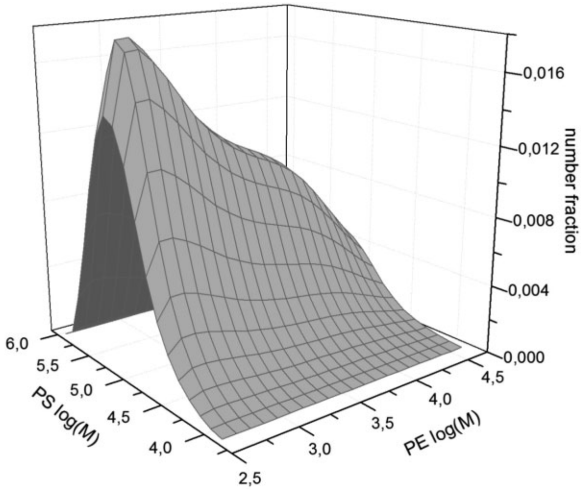
Graft Copolymers for Blend Compatibilization: Mathematical Modeling of the Grafting Process

Ioana A. Gianoglio Pantano, Mariano Asteasuain, Claudia Sarmoria,* Adriana Brandolin

The grafting of PE onto PS through a Friedel-Crafts reaction, which results in a mixture of PE-*g*-PS copolymer, unmodified PE, and modified PS, is investigated. The copolymer may be suitable for compatibilization of immiscible mixtures in the household plastic waste stream, where PE and PS are majority components. Since the compatibilization effect depends on the composition and block lengths in the copolymer, a model is presented for predicting the complete molecular weight distribution of the homopolymers and the chemical composition distribution of the graft copolymer. The model has potential for application in an optimization tool for the compatibilization process, as it is able to account for the opposing effects of competing reactions that characterize the graft reaction.



1. Introduction

Urban plastic waste streams are composed mainly by polystyrene (PS) and polyolefins (PO), such as polyethylene (PE) and poly(propylene) (PP). For example, the US Environmental Protection Agency reports[1] that in the United States in 2009 12 wt% of the municipal solid wastes (MSW) were plastic residues. When broken down by composition, those plastic residues contained 38.6% PE, 18.5% PP, 8.3% PS, and 11.8% PET. That same year, in Buenos Aires City (Argentina) almost 20% of MSW were plastics, containing 67.5% PE, 5.7% PP, 10.2% PS, and 10.4% PET.[2] In both examples, more than half of the plastic wastes were composed by PO, and the proportion of PS was significant.

The relative amount of plastics present in MSW poses a challenge for the local authorities responsible for solid waste management and sanitation, since discarded plastics take up large volumes in disposal sites due to their low density. An interesting alternative to disposal is plastic waste recycling, an approach that aims at converting waste into a resource. This alternative is not free of drawbacks. For instance, traditional recycling methods require the previous separation of resins, since mixtures of different polymers are often immiscible and show poor mechanical properties. PS and PO are an example of such immiscible polymer pairs. Methods that would allow recycling these resins together, avoiding the separation step, could save both time and money. A possible method of achieving this is the introduction of a compatibilizer to promote adhesion between phases, so as to improve the mechanical properties of the material.[3,4] Such an additive could be a copolymer, for example, that is obtained by grafting one of the immiscible homopolymers on the other one.

I. A. Gianoglio Pantano, M. Asteasuain, C. Sarmoria, A. Brandolin
Planta Piloto de Ingeniería Química (PLAPIQUI, UNS-CONICET),
Camino La Carrindanga km 7, 8000 Bahía Blanca, Argentina
E-mail: csarmoria@plapiqui.edu.ar

DOI: 10.1002/mren.201200025

To achieve the compatibilization, the copolymer could either be added to the mixture or generated in situ through reactive processing.[5,6]

There are reports in the literature about the synthesis of PE-*g*-PS copolymers from mixtures of PS and PE through Friedel-Crafts alkylations using a strong Lewis acid as catalyst.[7–12] It has been reported that the use of a cocatalyst such as styrene improves the yield of the reaction.[8,9,12] The studies conducted by Díaz et al.[9,12] on the reaction between PS and PE in the presence of the catalytic system $AlCl_3$/styrene revealed that shorter homopolymer molecules increase the amount of copolymer formed. However, compatibilization is more effective when the copolymer contains long homopolymer blocks.[9] These authors also found that at their operating conditions PE only participated in the grafting reaction, while PS was also involved in chain scission and chain combination.[9,13,14] In their works it was observed that the relative concentrations of the catalyst and cocatalyst influence the yield of the grafting reaction, the composition of the copolymer and the extent of the PS degradation process.

Given the number of variables and their opposing effects on the quantity and quality of the compatibilizing copolymer produced, finding the optimal operating conditions for the synthesis of the compatibilizer is not trivial. A mathematical model of the process would be a useful tool to aid in this task.

If we were to set up a mass balance for every molecular species present in the reacting system, an infinitely large system of equations would result because the degree of polymerization of PE, PS, and PE-*g*-PS chains ranges from 1 to infinity. Several transformation methods may be applied to this system in order to limit its size. One of them, the method of moments, allows calculation of several average molecular properties from the moments of the size distribution. Another one, the probability generating function (pgf) approach, is appropriate for obtaining the complete molecular weight distribution (MWD) and the chemical composition distribution (CCD) by applying the univariate and bivariate forms of the transform, respectively.

In previous works we modeled the copolymerization reaction taking into account the degradation of PS in the presence of $AlCl_3$.[15,16] In these works the method of moments was applied in order to predict the mass of grafted PS and the average molecular weights. Both quantities agreed well with experimental data. On the other hand, the pgf technique in its univariate form was successfully applied to predict the complete PS MWD during its degradation process in the presence of $AlCl_3$ and S.[17] First, the pgf transform was applied to the mass balances derived from the proposed kinetic mechanism, resulting in pgf balances for the MWD expressed in number fraction distribution, weight fraction distribution or differential-log distribution. The set of pgf balances constituted an initial value problem, which was solved numerically. The experimental MWD of the unmodified PS obtained from size exclusion chromatography (SEC) were used to calculate the necessary initial values. The second step was the numerical inversion of the pgfs calculated from the balances, producing as a result the MWD of the modified polymer. The inversion formula used in this work was the one proposed by Papoulis[18] for Laplace transforms, and adapted by Asteasuain et al.[19,20] for the inversion of pgf of MWD in polymeric systems.

In this context, we present a mathematical model of the graft copolymerization reaction between PS and PE, achieved through a Friedel-Crafts alkylation with $AlCl_3$ and styrene (S) as catalytic system. The model properly describes the MWD and the CCD by applying the univariate and bivariate pgf techniques. Kinetic parameters for the graft and PS side reactions were estimated previously,[15,16] using experimental data obtained in our laboratories. It should be noted that experimental data on complete MWD were not used in the parameter estimation; only average molecular weight data were used for that purpose.

2. Mathematical Model

In a previous work[16] we presented a preliminary mathematical model for the grafting process that accounts for the graft copolymerization of PS and PE as well as PS degradation reactions. In that work, the method of moments was used to calculate the mass of copolymer generated and the average molecular weights of PS. We also estimated the kinetic rate constants for the proposed reactions using experimental molecular weight data. In this section we present the description of the complete mathematical model that includes not only the calculation of those average properties but also the detailed prediction of MWDs.

The kinetic mechanism considered in this work is the same that was proposed previously.[16] In order to obtain a mechanism as simple as possible, the grafting reaction produced by a Friedel-Crafts alkylation, which has been reported to involve several steps and intermediate compounds,[14] is assumed to occur in a single step involving PS, PE, $AlCl_3$, and either S or benzene. Table 1 shows the kinetic equations considered in the model. This kinetic scheme involves PE-PS grafting (Equation 1 and 2), PS side reactions (Equation 3–10), and deactivation of the catalytic system (Equation 11 and 12). It is assumed that either benzene or S takes

Table 1. Kinetic Model.

Step	Reaction	No.
graft reactions		
	$PS_x + PE_y + A + B \xrightarrow{k_{gB}} G_{x+1,y} + A \quad x = 1, \ldots, \infty; \quad y = 1, \ldots, \infty$	(1)
	$PS_x + PE_y + A + S \xrightarrow{k_{gS}} G_{x+1,y} + A \quad x = 1, \ldots, \infty; \quad y = 1, \ldots, \infty$	(2)
PS side reactions		
chain scission through weak links I)	$PS_x + A \xrightarrow{k_{S1w}} PS_{x-y-1} + PS_y + A + B \quad x = 2, \ldots, \infty$	(3)
chain scission through weak links II)	$PS_x + A + S \xrightarrow{k_{S2w}} PS_{x-y-1} + PS_y + A + B + S \quad x = 2, \ldots, \infty$	(4)
chain scission through normal links I)	$PS_x + A \xrightarrow{k_{S1n}} PS_{x-y-1} + PS_y + A + B \quad x = 2, \ldots, \infty$	(5)
chain scission through normal links II)	$PS_x + A + S \xrightarrow{k_{S2n}} PS_{x-y-1} + PS_y + A + B + S \quad x = 2, \ldots, \infty$	(6)
formation of indane skeleton	$PS_x + A \xrightarrow{k_{In}} PS_{x-1} + A + B \quad x = 2, \ldots, \infty$	(7)
chain combination (I)	$PS_x + PS_y + A \xrightarrow{k_{c1}} PS_{x+y} + A \quad x = 2, \ldots, \infty$	(8)
chain combination (II)	$PS_x + PS_y + A + S \xrightarrow{k_{c2}} PS_{x+y} + A + S \quad x = 2, \ldots, \infty$	(9)
styrene polymerization	$PS_x + A + S \xrightarrow{k_p} PS_{x+1} + A \quad x = 1, \ldots, \infty$	(10)
catalytic system deactivation		
catalyst decomposition	$A \xrightarrow{k_i} Ai$	(11)
catalyst-Styrene reaction	$A + S \xrightarrow{k_d} Ai + Si$	(12)

part in the grafting reactions. The former appears in the reactive mixture as a product of several of the side reactions induced in PS by $AlCl_3$. Once reacted, the molecules of S or benzene are assumed to become part of the synthesized copolymer, where they are regarded as styrene monomeric units. The PS side reactions have already been described in another work,[17] where we modeled the complete MWD during PS degradation using the pgf technique.

