 = t$  and  $n - m = u$ . Then,  $u = 1$  when  $n = m + 1$ ,  $t = 1$  when  $j = k$ , and the derivation is as follows:

$$\begin{aligned} \sum_{n=1}^{\infty} n^a \sum_{j=0}^{j_n} \sum_{m=1}^{n-1} \sum_{k=0}^j (j - k + 1) [R_{m,k}] [P_{n-m,j-k+1}] (1 - \delta_{n,1}) &= \\ \sum_{n=2}^{\infty} n^a \sum_{j=0}^{j_n} \sum_{m=1}^{n-1} \sum_{k=0}^j (j - k + 1) [R_{m,k}] [P_{n-m,j-k+1}] &= \\ \sum_{m=1}^{\infty} n^a \sum_{k=0}^{k_m} \sum_{n=m+1}^{\infty} \sum_{j=k}^{j_n} n^a j^b t [R_{m,k}] [P_{u,t}] &= \\ \sum_{m=1}^{\infty} \sum_{k=0}^{k_m} \sum_{u=1}^{\infty} \sum_{t=1}^{t_u} (u + m)^a (t + k - 1)^b t [R_{m,k}] [P_{u,t}] &= \\ \sum_{r=0}^a \binom{a}{r} \sum_{s=0}^b \binom{b}{s} \sum_{m=1}^{\infty} \sum_{k=0}^{k_m} m^{a-r} k^{b-s} \sum_{u=1}^{\infty} \sum_{t=1}^{t_u} u^r (t - 1)^s t \times \\ [R_{m,k}] [P_{u,t}] &= \\ \sum_{r=0}^a \binom{a}{r} \sum_{s=0}^b \binom{b}{s} \sum_{q=0}^s \binom{s}{q} (-1)^{s-q} \sum_{m=1}^{\infty} \sum_{k=0}^{k_m} m^{a-r} k^{b-s} [R_{m,k}] \times \\ \sum_{u=1}^{\infty} \sum_{t=1}^{t_u} u^r t^{q+1} [P_{u,t}] &= \\ \sum_{r=0}^a \binom{a}{r} \sum_{s=0}^b \binom{b}{s} \sum_{q=0}^s \binom{s}{q} (-1)^{s-q} Y_{a-r,b-s} M_{r,a+1} \end{aligned} \quad (\text{A14})$$

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