

Modeling the Star-Branched Polymer Coupling Reaction in Continuous Reactors: Effects of the Operating Conditions on the Molecular Weight Distribution

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Star polymers, consisting of many arms connecting to a central core, represent a branched nanoscale material with compact structure and large surface area. Their synthesis is usually performed by making use of living polymers made by anionic polymerization as arms, and multifunctional compounds as linking agents. In general, polymer blends resulting from the star coupling process exhibit some polydispersity, which is influenced by (i) the polydispersity of the primary chains and (ii) the kinetics of the linking processes to the coupling agent.

In the present contribution we develop a mathematical model for the description of the star coupling process in continuous reactors. The proposed model is based on the following statements: (i) the characterization of the MWD of the branched polymer species is accomplished by exploiting a probabilistic approach and (ii) the concentration of the single species is evaluated through implementation of mass balance equations, where the reactions describing the linking of the living polymers to the active branched unit are modelled with first and second order kinetics. The final goal is to predict the MWD shape when varying the operating conditions (i.e.: concentration of polymers and multifunctional agents in the feed flow and residence time).

1. Introduction

Multi-arm star branched polymers contain a central core with linear polymer chains (arms) radiating outwards. These polymers are of great practical and theoretical interest due to their mechanical and thermal properties (Bywater, 1979). They are usually produced with an “arm-first, core-last” approach: living anionic polymers (hereafter referred also as parent polymers) are first produced through monomer initiation. After anionic polymerization is concluded, the star-coupling phase may take place: living polymers are reacted with a multifunctional linking agent to form star branched polymers (Higashihara et al., 2011). The final product is therefore a blend constituted by completed star polymers, partially reacted star polymers and unreacted parent polymers.

Controlling the Molecular Weight Distribution (MWD) of the blend is a crucial task in order to obtain a product with specified properties. For this reason, the development of effective mathematical models describing the polymerization is an important issue towards finding the optimal process conditions. With this regard, modelling the blend Molecular Weight Distribution (MWD) resulting from the star coupling process is an aspect so far approached in the framework of laboratory setup (i.e. discontinuous processes) by exploiting a probability approach (see e.g. Zhu, 1998 and Shiau, 2004) whereas there is still a lack of knowledge when dealing with continuous reactors, generally used for industrial production. To this end, the star coupling process is here modelled when occurring in Continuous Stirred Tank Reactors (CSTRs), using a probability approach, analogous to the one already proposed in the literature. The capability of the

proposed model to properly describe star-branched polymerization is assessed through experimental data related to industrial polymers composed of polydisperse star/linear blends.

2. Materials and characterization methods

The experimental data used to assess the model proposed in the present work were provided by Versalis S.p.A., and concern polydisperse star/linear 1,4-polybutadiene blends, with different composition and arm-average molar mass. The blends were obtained starting from linear parent polymers. In the first stage, a polydisperse mixture of living polymers (i.e. with a reactive end-group) was obtained via anionic polymerization. In the second stage, a chloro-silyl type tetrafunctional coupling agent was introduced, in order to obtain the blends from the living polymers. The illustrated procedure allows the association of a maximum of four linear chains, i.e. the creation of double linear, three-arm and four-arm star polymers.

Molecular weight distributions of the polymer blends were measured through GPC-multi-angle laser light scattering (MALLS) apparatus consisted of an Agilent 1100 isocratic pump, an Agilent 1200 auto-sampler, an Agilent 1100 DRI detector and a MALLS detector DAWN HELEOS (Wyatt Technology Corporation). All samples are dissolved in THF at a concentration of 0.15 % by weight. All measurements were carried out at room temperature.

3. Model assumptions and description

The star-coupling process described in the present work occurs in a CSTR, where a coupling agent (for the case at hand, the SiCl_4 species) reacts with living parent polymers.

3.1 Reaction scheme and kinetics

The living primary chains are assembled to form star polymers as schematically illustrated in Figure 1. The polybutadiene synthesis is regarded as a four step chain reaction with the formation of intermediary species i.e. stars with one, two or three arms.