In Equation 1–12, PS and PE chains with degree of polymerization x are indicated as PS_x and PE_x. Similarly, $G_{x,y}$ is a PE-*g*-PS copolymer molecule made up of x styrene monomeric units and y ethylene monomeric units. Finally, S is a styrene molecule, A is an active catalyst molecule, A_i and S_i are the inactive catalyst and cocatalyst molecules, and B is a benzene molecule.

The kinetic rate constants were estimated in a previous work.[16] The process is considered to be carried out in a constant volume, stirred batch reactor at isothermal conditions. It is also assumed that shorter polymer molecules are more reactive toward grafting than longer ones, in qualitative agreement with reported data.[3,9] As discussed in previous works,[15,17,21] PS chains contain several weak links that are easier to break than the remaining normal links. This difference in bond strength is also considered in the model.

Taking into account the above assumptions, the mass balances for the species that take part in the reactions described in Equation 1–12 lead to Equation 13–16 which represent the system of equations to be solved and their corresponding initial conditions.

PS molecules with x monomeric units ($x = 1, \ldots, \infty$):

$$\frac{d\mathbf{PS}(t)}{dt} = \mathbf{VPS}; \quad \mathbf{PS}(0) = \mathbf{PS0} \tag{13}$$

PE molecules with x monomeric units ($x = 1, \ldots, \infty$):

$$\frac{d\mathbf{PE}(t)}{dt} = \mathbf{VPE}; \quad \mathbf{PE}(0) = \mathbf{PE0} \tag{14}$$

PE-*g*-PS graft copolymer molecules with x styrene monomeric units and y ethylene monomeric units ($x = 2, \ldots, \infty$, $y = 1, \ldots, \infty$):

$$\frac{d\mathbf{G}(t)}{dt} = \mathbf{VG}; \quad \mathbf{G}(0) = \mathbf{0} \tag{15}$$

Other components:

$$\frac{\mathrm{d}\mathbf{X}(t)}{\mathrm{d}t} = \mathbf{VX};\quad \mathbf{X}(0) = \mathbf{X0} \tag{16}$$

where **PS**(t) and **PE**(t) are vector arrays of infinite size, **G**(t) is a matrix array with an infinite number of rows and columns and **X**(t) is a vector of length 4. Each element of **PS**(t), **PE**(t), and **G**(t) contains the molar concentration of the individual species that has the degree of polymerization indicated by its subscripts. For example, element PS_x of vector **PS**(t) is the concentration at time t of the PS chain with x monomeric units. Similarly, element $G_{x,y}$ of matrix **G**(t) is the concentration of the PS-*g*-PE chain with blocks of length x (PS) and y (PE). Vector **X**(t) contains the remaining concentrations necessary for the mass balances: those of benzene, styrene, catalyst and weak links, respectively. Finally, the various V vectors (**VPE**, **VPS**, **VG,** and **VX**) contain the reaction velocity terms. Further details about the expressions for the elements of these arrays are presented in the Appendix.

2.1. Method of Moments

Since the degree of polymerization of homopolymer and copolymer molecules may range between one and infinity, there are infinitely many mass balance equations. In order to reduce the size of the system, the well-known method of moments is used to calculate average properties. For that purpose, moment definitions are applied to the polymer distributions.

Taking advantage of vectorial notation, it is possible to define the vectors $\mathbf{M}^{\mathrm{PS}} = \left[M_0^{\mathrm{PS}}, M_1^{\mathrm{PS}}, M_2^{\mathrm{PS}}\right]^{\mathrm{T}}$ and $\mathbf{M}^{\mathrm{PE}} = \left[M_0^{\mathrm{PE}}, M_1^{\mathrm{PE}}, M_2^{\mathrm{PE}}\right]^{\mathrm{T}}$ for the moments of orders 0, 1, and 2 of PS and PE mass distributions, respectively, as:

$$M_a^{\mathrm{PS}} = (\mathbf{x}_a^{\mathrm{PS}})^T \mathbf{PS} \quad a = 0,\ 1,\ 2 \tag{17}$$

$$M_a^{\mathrm{PE}} = (\mathbf{x}_a^{\mathrm{PE}})^T \mathbf{PE} \quad a = 0,1,2 \tag{18}$$

In the above expressions, the infinitely sized vectors $\mathbf{x}_a^j$, $j =$ PS, PE are defined as

$$(x_a^{\mathrm{PS}})^{\mathrm{T}} = \left[(M_{\mathrm{S}})^a \quad (2M_{\mathrm{S}})^a \quad \cdots \quad (xM_{\mathrm{S}})^a \quad \cdots\right] \quad 1 \le x \le \infty \tag{19}$$

$$(x_a^{\mathrm{PE}})^{\mathrm{T}} = \left[(M_{\mathrm{E}})^a \quad (2M_{\mathrm{E}})^a \quad \cdots \quad (xM_{\mathrm{E}})^a \quad \cdots\right] \quad 1 \le x \le \infty \tag{20}$$

where M_{S} and M_{E} are the molecular weights of the PS and PE monomers, respectively.

The moments just defined involve a single variable, namely, the degree of polymerization. It is possible to define double moments involving two variables in an analogous way. In this work we are interested in using as variables the number of styrene and ethylene monomeric units in a graft copolymer. For example, the 1st, 2nd order moment for the PE-*g*-PS graft copolymer mass distribution is defined by

$$I_{1,2} = (\mathbf{x}_1^{\mathrm{PS}})^{\mathrm{T}} \mathbf{G} (\mathbf{x}_2^{\mathrm{PE}}) \tag{21}$$

All $I_{a,b}$ moments with $a = 0,1,2$ and $b = 0,1,2$, which compose matrix array **I**, are defined similarly.

Average molecular weights for PE and PS homopolymers and the amount of grafted PS, for which experimental data is available, may be calculated in terms of several moments of their mass distributions. The corresponding expressions used in this work are

Number-average molecular weight for PS and PE homopolymers:

$$\overline{M}_{\mathrm{n}}^j = \frac{M_1^j}{M_0^j} \qquad j = \mathrm{PS}, \mathrm{PE} \tag{22}$$

Weight-average molecular weight for PS and PE homopolymer:

$$\overline{M}_{\mathrm{w}}^j = \frac{M_2^j}{M_1^j} \qquad j = \mathrm{PS}, \mathrm{PE} \tag{23}$$

Concentration (wt%) of grafted PS:

$$\mathrm{Gr} = 100 \frac{I_{1,0}}{M_1^{\mathrm{PS}}(t = 0)} \tag{24}$$

It is also possible to calculate the number and weight-average molecular weights for the graft copolymer. Even though we have no experimentally measured values against which model predictions could be compared, these calculated quantities have value for the insight they provide. The expressions used in this work are

$$\overline{C}_{\mathrm{n}} = \frac{I_{1,0} + I_{0,1}}{I_{0,0}} \qquad \overline{C}_{\mathrm{w}} = \frac{I_{2,0} + 2I_{1,1} + I_{0,2}}{I_{1,0} + I_{0,1}} \tag{25}$$

In order to transform the mass balances to include moments, vectorial Equation 13 is premultiplied by either $(\mathbf{x}_0^{\mathrm{PS}})^{\mathrm{T}}$, $(\mathbf{x}_1^{\mathrm{PS}})^{\mathrm{T}}$ or $(\mathbf{x}_2^{\mathrm{PS}})^{\mathrm{T}}$, while vectorial Equation 14 is premultiplied by either $(\mathbf{x}_0^{\mathrm{PE}})^{\mathrm{T}}$, $(\mathbf{x}_1^{\mathrm{PE}})^{\mathrm{T}}$ or $(\mathbf{x}_2^{\mathrm{PE}})^{\mathrm{T}}$. As a result of those operations, balance equations for the first three moments of the length distributions are obtained. Similarly, Equation 15 is premultiplied by either $(\mathbf{x}_0^{\mathrm{PS}})^{\mathrm{T}}$, $(\mathbf{x}_1^{\mathrm{PS}})^{\mathrm{T}}$ or

$(\mathbf{x}_2^{\mathrm{PS}})^{\mathrm{T}}$ and postmultiplied by either $(\mathbf{x}_0^{\mathrm{PE}})^{\mathrm{T}}$, $(\mathbf{x}_1^{\mathrm{PE}})^{\mathrm{T}}$, or $(\mathbf{x}_2^{\mathrm{PE}})^{\mathrm{T}}$ to obtain balance equations for the nine $I_{a,b}$ moments. After rearranging terms, the following system of equations results

a^{th}-order homopolymer moments, $a = 0,1,2$

$$\frac{d\mathbf{M}^{\mathrm{PS}}(t)}{dt} = \mathbf{VM}^{\mathrm{PS}}; \qquad \mathbf{M}^{\mathrm{PS}}(0) = \mathbf{M0}^{\mathrm{PS}} \tag{26}$$

$$\frac{d\mathbf{M}^{\mathrm{PE}}(t)}{dt} = \mathbf{VM}^{\mathrm{PE}}; \qquad \mathbf{M}^{\mathrm{PE}}(0) = \mathbf{M0}^{\mathrm{PE}} \tag{27}$$

$a^{\mathrm{th}} - b^{\mathrm{th}}$-order copolymer moments, $a = 0,1,2$; $b = 0,1,2$

$$\frac{d\mathbf{I}(t)}{dt} = \mathbf{VI}; \quad \mathbf{I}(0) = \mathbf{0} \tag{28}$$

Besides, the elements of the vector array **VX** in Equation 16 can be put in terms of vectors $\mathbf{M}^{\mathrm{PS}}$ and $\mathbf{M}^{\mathrm{PE}}$, obtaining the new vector array **VMX**. With this substitution, Equation 29 results,

Other components:

$$\frac{d\mathbf{X}(t)}{dt} = \mathbf{VMX}; \quad \mathbf{X}(0) = \mathbf{X0} \tag{29}$$

The elements of vectors **VMX**, $\mathbf{VM}^{\mathrm{PS}}$, $\mathbf{VM}^{\mathrm{PE}}$, and **VI** are detailed in the Appendix.

2.2. Probability-Generating Function (pgf) Transform

The above method of moments is a transform technique that changes an unsolvable, detailed, infinitely sized system of equations into a finite-size lumped system that can be solved to give useful results. Other transform techniques may be applied in order to yield different useful information. One of the applicable transform techniques uses pgf, both univariate and bivariate. Inversion of the pgf allows recovering the MWD of the unreacted homopolymers and the CCD of the synthesized graft copolymer.

The method applied is similar to that applied in a previous work.[17] First, mass balances were transformed to obtain pgf balances. Univariate pgf are used as transforms of the MWD of the homopolymers, while bivariate pgfs are employed for the CCD of the graft copolymer. A detailed description of the application of this technique is given elsewhere.[19,20,22] For this system we employ the following pgf definitions.

Homopoymer pgf:

$$\phi^j(z) = [\phi_0^j(z), \phi_1^j(z), \phi_2^j(z)], \qquad j = \mathrm{PS, PE} \tag{30}$$

with

$$\phi_a^j(z) = \mathbf{z}^{\mathrm{T}}\mathbf{p}_a^j \qquad a = 0,1,2 \tag{31}$$

Copolymer pgf:

$$\psi(z_1, z_2) = \begin{bmatrix} \psi_{0,0}(z) & \psi_{0,1}(z) & \psi_{0,2}(z) \\ \psi_{1,0}(z) & \psi_{1,1}(z) & \psi_{1,2}(z) \\ \psi_{2,0}(z) & \psi_{2,1}(z) & \psi_{2,2}(z) \end{bmatrix} \tag{32}$$

with

$$\psi_{a,b}(z_1, z_2) = \mathbf{z}_1^{\mathrm{T}} \cdot \mathbf{p}_{a,b} \cdot \mathbf{z}_2 \qquad a = 0,1,2; \quad b = 0,1,2 \tag{33}$$

where the vector arrays **z**, $\mathbf{z}_1$, $\mathbf{z}_2$, and $\mathbf{p}_a$, and the matrix array $\mathbf{p}_{a,b}$ are defined as

$$\mathbf{z}^{\mathrm{T}} = \begin{bmatrix} z^1 & z^2 & \dots & z^x & \dots \end{bmatrix} \qquad 1 \le x \le \infty \tag{34}$$

$$\mathbf{z}_1^{\mathrm{T}} = \begin{bmatrix} z_1^1 & z_1^2 & \dots & z_1^x & \dots \end{bmatrix} \qquad 1 \le x \le \infty \tag{35}$$

$$\mathbf{z}_2^{\mathrm{T}} = \begin{bmatrix} z_2^1 & z_2^2 & \dots & z_2^x & \dots \end{bmatrix} \qquad 1 \le x \le \infty \tag{36}$$

$$\left(\mathbf{p}_a^j\right)^{\mathrm{T}} = \begin{bmatrix} p_a^j(1) & p_a^j(2) & \dots & p_a^j(x) & \dots \end{bmatrix} \quad 1 \le x \le \infty \tag{37}$$

$$p_{a,b} = \begin{bmatrix} p_{a,b}(1,1) & p_{a,b}(1,2) & \dots & p_{a,b}(1,y) & \dots \\ p_{a,b}(2,1) & & & & \\ \vdots & & & \vdots & \\ p_{a,b}(x,1) & & \dots & p_{a,b}(x,y) & \dots \\ \vdots & & & \vdots & \end{bmatrix} \quad \begin{matrix} 1 \le x \le \infty \\ 1 \le y \le \infty \end{matrix} \tag{38}$$

In these equations, z_i are the dummy transform variables, $0 \le |z_i| \le 1$, and $p_a^j(x)$ is the "a" probability function of the length distribution of the homopolymers, while $p_{a,b}(x,y)$ is the "a,b" probability function of the length distribution of the copolymer. They may be calculated through Equation 39–41 as follows:

$$\mathbf{p}_a^{\mathrm{PS}} = \frac{\mathbf{XPS}_a}{M_a^{\mathrm{PS}}} \qquad a = 0,1,2 \tag{39}$$

$$\mathbf{p}_a^{\mathrm{PE}} = \frac{\mathbf{XPE}_a}{M_a^{\mathrm{PE}}} \qquad a = 0,1,2 \tag{40}$$

$$\mathbf{p}_{a,b} = \frac{\mathbf{XYG}_{a,b}}{I_{a,b}} \qquad a = 0,1,2; \quad b = 0,1,2 \tag{41}$$

where $\mathbf{XPS}_a$, $\mathbf{XPE}_a$, and $\mathbf{XYG}_{a,b}$ are defined as

$$(\mathbf{XPS}_a)^{\mathrm{T}} = \left[(M_{\mathrm{S}}1)^a \mathrm{PS}_1 \quad (M_{\mathrm{S}}2)^a \mathrm{PS}_2 \quad \ldots \quad (M_{\mathrm{S}}x)^a \mathrm{PS}_x \quad \ldots \right] \qquad 1 \leq x \leq \infty \tag{42}$$

$$(\mathbf{XPE}_a)^{\mathrm{T}} = \left[(M_{\mathrm{E}}1)^a \mathrm{PE}_1 \quad (M_{\mathrm{E}}2)^a \mathrm{PE}_2 \quad \ldots \quad (M_{\mathrm{E}}x)^2 \mathrm{PE}_x \quad \ldots \right] \qquad 1 \leq x \leq \infty \tag{43}$$

$$\mathbf{XYG}_{a,b} = \begin{bmatrix} (M_{\mathrm{S}}1)^a (M_{\mathrm{E}}1)^b G_{1,1} & (M_{\mathrm{S}}1)^a (M_{\mathrm{E}}2)^b G_{1,2} & \ldots & (M_{\mathrm{S}}1)^a (M_{\mathrm{E}}y)^b G_{1,y} & \ldots \\ (M_{\mathrm{S}}2)^a (M_{\mathrm{E}}1)^b G_{2,1} & & & & \\ \vdots & & & \vdots & \\ (M_{\mathrm{S}}x)^a (M_{\mathrm{E}}1)^b G_{x,1} & & \ldots & (M_{\mathrm{S}}x)^a (M_{\mathrm{E}}y)^b G_{x,y} & \ldots \\ \vdots & & & \vdots & \end{bmatrix} \qquad \begin{array}{l} 1 \leq x \leq \infty \\ 1 \leq y \leq \infty \end{array} \tag{44}$$

Replacing Equation 39–41 in Equation 31 and 33, the following pgf expressions are obtained.