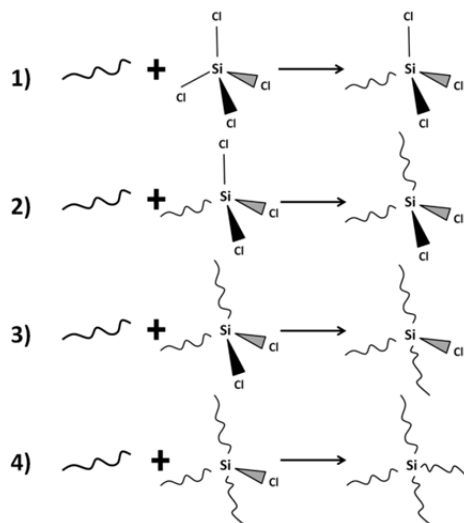
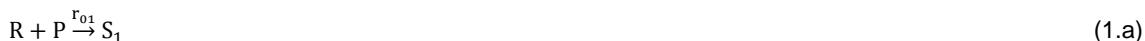


Figure 1: Reactions scheme of the star coupling process: the coupling agent here considered is the SiCl_4 .

This leads to the following reaction scheme:



In equations (1), R is the coupling agent, P is the living parent polymer, S_m is the m -arms star branched polymer, $r_{j,j+1}$ is the reaction rate for the formation of the $(j+1)$ -arms star. Hereafter it is assumed that the linking reactions become slower as the number of arms increases (i.e. $r_{j,j+1} \ll r_{j-1,j}$), as supported by the

experimental evidences (see e.g. Lee et al., 1998). This allows simplifying the mathematical model: in more detail the two reactions related to the coupling of first and second arm (equations 1.a and 1.b) are assumed to take place instantaneously.

Two different kinetic expressions are investigated for the $r_{j,j+1}$ terms ($j = 2,3$). A second order scheme is suggested in the literature (Lee et al., 1998)

$$r_{j,j+1} = k_{j,j+1} C_{S_j} C_P \quad (2)$$

In addition, a first order kinetics is here also considered:

$$r_{j,j+1} = k_{j,j+1} C_{S_j} \quad (3)$$

3.2 The mass-balance model

According with the assumptions on the kinetic rates, the mass balance equations for a CSTR are:

$$\begin{cases} V \frac{dC_{S_2}}{dt} = -QC_{S_2} + QC_{R_0} - r_{23}V \\ V \frac{dC_{S_3}}{dt} = -QC_{S_3} + r_{23}V - r_{34}V \\ V \frac{dC_{S_4}}{dt} = -QC_{S_4} + r_{34}V \end{cases} \quad (4)$$

In equation (4) Q is the inlet flow-rate, V is the reactor volume, C_x is the molar concentration of the generic species x , C_{R_0} is the inlet feed concentration of the coupling agent. It should be noticed that the generation term for the species S_2 is equal to the amount of the coupling agent entering the reactor ($Q C_{R_0}$) as a consequence of the instantaneous reaction for the formation of first and second arms.

The mathematical model can be thus rewritten in dimensionless form:

$$\begin{cases} \frac{dc_{S_2}}{d\tau} = \frac{1}{\eta} - c_{S_2} - Da_{23} c_{S_2} c_p^\alpha \\ \frac{dc_{S_3}}{d\tau} = -c_{S_3} + Da_{23} c_{S_2} c_p^\alpha - Da_{34} c_{S_3} c_p^\alpha \\ \frac{dc_{S_4}}{d\tau} = -c_{S_4} + Da_{34} c_{S_3} c_p^\alpha \end{cases} \quad (5)$$