PS pgf:

$$\phi_a^{\mathrm{PS}}(z) = \frac{\mathbf{z}^{\mathrm{T}} \cdot \mathbf{XPS}_a}{M_a^{\mathrm{PS}}} \qquad a = 0, 1, 2 \tag{45}$$

PE pgf:

$$\phi_a^{\mathrm{PE}}(z) = \frac{\mathbf{z}^{\mathrm{T}} \cdot \mathbf{XPE}_a}{M_a^{\mathrm{PE}}} \qquad a = 0, 1, 2 \tag{46}$$

Copolymer pgf:

$$\psi_{a,b}(z_1, z_2) = \frac{(\mathbf{z}_1)^T \cdot \mathbf{XYG}_{a,b} \cdot \mathbf{z}_2}{I_{a,b}} \qquad a = 0, 1, 2; \quad b = 0, 1, 2 \tag{47}$$

The pgf $\phi_0^j(z)$ are the transforms of the homopolymers' MWD expressed in number fraction, since $\mathbf{p}_0^j$ is the number fraction MWD (i.e., $n^{\mathrm{PS}}(x) = p_{0,x}^{\mathrm{PS}} = \mathrm{PS}_x / M_0$). Accordingly, $\phi_1^j(z)$ are the transforms of the MWD expressed in weight fraction (i.e., $w^{\mathrm{PS}}(x) = p_{1,x}^{\mathrm{PS}} = M_{\mathrm{S}} x \mathrm{PS}_x / M_1^{\mathrm{PS}}$) and $\phi_2^j(z)$ are the transforms of the MWD expressed as what we refer to as chromatographic fraction (i.e., $c^{\mathrm{PS}}(x) = (M_{\mathrm{S}})^2 x^2 \mathrm{PS}_x / M_2^{\mathrm{PS}}$). The chromatographic distributions are related to the differential log distributions by

$$\mathrm{d}W/\mathrm{d}\log_{10} M(x)^{\mathrm{PS}} = \frac{1}{\log_{10}(e)} c^{\mathrm{PS}}(x) \frac{M_2^{\mathrm{PS}}}{M_{\mathrm{S}} M_1^{\mathrm{PS}}}$$

and

$$\mathrm{d}W/\mathrm{d}\log_{10} M(x)^{\mathrm{PE}} = \frac{1}{\log_{10}(e)} c^{\mathrm{PE}}(x) \frac{M_2^{\mathrm{PE}}}{M_{\mathrm{E}} M_1^{\mathrm{PE}}}$$

In the case of the copolymer, the different combinations of values of a and b lead to several different pgf, each of them being the transform of different representations of the copolymer bivariate MWD (also referred to as CCD in this work). In this work we only consider $\psi_{0,0}(z_1,z_2)$, which is the transform of the copolymer MWD expressed in number fraction as

$$n^{\mathrm{PE-g-PS}}(x, y) = P_{0,0,x,y} = \frac{G_{x,y}}{I_{0,0}}$$

To transform the mass balances using pgf, every term in Equation 13 and 14 is multiplied by $x^a z^x$, and added up for all possible values of x. In the same way, every term in Equation 15 is multiplied by $z_1^x z_2^y$ (in the general case the multiplication would be by $x^a y^b z_1^x z_2^y$, but since we consider only the number distribution, $a = 0$ and $b = 0$) and added up for all possible values of x and y. The result is reordered in terms of the moments and the pgf, yielding a system of differential equations for the different pgf. For our particular grafting process, the corresponding equations are

Copolymer number distribution pgf:

$$\frac{\partial \left(I_{00} \psi_{0,0}(z_1, z_2) \right)}{\partial t} = 2A(Bk_{gB} + Sk_{gS}) \frac{M_0^{\mathrm{PS}}}{M_1^{\mathrm{PS}}} z_1 \times \frac{\partial \left(M_0^{\mathrm{PS}} \phi_0^{\mathrm{PS}}(z_1) \right)}{\partial z_1} \frac{M_0^{\mathrm{PE}}}{M_1^{\mathrm{PE}}} \left(M_0^{\mathrm{PE}} \phi_0^{\mathrm{PE}}(z_2) \right) \tag{48}$$

PE number distribution pgf:

$$\frac{\partial \left(M_0^{\mathrm{PS}} \phi_0^{\mathrm{PS}}(z) \right)}{\partial t} = -2A(Bk_{gB} + Sk_{gS}) \times \frac{M_0^{\mathrm{PS}} M_0^{\mathrm{PE}}}{M_{\mathrm{S}} M_1^{\mathrm{PE}}} \left(M_0^{\mathrm{PE}} \phi_0^{\mathrm{PE}}(z) \right) \tag{49}$$

PE weight distribution pgf:

$$\frac{\partial \left(M_1^{\mathrm{PE}} \phi_1^{\mathrm{PE}}(z) \right)}{\partial t} = -2A(Bk_{gB} + Sk_{gS}) \times \frac{M_0^{\mathrm{PS}} M_0^{\mathrm{PE}}}{M_{\mathrm{S}} M_1^{\mathrm{PE}}} \left(M_1^{\mathrm{PE}} \phi_1^{\mathrm{PE}}(z) \right) \tag{50}$$

PE chromatographic distribution pgf:

$$\frac{\partial\left(M_2^{\mathrm{PE}}\phi_2^{\mathrm{PE}}(z)\right)}{\partial t} = -2A(Bk_{gB} + Sk_{gS}) \times \frac{M_0^{\mathrm{PS}}M_0^{\mathrm{PE}}}{M_{\mathrm{S}}M_1^{\mathrm{PE}}}\left(M_2^{\mathrm{PE}}\phi_2^{\mathrm{PE}}(z)\right) \tag{51}$$

PS number distribution pgf:

$$\begin{aligned}\frac{\partial\left(M_0^{\mathrm{PS}}\phi_0^{\mathrm{PS}}(z)\right)}{\partial t} &= \begin{pmatrix} k_{s1w}f_wA^2 + k_{s2w}f_wA^2S^2 \\ +k_{s1n}f_nA^4 + k_{s2n}f_nA^4S \end{pmatrix} \\ &\times \left[-z\frac{\partial\left(M_0^{\mathrm{PS}}\phi_0^{\mathrm{PS}}(z)\right)}{\partial z} + 2\frac{\left(\left(M_0^{\mathrm{PS}}\phi_0^{\mathrm{PS}}(z)\right) - zM_0^{\mathrm{PS}}\right)}{z-1}\right] \\ &+ k_{\mathrm{In}}A^2\frac{\partial\left(M_0^{\mathrm{PS}}\phi_0^{\mathrm{PS}}(z)\right)}{\partial z}(1-z) \\ &\times \left(k_{cl}A^2 + k_{c2,1}A^2S + k_{c2,2}A^4S^4\right)z\frac{\partial\left(M_0^{\mathrm{PS}}\phi_0^{\mathrm{PS}}(z)\right)}{\partial z}\begin{bmatrix}\frac{z}{2}\frac{\partial\left(M_0^{\mathrm{PS}}\phi_0^{\mathrm{PS}}(z)\right)}{\partial z} \\ -\frac{M_1^{\mathrm{PS}}}{M_{\mathrm{S}}}\end{bmatrix} \\ &+ 2k_{\mathrm{p}}A^2S^2(z-1)\left(M_0^{\mathrm{PS}}\phi_0^{\mathrm{PS}}(z)\right) \\ &- 2A(k_{\mathrm{g}B}B + k_{\mathrm{g}S}S)\frac{M_0^{\mathrm{PS}}\left(M_0^{\mathrm{PE}}\right)^2}{M_1^{\mathrm{PS}}M_1^{\mathrm{PE}}}z\frac{\partial\left(M_0^{\mathrm{PS}}\phi_0^{\mathrm{PS}}(z)\right)}{\partial z}\end{aligned} \tag{52}$$

PS weight distribution pgf:

$$\begin{aligned}\frac{\mathrm{d}\left(M_1^{\mathrm{PS}}\phi_1^{\mathrm{PS}}(z)\right)}{\mathrm{d}t} &= \begin{bmatrix} f_w(k_{s1w}A^2 + k_{s2w}A^2S^2) \\ +f_n(k_{s1n}A^4 + k_{s2n}A^4S) \end{bmatrix} \\ &\times \left\{\begin{matrix} -z\frac{\partial\left(M_1^{\mathrm{PS}}\phi_1^{\mathrm{PS}}(z)\right)}{\partial z} + \frac{2\left(M_1^{\mathrm{PS}}\phi_1^{\mathrm{PS}}(z)\right)}{(z-1)} \\ + \frac{2M_Sz\left(M_0^{\mathrm{PS}} - \left(M_0^{\mathrm{PS}}\phi_0^{\mathrm{PS}}(z)\right)\right)}{(z-1)^2} \end{matrix}\right\} \\ &+k_{\mathrm{In}}A^2\left[\frac{\partial\left(M_1^{\mathrm{PS}}\phi_1^{\mathrm{PS}}(z)\right)}{\partial z}(1-z) - \frac{\left(M_1^{\mathrm{PS}}\phi_1^{\mathrm{PS}}(z)\right)}{z}\right] \\ &+\left(k_{c1}A^2 + k_{c2,1}A^2S + k_{c2,2}A^4S^4\right) \\ &\times\left(z\frac{\partial\left(M_1^{\mathrm{PS}}\phi_1^{\mathrm{PS}}(z)\right)}{\partial z}\left[z\frac{\partial\left(M_0^{\mathrm{PS}}\phi_0^{\mathrm{PS}}(z)\right)}{\partial z} - \frac{M_1^{\mathrm{PS}}}{M_{\mathrm{S}}}\right]\right) \\ &+2k_{\mathrm{p}}A^2S^2\left[\left(M_1^{\mathrm{PS}}\phi_1^{\mathrm{PS}}(z)\right)(z-1) + M_Sz\left(M_0^{\mathrm{PS}}\phi_0^{\mathrm{PS}}(z)\right)\right] \\ &-2A\left(k_{\mathrm{g}B}B + k_{\mathrm{g}S}S\right)\frac{M_0^{\mathrm{PS}}\left(M_0^{\mathrm{PE}}\right)^2}{M_1^{\mathrm{PS}}M_1^{\mathrm{PE}}}z\frac{\partial\left(M_1^{\mathrm{PS}}\phi_1^{\mathrm{PS}}(z)\right)}{\partial z}\end{aligned} \tag{53}$$