where, in Equation 5, the dimensionless variables $c_{sx} = C_{sx}/C_{p0}$ are introduced, the time is made dimensionless with the residence time V/Q , $\eta = C_{p0}/C_{R0}$ is the feed ratio between the feed concentration of primary chains (C_{p0}) and coupling agent (C_{R0}) ($\eta = 4$ corresponds to stoichiometric feed ratio), the Damkohler numbers are defined as $Da_{23} = k_{23} C_{p0}^\alpha \tau$, $Da_{34} = k_{34} C_{p0}^\alpha \tau$ ($\alpha = 1$ refers to the second order kinetic model, see eq. 2, whereas $\alpha = 0$ refers to the first order kinetic model, see eq. 3). In order to simplify the analysis of the considered reacting system, it is also assumed that $Da_{23} = 10 \cdot Da_{34}$. This choice is corroborated by the literature, where it is recognized that there is one order magnitude between the rates of two successive reactions (Lee et al, 1998). Eventually, two parameters appear in the proposed models: the Damköhler number Da_{34} (simply referred in the following as Da) and the feed ratio η between parent polymers and coupling agent.

3.3 Molecular weight distributions

A quantitative description of the molecular dispersity in the polymer sample is carried out by estimating the number chain length density distribution $\psi_{num}(r)$. Generally, the distribution is described in simple terms by resorting to some scalars. The most used are the number average molecular weight M_n :

$$M_n = \int_0^\infty r \psi(r) dr \quad (6)$$

the weight average molecular weight M_m :

$$M_m = \int_0^\infty r^2 \psi(r) dr \quad (7)$$

and the polydispersity index PDI :

$$PDI = \frac{M_m}{M_n^2} = \frac{\int_0^\infty r^2 \psi(r) dr}{\left(\int_0^\infty r \psi(r) dr\right)^2} \quad (8)$$

As a first step, the distributions of the parent polymers entering the reactor are modeled by looking for the class of distributions suited for its description. For the case at hand, it was found that the primary chains distributions are fairly described by two different distributions, a Beasley and a Schulz-Zimm distribution (see e.g. Graessley, 2004). The comparison with the experimental data provided by van Ruymbeke et al.

(2010) is reported in Figure 2. It is shown that both the distributions exhibit an excellent capability to describe the experimental distribution, with a slight improvement when the Beasley distribution is used. Table 1 reports the estimated parameters for the experimental data and some performance measurements of the fitting together with the analytical expression of the distributions.

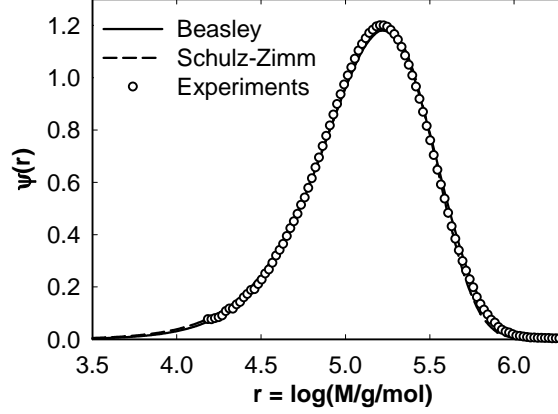


Figure 2: Comparison between the molecular weight distribution of the parent polymers and the theoretical distributions

Table 1: Estimated parameters for the experimental parent polymer distribution

Distribution	Number density distribution	Weight density distribution	Average molecular weight	Polidispersity index	Estimated Parameters	MSE
Beasley distribution	$\frac{(1 + \frac{\beta r}{v})^{-\frac{1+\beta}{\beta}}}{v}$	$\frac{(1 - \beta)r(1 + \frac{\beta r}{v})^{-\frac{1+\beta}{\beta}}}{v^2}$	$\frac{v}{1 - \beta}$	$2 \frac{1 - \beta}{1 - 2\beta}$	$\beta=0.05686$ $v=78300$	$1.05 \cdot 10^{-4}$
Schulz-Zimm distribution	$\frac{e^{-\frac{r\sigma}{\theta}} (\frac{r\sigma}{\theta})^\sigma}{r \Gamma[\sigma]}$	$\frac{e^{-\frac{r\sigma}{\theta}} (\frac{r\sigma}{\theta})^\sigma}{\theta \Gamma[\sigma]}$	θ	$\frac{\sigma + 1}{\sigma}$	$\theta=76700$ $\sigma=0.8236$	$9.06 \cdot 10^{-4}$