PS chromatographic distribution pgf:

$$\begin{aligned}\frac{\partial\left(M_2^{\mathrm{PS}}\phi_2^{\mathrm{PS}}(z)\right)}{\partial t} &= \begin{bmatrix} f_w\left(k_{s1w}A^2 + k_{s2w}A^2S^2\right) \\ +f_n\left(k_{1n}A^4 + k_{2n}A^4S\right) \end{bmatrix} \\ &\times \begin{bmatrix} -z\frac{\partial\left(M_2^{\mathrm{PS}}\phi_2^{\mathrm{PS}}(z)\right)}{\partial z} + \frac{2\left(M_2^{\mathrm{PS}}\phi_2^{\mathrm{PS}}(z)\right)}{(z-1)} \\ -\frac{4zM_S\left(M_1^{\mathrm{PS}}\phi_1^{\mathrm{PS}}(z)\right)}{(z-1)^2} \\ +\frac{2(z+z^2)(M_S)^2\left(\left(M_0^{\mathrm{PS}}\phi_0^{\mathrm{PS}}(z)\right) - M_0^{\mathrm{PS}}\right)}{(z-1)^3} \end{bmatrix} \\ &+ k_{\mathrm{In}}A^2\left[\frac{\partial\left(M_2^{\mathrm{PS}}\phi_2^{\mathrm{PS}}(z)\right)}{\partial z}(1-z) + \frac{1}{z}\left(M_S\left(M_1^{\mathrm{PS}}\phi_1^{\mathrm{PS}}(z)\right) - 2\left(M_2^{\mathrm{PS}}\phi_2^{\mathrm{PS}}(z)\right)\right)\right] \\ &+ \begin{pmatrix} k_{c1}A^2 + k_{c2,1}A^2S \\ +k_{c2,2}A^4S^4 \end{pmatrix}\left\{\begin{matrix} z\frac{\partial\left(M_2^{\mathrm{PS}}\phi_2^{\mathrm{PS}}(z)\right)}{\partial z}\left(z\frac{\partial\left(M_0^{\mathrm{PS}}\phi_0^{\mathrm{PS}}(z)\right)}{\partial z} - \frac{M_1^{\mathrm{PS}}}{M_S}\right) \\ +z^2\left(\frac{\partial\left(M_1^{\mathrm{PS}}\phi_1^{\mathrm{PS}}(z)\right)}{\partial z}\right)^2 \end{matrix}\right\} \\ &+ 2k_{\mathrm{p}}A^2S^2\left[(z-1)\left(M_2^{\mathrm{PS}}\phi_2^{\mathrm{PS}}(z)\right) + z\begin{pmatrix} 2M_S\left(M_1^{\mathrm{PS}}\phi_1^{\mathrm{PS}}(z)\right) \\ +(M_S)^2\left(M_0^{\mathrm{PS}}\phi_0^{\mathrm{PS}}(z)\right) \end{pmatrix}\right] \\ &- 2A\left(k_{\mathrm{g}B}B + k_{\mathrm{g}S}S\right)\frac{M_0^{\mathrm{PS}}\left(M_0^{\mathrm{PE}}\right)^2}{M_1^{\mathrm{PS}}M_1^{\mathrm{PE}}}z\frac{\partial\left(M_2^{\mathrm{PS}}\phi_2^{\mathrm{PS}}(z)\right)}{\partial z}\end{aligned} \tag{54}$$

Equation 48–54 must be solved and the resulting pgf must be inverted numerically to obtain the MWD of each homopolymer and the CCD of the copolymer.

The inversion method of univariate pgf used in this work is an adaptation of the method originally proposed by Papoulis[18] for the inversion of Laplace transforms.[19,20] Bivariate pgf inversion was carried out by means of the approach recently proposed by Asteasuain and Brandolin.[22] The inversion methods and the grid of molecular weights at which the MWD and CCD are to be calculated, determine the number of elements and their values of arrays **z**, $\mathbf{z}_1$, and $\mathbf{z}_2$, at which the pgf transforms are required. Equation 46–52 must be parameterized for each of these values. The size of the mathematical model is mostly dependent on the number of pgf equations. In this work, the model consisted in more than 800 000 differential algebraic equations.

The complete procedure for inversion to obtain the number fraction MWD, $n^{\mathrm{PE}\text{-}g\text{-}\mathrm{PS}}(x,y)$, from $\psi_{0,0}(z_1,z_2)$ is carefully developed in the literature.[22] This inversion method recovers the probability mass fractions from their pgf transforms by means of Equation 55–58.

$$n^{\mathrm{PE\text{-}g\text{-}PS}}(x,y) = \frac{(\ln(2))^2}{xy}\mathbf{v}^{\mathrm{T}}\mathbf{D}\mathbf{v} \tag{55}$$

where $\mathbf{v}$ is a vector that may be calculated by solving the following system of linear equations:

$$\mathbf{C}^{\mathrm{T}}\mathbf{v} = \mathbf{P}\left(\frac{1}{2}\right) \tag{56}$$

In Equation 56, $\mathbf{P}(1/2)$ is a vector containing Legendre polynomials of order $2n$ ($n = 0\ldots N$) and $\mathbf{C}$ is a lower-triangular matrix whose elements $c_{k,n}$, are defined as

$$c_{k,n} = \sum_{m=0}^{k} \frac{(k-m+1)_m}{2(k+(1/2))_{m+1}} \quad k = 0,\ldots,n; \quad n = 0,\ldots,N \tag{57}$$

Besides, $\mathbf{D}$ is a matrix that contains the bivariate pgf values corresponding to each (z_1, z_2) pair:

$$\mathbf{D} = \begin{bmatrix} \psi_{0,0}(z_{10},z_{20}) & \psi_{0,0}(z_{10},z_{21}) & \ldots & \psi_{0,0}(z_{10},z_{2N}) \\ \psi_{0,0}(z_{11},z_{20}) & \psi_{0,0}(z_{11},z_{21}) & \ldots & \psi_{0,0}(z_{11},z_{2N}) \\ \ldots & \ldots & \ldots & \ldots \\ \psi_{0,0}(z_{1N},z_{20}) & \psi_{0,0}(z_{1N},z_{21}) & \ldots & \psi_{0,0}(z_{1N},z_{2N}) \end{bmatrix},$$

$$\begin{aligned} z_{1j} &= \mathrm{e}^{-(2j+1)\ln(2)/x} \\ z_{2j} &= \mathrm{e}^{-(2j+1)\ln(2)/y} \\ j &= 0,\ldots,N \end{aligned} \tag{58}$$

The mathematical model of the system is composed by the set of equations required to compute the average properties, Equation 22–29, plus the equations needed for the calculation of the pgf, Equation 48–54 parameterized for the z_i, the equations of the inversion method of the bivariate pgf, Equation 55–58, and the equations for the inversion method of the univariate pgf for recovering the homopolymers' MWD. This differential-algebraic system of equations (DAE) was implemented and solved numerically using the commercial software gPROMS (Process Systems Enterprise, Ltd.). This software allows performing simulation activities involving complex mathematical models with large numbers of equations and variables. The built-in method DASOLV was employed to solve the DAE system.[23] This is a variable-step and variable-order method, suitable for rigid systems such as those discussed in this work. Besides, external routines developed in FORTRAN were linked to the gPROMS model for some ancillary calculations related to the initial values of the pgf and the evaluations of the derivatives of the pgf with respect to the dummy variable z.

3. Results and Discussion

In order to solve the proposed model and obtain the MWD, the kinetic parameters obtained in a previous work[16] were used. They are shown in Table 2. They correspond to a reaction carried out in a batch mixer at 190 °C under N_2 atmosphere and a ratio PS/PE of 20/80 wt%.[9]

In what follows, we show the model predictions for homopolymer MDW and copolymer CCD. All curves have been normalized so that the maximum height is unity. The reaction conditions are indicated in Table 3.

As mentioned earlier, Díaz et al.[9,13,14] reported that for the reaction between PS and PE in the presence of the catalytic system $AlCl_3$/styrene the two homopolymers were not equally active: while PE was only involved in the grafting reaction, PS was also subjected to several side reactions including chain scission and chain combination. As the reaction advanced, the MWD of PS shifted toward lower molecular weights, while that of PE remained unchanged.[9] Bearing those observations in mind, our kinetic model includes side reactions for PS only.

Table 2. Model kinetic parameters.

Parameter	Value
k_{gB} (copolymerization)	6.263×10^{10} L^3 mol^{-3} min^{-1}
k_{gS} (copolymerization)	1.553×10^{9} L^3 mol^{-3} min^{-1}
k_{S1w} (PS chain scission)	4.26 L^2 mol^{-2} min^{-1}
k_{S1n} (PS chain scission)	1.21 L^4 mol^{-4} min^{-1}
k_{In} (Indane formation)	3.39×10^{-2} L^2 mol^{-2} min^{-1}
k_{c1} (PS chain combination)	8.71×10^{-5} L^3 mol^{-3} min^{-1}
k_{i} (catalyst decomposition)	1.00×10^{-3} min^{-1}
k_{S2w} (PS chain scission)	1.56×10^{5} L^5 mol^{-5} min^{-1}
k_{S2n} (PS chain scission)	6.87×10^{2} L^4 mol^{-4} min^{-1}
$k_{\mathrm{c2,1}}$ (PS chain combination)	7.23×10^{-2} L^4 mol^{-4} min^{-1}
$k_{\mathrm{c2,2}}$ (PS chain combination)	7.83×10^{6} L^9 mol^{-9} min^{-1}
k_{p} (PS polymerization)	1.21×10^{6} L^4 mol^{-4} min^{-1}
k_{d} (catalyst-cocatalyst reaction)	1.329×10^{7} L^4 mol^{-4} min^{-1}

Table 3. Conditions used for the graft reaction experiments.[9,13]

Parameter	**Value**
neat PE	$\overline{M}_w^{PE} = 52\,000$; $\overline{M}_n^{PE} = 16\,700$
neat PS	$\overline{M}_w^{PS} = 271\,000$; $\overline{M}_n^{PS} = 136\,000$
PS/PE	20/80 wt%
reaction time	10 min
initial styrene concentration	0.3 wt%
initial AlCl$_3$ concentration	0.1 wt% 0.3 wt% 0.5 wt% 0.7 wt% 1 wt% 1.5 wt%
reaction conditions	batch mixer at 190 °C under N$_2$ atmosphere

In Figure 1 we show a comparison between the experimental and calculated dW/dlog$_{10}$ M of each homopolymer at initial reaction time, and the calculated distributions after a 10 min reaction. Part (a) of the figure corresponds to PS, and part *b* to PE. It may be observed that the MWD of both virgin resins are calculated accurately with the model. After a reaction time of 10 min, the model predicts a MWD shift to lower molecular weights in the PS homopolymer, indicating a predominance of scission over chain combination and homopolymerization. On the other hand, the model predicts a negligible change in the MWD of the PE homopolymer, which is consistent with the experimental observation that PE only takes part in the grafting reaction, suffering neither scission nor chain combination.