The distributions related to the two-arms population, $\psi_{S2}(r)$, three-arms population $\psi_{S3}(r)$, and four-arms population $\psi_{S4}(r)$, can be calculated as a combination of parent polymers according to the convolution integrals (Zhu, 1998):

$$\psi_{S2}(r) = (\Psi_P * \Psi_P)(r) = \int_0^r \psi_P(r-s)\psi_P(s)ds \quad (9)$$

$$\psi_{S3}(r) = \int_0^r \psi_{S2}(r-s)\psi_P(s)ds = \int_0^r \psi_P(r-s)\psi_P(s-t)\psi_P(t)dt \quad (10)$$

$$\psi_{S4}(r) = \int_0^r \psi_{S3}(r-s)\psi_P(s)ds = \int_0^r \psi_P(r-s)\psi_P(s-t)\psi_P(t-v)\psi_P(v)dv \quad (11)$$

It should be remarked that equations (9-11) are valid with an arbitrary distribution of parent polymers. When considering a Schulz Zimm distribution one can obtain an analytical expression:

$$\psi_{Sm}(r) = \frac{e^{-\frac{r\sigma}{\theta}} (\frac{r\sigma}{\theta})^{m\sigma}}{r \Gamma[m\sigma]} \quad (12)$$

where index m refers to the m -arms star. No analytical solution is instead available for the Beasley distribution. The whole distribution ψ_B for the blend can be finally calculated as the sum of the different population distributions, where each term is weighted with the corresponding mole fraction:

$$\psi_B(r) = x_P \psi_P(r) + \sum_{m=1}^4 x_{Sm} \psi_{Sm}(r) \quad (13)$$

where x_P is the mole fraction of parent polymers, x_{Sm} is the mole fraction of the star polymer with m arms. It should be noted that, again, an analytical expression is available for both number average molecular weight and polydispersity, provided that parent polymers are modeled in terms of Schulz-Zimm distributions:

$$M_{Bn}(x_{s2}, x_{s3}, x_{s4}) = (1 + x_{s2} + 2x_{s3} + 3x_{s4})\theta \quad (14)$$

$$PDI_B(x_{s2}, x_{s3}, x_{s4}) = \frac{1+x_{s2}+3x_{s3}+\sigma+3x_{s2}\sigma+15x_{s4}\sigma+x_{s3}(2+8\sigma)}{(1+x_{s2}+2x_{s3}+3x_{s4})^2\sigma} \quad (15)$$

It should be reminded that the parameters θ and σ refer to the parent polymer distribution as reported in Table 1.

4. Results

The coupling reaction is investigated through resolution of equations (5) and (14-15) for both first and second order kinetic modes (see Eqs. 2 and 3) as the Damkohler number varies. In equations 14 and 15, the distribution parameters adopted (θ and σ for the Schulz-Zimm distribution, β and ν for the Beasley distribution) are the ones estimated for the parent polymer distribution as reported in Table 1.

Figure 3.a shows the number average molecular weight of the blend for three different feed ratios: $\eta=4$ (stoichiometric feed ratios), slight ($\eta=5$) and large ($\eta=8$) excess of parent polymers, both for the first (solid line) and second (dashed line) order kinetic model. For sake of brevity, only the results related to the Schulz-Zimm distribution are reported, in the understanding that the Beasley distribution gives the very same results. It is evident that the process performance is quite sensitive to parameter changes: the average molecular weight is always an increasing function of the Da parameter and a decreasing function of the feed ratio. With this regard, the impact of η is crucial, and even a slight excess of parent polymers leads to an important decay of the product quality with an abrupt decrease of the molecular weight.

The impact of the feed ratio is evident also when examining the polydispersity index PDI, as reported in Figure 3.b. In more detail, it was found again that the product quality improves as Da increases and η decreases, at least when considering lower values of feed ratio. The behavior changes at a large excess of parent polymers where the PDI increases with Da . As a final remark it should be noted that the qualitative behavior is not affected by the reaction order.