Copolymer CCD resulting from the grafting process presented similar shapes for all catalyst concentrations. Figure 2 shows a representative result, calculated for 0.7 wt% catalyst concentration. As may be observed in the figure, the distribution of PS segments is bell-shaped, while the distribution of PE segments shows a maximum in the low-molecular-weight region. This is the expected behavior since the model considers that shorter PE molecules are more reactive toward grafting. In the case of PS this effect is attenuated because the rate of formation of the graft copolymer is proportional to the number of monomeric units in the PS homopolymer.

We have found that all CCD show signs of inaccuracy in the high molecular weight region, probably due to error propagation inherent to the numerical inversion method used.[24–26]

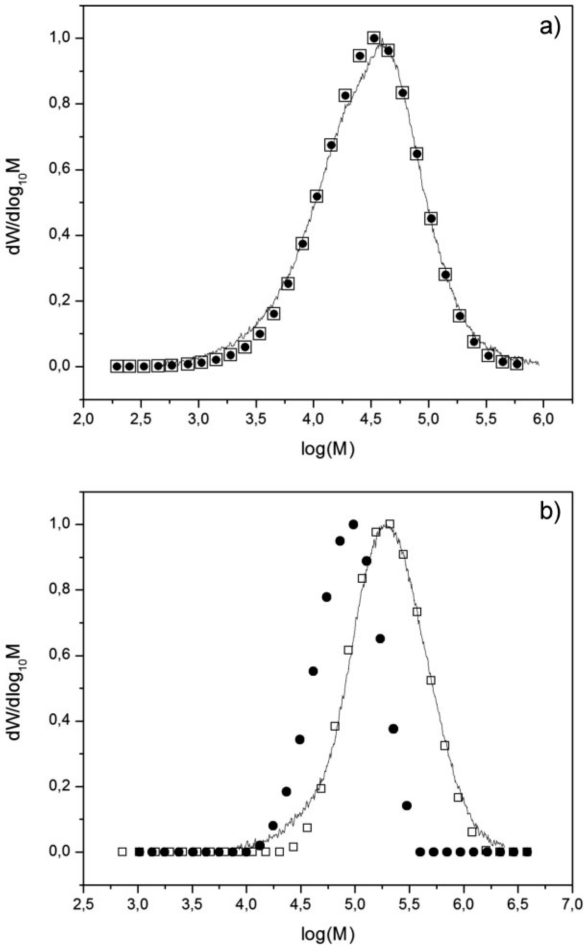


Figure 1. (a) PE and (b) PS Homopolymers dW/dlog$_{10}$ M for material treated with 1% AlCl$_3$ and 0.3% S. Line: experimental at $t = 0$, symbols: calculated, □: $t = 0$ min, ●: $t = 10$ min.

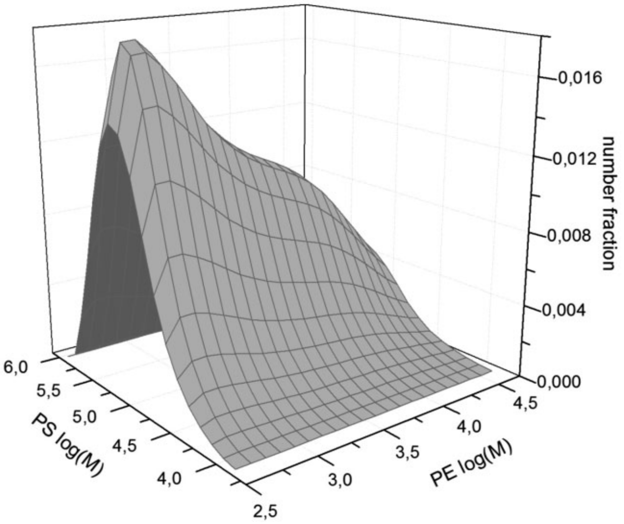


Figure 2. Copolymer CCD at 0.7 wt% AlCl$_3$ and 0.3 wt% S at final reaction time, $t = 10$ min.

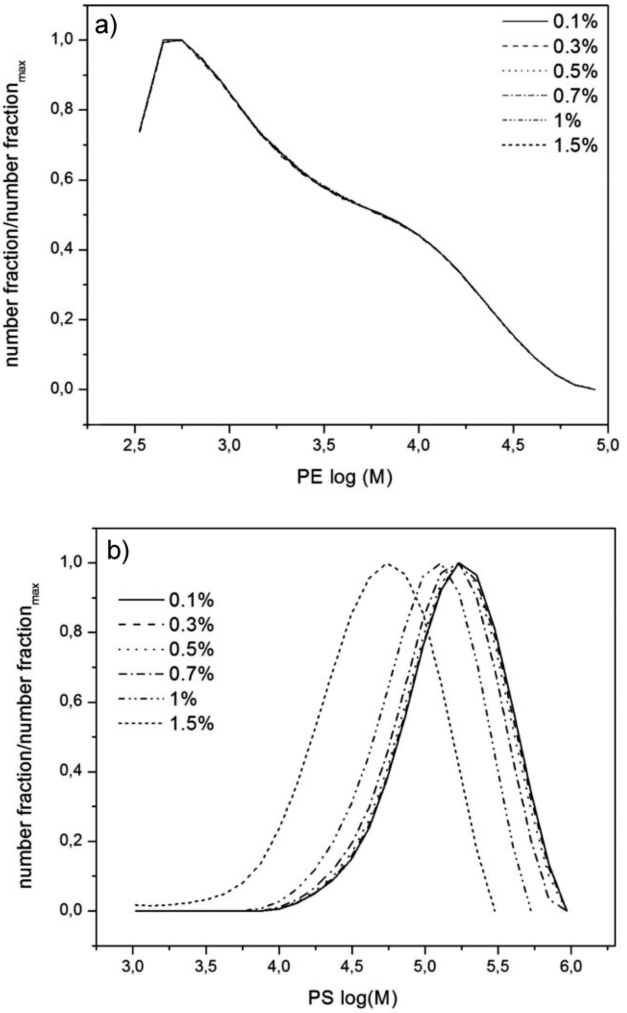


Figure 3. Number MWD corresponding to one of the copolymer blocks at various [$AlCl_3$]. (a) constant-weight PS block (170 000 g · mol^{-1}); (b) constant-weight PE block (570 g · mol^{-1}).

The graft copolymers consist in PE blocks grafted onto PS blocks. In Figure 3 we show the calculated MWD of one of the copolymer blocks for a fixed length of the other one. This is equivalent to a selecting one of the contour curves in the 3D plots of the CCD at different $AlCl_3$ concentrations, such as the one shown in Figure 2 for 0.7% $AlCl_3$.

The effect of the concentration of catalyst is illustrated in Figure 3. In Figure 3a, the distributions of the PE blocks are identical, as expected since in this model PE only participates in the grafting reaction. However, Figure 3b shows that the number MWD of the PS block is sensitive to the concentration of catalyst. The distributions shift toward the lower molecular weights. This is probably due to the degradation of PS, which leaves shorter molecules available for grafting.

4. Conclusion

We propose a model for the synthesis of graft PS/PE copolymer for blend compatibilization capable of calculating copolymer CCD and homopolymers MWD using the pgf technique. Even though the kinetic constants of the model were obtained by fitting average molecular weights, the predictions of the MWD of the homopolymers agree very well with experimental measurements. The trends observed in the calculated CCD and MWD are consistent with reported experimental data.

The proposed model has potential as a component of an optimization tool for the compatibilization process because it is able to account for the opposing effects of competing reactions that characterize the studied graft reaction. This tool would aid the search of operating conditions under which one could synthesize a sufficient amount of a graft copolymer with appropriate block lengths to optimize the compatibilization. The model also helps understand several aspects of this complex process.

To be able to avoid resin separation to a large degree, a compatibilization method that includes other significant components in MSW streams, such as PET and PP, should be devised. In this context, the strategy and the model discussed in this work are but a first step in that direction.

Appendix

Mass Balances

In what follows, the elements of each vector and matrix used in Equation 13–15 are presented.

Molar concentrations of PS homopolymer chains:

$$\mathbf{PS}^{\mathrm{T}} = [\mathrm{PS}_1, \mathrm{PS}_2, \ldots, \mathrm{PS}_x, \ldots], \qquad x = 1, \ldots \infty \tag{A1}$$

Molar concentrations of PE homopolymer chains:

$$\mathbf{PE}^{\mathrm{T}} = [\mathrm{PE}_1, \mathrm{PE}_2, \ldots, \mathrm{PE}_x, \ldots], \qquad x = 1, \ldots \infty \tag{A2}$$

Molar concentrations of PE-*g*-PS copolymer molecules:

$$\mathbf{G} = \begin{bmatrix} G_{1,1} = 0 & G_{1,2} = 0 & \ldots & \ldots & G_{1,y} = 0 & \ldots \\ G_{2,1} & G_{2,2} & G_{2,3} & \ldots & \ldots & \ldots \\ G_{3,1} & G_{3,2} & G_{3,3} & \ldots & \ldots & \ldots \\ G_{4,1} & G_{4,2} & G_{4,3} & \ldots & \ldots & \ldots \\ \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\ \ldots & \ldots & \ldots & \ldots & G_{x,y} & \ldots \\ \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \end{bmatrix},$$
$$x = 1, \ldots \infty; \; y = 1, \ldots \infty \tag{A3}$$

The model considers that the minimum length of the PS blocks in the copolymer is $x = 2$. However, in order to make matrix G compatible with the different vector-matrix operations involved in the model equations, a row corresponding to copolymer molecules with PS blocks of unit length has been added, with zero concentration.

Other molar concentrations:

$$\mathbf{X}^{\mathrm{T}} = [B, S, A, e_w] \tag{A4}$$

For the reaction arrays, the elements of **VPS**, **VPE**, and **VG** have the following general expressions:

$$\begin{aligned}\mathrm{VPS}_x = {} & \sum_{i=3}^{6} R_i(x)(1-\delta_{x,1}) + 2\sum_{y=x+1}^{\infty} \Omega(x,y)\sum_{i=3}^{6} R_i(y) \\ & - R_7(x)(1-\delta_{x,1}) + R_7(x+1) - R_{10}(x) \\ & + R_{10}(x-1) - \sum_{y=1}^{\infty}(R_8(x,y)+R_9(x,y)) \\ & + \frac{1}{2}\sum_{y=1}^{x-1} R_8(x-y,y)(1-\delta_{x,1}) \\ & - \sum_{y=1}^{\infty}(R_1(x,y)+R_2(x,y))\end{aligned} \tag{A5}$$

$$\mathrm{VPE}_x = \sum_{y=1}^{\infty}(R_1(y,x)+R_2(y,x)) \tag{A6}$$

$$\mathrm{VG}_{x,y} = R_1(x-1,y) + R_2(x-1,y) \tag{A7}$$

The reaction velocity vector **VX** has four elements. It is expressed as

$$\mathbf{VX} = \begin{bmatrix} \sum\limits_{x=2}^{\infty}\sum\limits_{i=3}^{7} R_i(x) - \sum\limits_{x=1}^{\infty}\sum\limits_{y=1}^{\infty} R_1(x,y) \\ -\sum\limits_{x=1}^{\infty} R_{10}(x) - R_{12} - \sum\limits_{x=1}^{\infty}\sum\limits_{y=1}^{\infty} R_2(x,y) \\ -R_{11} - R_{12} \\ -r_{sw}e_w \end{bmatrix} \tag{A8}$$

In the above equations, the reaction rate terms R_i correspond to the rate of reaction of the ith reaction in the kinetic mechanism in Table 1. They are defined as

$$R_1(x,y) = 2f_r k_{gB} AB x\mathrm{PS}_x\mathrm{PE}_y \tag{A9}$$

$$R_2(x,y) = 2f_r k_{gS} AS x\mathrm{PS}_x\mathrm{PE}_y \tag{A10}$$

$$R_3(x) = k_{s1w} f_w A^2 x\mathrm{PS}_x \tag{A11}$$

$$R_4(x) = k_{s2w} f_w A^2 S^2 x\mathrm{PS}_x \tag{A12}$$

$$R_5(x) = k_{s1n} f_n A^4 x\mathrm{PS}_x \tag{A13}$$

$$R_6(x) = k_{s2n} f_n A^4 S x\mathrm{PS}_x \tag{A14}$$

$$R_7(x) = k_{\mathrm{In}} A^2 x PS_x \tag{A15}$$

$$R_8(x,y) = k_{c1} A^2 x\mathrm{PS}_x y\mathrm{PS}_y \tag{A16}$$

$$R_9(x,y) = (k_{c2,1}A^2S + k_{c2,2}A^4S^4)x\mathrm{PS}_x y\mathrm{PS}_y \tag{A17}$$

$$R_{10}(x) = 2k_{\mathrm{p}} A^2 S^2 \mathrm{PS}_x \tag{A18}$$

The orders of the reactions with respect to the different reactants were those previously reported.[15,16]

PS0 and **PE0** are the vectors of the initial molar concentrations for the homopolymers PS and PE. $\mathbf{X0} = [0, S_0, [\mathrm{AlCl_3}]_0, ew_0]$ is the vector that contains the initial molar concentrations of benzene, styrene, catalyst, and weak links.

The factor f_r that appears in Equation A9 and A10 takes into account the difference in reactivity of polymer chains of different lengths. The expression we adopted for this factor is $f_{\mathrm{r}} = 1/(\overline{M}_{\mathrm{n}}^{\mathrm{PS}}\overline{M}_{\mathrm{n}}^{\mathrm{PE}})$, where $\overline{M}_{\mathrm{n}}^{\mathrm{PS}}$ and $\overline{M}_{\mathrm{n}}^{\mathrm{PE}}$ are the number-average molecular weights of PS and PE, respectively. The consequence of the use of this expression is that in our model shorter chains are more reactive toward grafting than longer ones, a trend that agrees qualitatively with reported data.[3,9]

The function $\Omega(x, y)$ determines how the scission products are distributed. In this work we assumed random scission, for which $\Omega(x, y) = 1/y$.[27] Finally, the fraction of weak (f_w) and normal links (f_n) is calculated as

$$f_w = \frac{e_w}{e_n + e_w} = \frac{e_w}{\sum\limits_{x=1}^{\infty} xPS_x - \sum\limits_{x=1}^{\infty} PS_x} = 1 - f_n \tag{A19}$$

Method of Moments

In what follows, the elements of each vector **V** used in Equation 26–28 are presented:

$$\begin{aligned}\mathrm{VM}_0^{\mathrm{PS}} = {} & \left[f_w(k_{S1w}A^2 + k_{S2w}A^2S^2) + f_n(k_{S1n}A^4 + k_{S2n}A^4S^4)\right] \\ & \times \left(\frac{M_1^{\mathrm{PS}}}{M_S} - 2M_0^{\mathrm{PS}}\right) - \frac{1}{2}(k_{c1}A^2 + k_{c2,1}A^2S + k_{c2,2}A^4S^4)\frac{(M_1^{\mathrm{PS}})^2}{M_S} \\ & - 2A(k_{gB}B + k_{gS}S)\frac{M_1^{\mathrm{PS}}M_0^{\mathrm{PE}}}{M_S\overline{M}_n^{\mathrm{PS}}\overline{M}_n^{\mathrm{PE}}}\end{aligned} \tag{A20}$$

$$\begin{aligned}\mathrm{VM}_1^{\mathrm{PS}} &= -\left[f_w(k_{S1w}A^2 + k_{S2w}A^2S^2) + f_n(k_{S1n}A^4 + k_{S2n}A^4S^4)\right]M_1^{\mathrm{PS}}\\ &\quad - k_{\mathrm{In}}A^2M_1^{\mathrm{PS}} + M_Sk_pA^2S^2M_0^{\mathrm{PS}} - 2A(k_{gS}S + k_{gB}B)\,\frac{M_2^{\mathrm{PS}}M_0^{\mathrm{PS}}}{M_S\overline{M}_n^{\mathrm{PS}}\overline{M}_n^{\mathrm{PE}}}\end{aligned} \tag{A21}$$

$$\begin{aligned}\mathrm{VM}_2^{\mathrm{PS}} &= \left[f_wA^2(k_{S1w} + k_{S2w}S^2) + f_nA^4(k_{S1n} + k_{S2n}S^4)\right]\\ &\quad\times\left(-\frac{M_3^{\mathrm{PS}}}{3M_S} - M_2^{\mathrm{PS}} + \frac{M_SM_1^{\mathrm{PS}}}{3}\right) + k_{\mathrm{In}}A^2(-2M_2^{\mathrm{PS}} + M_SM_1^{\mathrm{PS}})\\ &\quad + A^2(k_{c1} + k_{c2,1}S + k_{c2,2}A^2S^4)\left(\frac{M_2^{\mathrm{PS}}}{M_S}\right)^2\\ &\quad + k_pA^2S^2(2M_SM_1^{\mathrm{PS}} + M_S^2M_0^{\mathrm{PS}})\\ &\quad - 2A(Sk_{gS} + Bk_{gB})\,\frac{M_3^{\mathrm{PS}}M_0^{\mathrm{PE}}}{M_S\overline{M}_n^{\mathrm{PS}}\overline{M}_n^{\mathrm{PE}}}\end{aligned} \tag{A22}$$