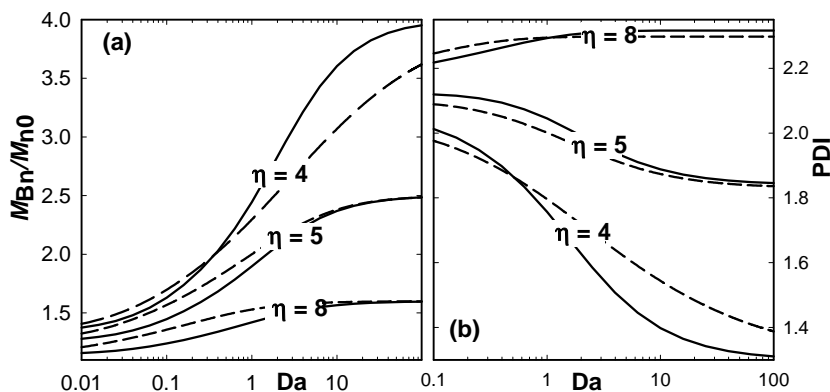


Figure 3: Number Average Molecular Weight (figure 3.a) and PDI (figure 3.b) with respect to the Da number for a first order (solid line) and a second order kinetic model (dashed line) at different feed rates η .

The capability of the proposed model to describe the polymerization process, considering both first order and second order kinetics (equation 2 and 3), is finally carried out using the experimental data already reported in van Ruymbeck et al. (2010). The PB blend experimental distribution is obtained for a feed ratio $\eta = 5$. The parent polymer distribution fed in the CSTR is assumed to be the Beasley distribution with the parameters ν and β reported in Table 1. It should be remarked that the Da numbers are not a priori known (since the kinetic constants $k_{i,i+1}$ in equations 3 and 4 are not available) and thus they have been estimated looking for the best fit model to the experimental data through a least square algorithm. Table 2 shows the estimated Da values and the Mean Square Error (MSE), which indicates that a slightly better agreement is obtained for the first order kinetic scheme. Figure 4 shows a comparison between experiments and model predictions. The estimated distributions for first order (solid line) and second order kinetics (dashed line) are shown in the figure.

Table 2: Estimated parameters and performance index for the estimated distributions

Order kinetic	Da	MSE
First order	0.658	3e-3
Second order	0.111	8e-3

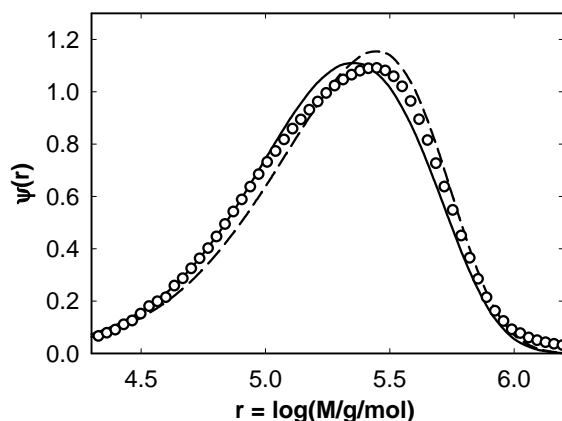


Figure 4: comparison between the molecular weight distribution of the blends and the theoretical distribution predicted by the first and the second order model (respectively solid and dashed line).

5. Conclusions

A probabilistic approach has been applied for modeling the star-branched polymer coupling reaction in continuous mode, extending a procedure already used for batch reactors. The study evidenced how two important process conditions, such as the excess of parent polymer (with respect to the stoichiometric amount) and the residence time greatly affects the characteristic of the product in terms of number average molecular weight and polydispersity index. The investigation has been carried out by considering two different kinetic rate laws: second order (as reported in literature) and first order, which simplify the model. It is worth noting that the qualitative behaviour of the product characteristics is not influenced by the order of the kinetic rate here considered. Furthermore, the use of a first order reaction rate has shown a better fitting with experimental data. These results are important when considering that a simple model can be more easily used for on-line application, such as process control and optimization.

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