$$\mathrm{VM}_0^{\mathrm{PE}} = -2A(k_{gB}B + k_{gS}S)\,\frac{M_1^{\mathrm{PS}}M_0^{\mathrm{PE}}}{M_S\overline{M}_n^{\mathrm{PS}}\overline{M}_n^{\mathrm{PE}}} \tag{A23}$$

$$\mathrm{VM}_1^{\mathrm{PE}} = -2A(k_{gB}B + k_{gS}S)\,\frac{M_1^{\mathrm{PS}}M_1^{\mathrm{PE}}}{M_S\overline{M}_n^{\mathrm{PS}}\overline{M}_n^{\mathrm{PE}}} \tag{A24}$$

$$\mathrm{VM}_2^{\mathrm{PE}} = -2A(k_{gB}B + k_{gS}S)\,\frac{M_1^{PS}M_2^{\mathrm{PE}}}{M_S\overline{M}_n^{\mathrm{PS}}\overline{M}_n^{PE}} \tag{A25}$$

$$\mathrm{VI}_{0,0} = 2A(k_{gB}B + k_{gS}S)\,\frac{M_1^{\mathrm{PS}}M_0^{\mathrm{PE}}}{M_SM_n^{\mathrm{PS}}M_n^{\mathrm{PE}}} \tag{A26}$$

$$\mathrm{VI}_{1,0} = 2A(k_{gB}B + k_{gS}S)\left(\frac{M_2^{\mathrm{PS}}}{M_S} + M_1^{\mathrm{PS}}\right)\frac{M_0^{\mathrm{PE}}}{\overline{M}_n^{\mathrm{PS}}\overline{M}_n^{\mathrm{PE}}} \tag{A27}$$

$$\mathrm{VI}_{0,1} = 2A(k_{gB}B + k_{gS}S)\,\frac{M_1^{\mathrm{PS}}M_1^{\mathrm{PE}}}{M_S\overline{M}_n^{\mathrm{PS}}\overline{M}_n^{\mathrm{PE}}} \tag{A28}$$

$$\mathrm{VI}_{1,1} = 2A(k_{gB}B + k_{gS}S)\left(\frac{M_2^{\mathrm{PS}}}{M_S} + M_1^{\mathrm{PS}}\right)\frac{M_1^{\mathrm{PS}}}{\overline{M}_n^{\mathrm{PS}}\overline{M}_n^{\mathrm{PE}}} \tag{A29}$$

$$\mathrm{VI}_{2,0} = 2A(k_{gB}B + k_{gS}S)\left(\frac{M_3^{\mathrm{PS}}}{M_S} + 2M_2^{\mathrm{PS}} + M_SM_1^{\mathrm{PS}}\right)\frac{M_0^{\mathrm{PE}}}{\overline{M}_n^{\mathrm{PS}}\overline{M}_n^{\mathrm{PE}}} \tag{A30}$$

$$\mathrm{VI}_{0,2} = 2A(k_{gB}B + k_{gS}S)\,\frac{M_1^{\mathrm{PS}}M_2^{\mathrm{PE}}}{M_S\overline{M}_n^{\mathrm{PS}}\overline{M}_n^{\mathrm{PE}}} \tag{A31}$$

$$\begin{aligned}\mathrm{VMX}_1 &= \left[f_wA^2(k_{S1w} + k_{S2w}S^2) + f_nA^4(k_{S1n} + k_{S2n}S^4) + k_{\mathrm{In}}A^2\right]\frac{M_1^{\mathrm{PS}}}{M_S}\\ &\quad - 2k_{gB}ABf_r\,\frac{M_1^{\mathrm{PS}}M_0^{\mathrm{PE}}}{M_S}\end{aligned} \tag{A32}$$

$$\mathrm{VMX}_2 = -k_pA^2S^2M_0^{\mathrm{PS}} - R_{12} - 2k_{gS}ASf_r\,\frac{M_1^{\mathrm{PS}}M_0^{\mathrm{PE}}}{M_S} \tag{A33}$$

$$\mathrm{VMX}_3 = -R_{11} - R_{12} \tag{A34}$$

$$\mathrm{VMX}_4 = -r_{ew}e_w \tag{A35}$$

$$f_w = \frac{e_w}{(M_1/M_S) - M_0} \tag{A36}$$

The selected moment definitions correspond to mass distributions, not to length distributions. Since the latter appear in some of the terms in the original mass balances (Equation A5–A19), a factor $1/M_S$ is used to make the conversion between mass and length distributions.

Acknowledgements: The authors wish to thank Dr. Mónica Díaz for helpful discussions. They are also grateful for the financial support from CONICET (National Research Council of Argentina), ANPCyT (National Agency for Promotion of Science and Technology of Argentina), and UNS (Universidad Nacional del Sur).

Received: April 9, 2012; Revised: May 28, 2012; Published online: July 24, 2012; DOI: 10.1002/mren.201200025

Keywords: chemical composition distribution; graft copolymers; molecular weight distribution/molar mass distribution; polyethylene (PE); polystyrene (PS)

[1] *Municipal Solid Waste in The United States: 2009 Facts and Figures*, United States Environmental Protection Agency, Office of Solid Waste, Washington 2010.
[2] N. F. Giorgi, M. Rosso, C. Fontán, O. Nielsen, M. De Luca, M. E. Guaresti, N. A. Giorgi, C. R. Rueda Serrano, D. Passeman, N. Alvarado, F. Jassón, I. Marcolini, L. Prieto, M. Rebuffo, J. P. Vásquez, A. Meneguzzi, "*Estudio de Calidad de los Residuos Sólidos de la Ciudad Autónoma de Buenos Aires, 2009, Resumen Ejecutivo*," CEAMSE–Instituto de Ingeniería Sanitaria–Secretaría Técnica, Facultad de Ingeniería, Universidad de Buenos Aires, Buenos Aires **2009**.
[3] B. O'Shaughnessy, U. Sawhney, *Macromolecules* **1996**, *29*, 7230.
[4] U. Sundararaj, C. W. Macosko, *Macromolecules* **1995**, *28*, 2647.
[5] W. M. Barentsen, D. Heikens, P. Piet, *Polymer* **1974**, *15*, 119.
[6] A. L. Bisio, M. Xanthos, "*How to Manage Plastics Waste: Technology and Market Opportunities*,", Hanser, Munich **1995**.
[7] W. L. Carrick, *J. Polym. Sci., Part A:Polym. Chem.* **1970**, *8*, 215.
[8] Y.-J. Sun, W. E. Baker, *J. Appl. Polym. Sci.* **1997**, *65*, 1385.
[9] M. F. Díaz, S. E. Barbosa, N. J. Capiati, *Polymer* **2007**, *48*, 1058.

[10] Y. Gao, H. Huang, Z. Yao, D. Shi, Z. Ke, J. Yin, *J. Polym. Sci., Part B: Polym. Phys.* **2003**, *41*, 1837.
[11] Z. Guo, Z. Fang, L. Tong, Z. Xu, *Polym. Degrad. Stabil.* **2007**, *92*, 545.
[12] M. F. Díaz, S. E. Barbosa, N. J. Capiati, *Polymer* **2002**, *43*, 4851.
[13] M.F. Díaz, S.E. Barbosa, N.J. Capiati, "Reactive Compatibilization of Binary and Ternary Blends Based on PE, PP, and PS," in *Polyolefin Blends* (Eds: T. Kyu, D. Nwabunma) Wiley-Interscience, Hoboken **2008**, p. 600.
[14] M. F. Díaz, S. E. Barbosa, N. J. Capiati, *J. Appl. Polym. Sci.* **2009**, *114*, 3081.
[15] I. A. Gianoglio Pantano, M. F. Díaz, A. Brandolin, C. Sarmoria, *Polym. Degrad. Stabil.* **2009**, *94*, 566.
[16] I. A. Gianoglio Pantano, A. Brandolin, C. Sarmoria, *Polym. Degrad. Stabil.* **2011**, *96*, 416.
[17] I. A. Gianoglio Pantano, M. Asteasuain, M. F. Díaz, C. Sarmoria, A. Brandolin, *Macromol. React. Eng.* **2011**, *5*, 243.
[18] A. Papoulis, *Quart. Appl. Math.* **1956**, *14*, 405.
[19] M. Asteasuain, A. Brandolin, C. Sarmoria, *Polymer* **2002**, *43*, 2529.
[20] M. Asteasuain, C. Sarmoria, A. Brandolin, *Polymer* **2002**, *43*, 2513.
[21] I. A. Gianoglio Pantano, M. F. Diaz, A. Brandolin, C. Sarmoria, *Polym. Degrad. Stabil.* **2009**, *94*, 566.
[22] M. Asteasuain, A. Brandolin, *Macromol. Theory Simul.* **2010**, *19*, 342.
[23] "*gPROMS User Guides,*", Process Systems Enterprise Ltd., **2009**.
[24] A. Brandolin, M. Asteasuain, C. Sarmoria, A. López-Rodríguez, K. S. Whiteley, B. Del Amo Fernández, *Polym. Eng. Sci.* **2001**, *41*, 1156.
[25] M. Asteasuain, M. V. Pérez, C. Sarmoria, A. Brandolin, *Lat. Am. Appl. Res.* **2003**, *33*, 241.
[26] M. Asteasuain, C. Sarmoria, A. Brandolin, *J. Appl. Polym. Sci.* **2003**, *88*, 1676.
[27] B. J. McCoy, M. Wang, *Chem. Eng. Sci.* **1994**, *49*, 3773.