Mathematical Model for the Bulk Polymerization of Styrene Chemically Initiated by Sequential and Total Decomposition of the Trifunctional Initiator Diethyl Ketone Triperoxide

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This work experimentally and theoretically investigates the use of the symmetrical cyclic trifunctional initiator diethyl ketone triperoxide (DEKTP) in the bulk polymerization of styrene (St). The study focused on temperatures of 150 to 200°C, considering chemical initiation by both sequential and total decomposition reactions. The experimental work consisted of a series of isothermal batch polymerizations at higher temperatures, 150 and 200°C, with an initiator concentration of 0.01 mol/L. The mathematical model is based on a kinetic mechanism that includes thermal and chemical initiation (both sequential and total decomposition reactions), propagation, transfer to monomer, termination by combination and re-initiation reactions. Experimental and theoretical results show that the decomposition mechanism of the initiator is modified by the reaction temperature and can be modeled as a set of two parallel reactions with different temperature dependences. The developed mathematical model simulates the bulk polymerization of St in the presence of DEKTP for a wide temperature range (120–200°C). It was found that due to these two decomposition mechanisms, the system may behave as a "dead-end" polymerization system above a certain temperature, yielding low molecular weights and a limiting conversion value. Simulation results indicate the value of this temperature to be about 185°C. POLYM. ENG. SCI., 00:000–000, 2014. © 2014 Society of Plastics Engineers

INTRODUCTION

The use of multifunctional initiators in the bulk polymerization of styrene (St) allows obtaining both high reaction rates and molecular weights, as well as enhanced mechanical properties compared to polystyrene (PS) obtained by using traditional monofunctional initiators [1–5]. The use of multifunctional initiators may help overcome the difficulty of obtaining an adequate balance between reaction rate, molecular weight, polydispersity and monomer conversion that can be observed when a monofunctional initiator is used [6, 7]. In the last few decades, there has been a growing interest in the industrial use of multifunctional initiators. Numerous works have studied, both experimentally and theoretically, the use of bifunctional initiators in the bulk polymerization of St [1–3, 6–10]. The mathematical models developed allow prediction of reacting species' concentrations, as well as molecular structure of the obtained polymer during the course of the polymerization reaction. Choi and Lei [1] and Kim et al. [3] developed detailed kinetic models for the bulk St homopolymerization with symmetrical and asymmetrical diperoxyester initiators. González et al. [5] developed a model to simulate the bulk polymerization of St using mixtures of mono- and bifunctional initiators. Villalobos et al. [8] theoretically and experimentally investigated the polymerization of St with the bifunctional initiators 2,5-dimethyl-2,5-bis(2-ethylhexanol peroxy) hexane (Lupersol-256, L-256), 1,1-di(t-butyl-peroxy) cyclohexane (Lupersol-331-80B), and 1,4-bis(t-butyl peroxycarbo) cyclohexane, (D-162). Compared with the standard monofunctional case, bifunctional initiators reduced polymerization times as much as 75%, without substantial changes in the final product properties. These experimental and theoretical results for diperoxyesters as initiators were also reported in the work of Benbachir and Benjelloun [10]. In Estenoz et al. [11] a detailed mathematical model was developed to simulate the synthesis of high-impact polystyrene (HIPS) using symmetrical bifunctional initiators such as L-256 and L-118 [2,5-dimethyl-2,5-bis(benzoyl peroxyl) hexane].

There are a limited number of works dealing with the use of multifunctional initiators (i.e. initiators containing more than two labile groups per molecule) [12–21]. Cerna et al. [12, 13] studied the particular case of the bulk polymerization of St using a cyclic trifunctional peroxide initiator, the diethyl ketone triperoxide (DEKTP). Results showed that, at 120 to 130°C, polymers with high molecular weights (250,000–450,000 g/mol) could be obtained at relatively short polymerization times (4–6 h). Additionally, based on the experimental results at higher reaction temperatures, two separate mechanisms were proposed for the decomposition of DEKTP: a sequential decomposition of the O—O groups at temperatures between 110 and 130°C and a total decomposition of the three O—O groups at temperatures higher than 130°C [12, 13]. The first stage in the sequential decomposition reaction for DEKTP is presented in Fig. 1a, where only one peroxide group of the DEKTP molecule suffers a decomposition reaction. Further stages of the sequential decomposition arise as polymerization reaction generates polymer chains with undecomposed peroxide groups. The total decomposition reaction is shown in Fig. 1b. In this reaction, all peroxide groups decompose, generating three di-radicals without undecomposed peroxide groups. The use of this trifunctional initiator in the synthesis of HIPS was experimentally studied by Acuña et al. [20]. Sheng et al. [16] studied the use of the cyclic
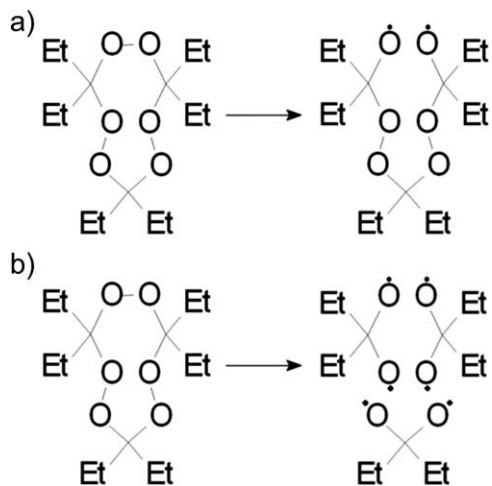
FIG. 1. a) First stage of the sequential decomposition of DEKTP; b) Total decomposition of DEKTP.

trifunctional initiator 3,6,9-triethyl-3,6,9-trimethyl-1,4,7-triperoxonane in the bulk polymerization of St. Experimental results showed that it was possible to produce polymers with higher molecular weights and lower polydispersities at a higher rate. The obtained PS had residual O—O bonds in the molecular chains.

In Scorah [17, 18], the bulk polymerization of St and methyl methacrylate in the presence of the tetrafunctional initiator polyether tetrakis(*tert*-butylperoxy carbonate) (JWEB50) was experimentally and theoretically studied. The developed model was validated with experimental results. The concentration and chain length of the various polymeric structures formed was found to depend on monomer type [19].

The majority of the mathematical models developed for the case of multifunctional initiators in the literature do not compute the detailed molecular structure of the obtained polymer, only the moments of the molecular weight distributions are calculated. In addition, there are no works in the available literature containing mathematical models including both sequential and total decomposition mechanisms for multifunctional initiators.

In Berkenwald et al. [21], a detailed mathematical model for the bulk polymerization of St in the presence of DEKTP was developed, considering reaction temperatures at which the initiator decomposition is mostly sequential (120–130°C). This model allowed obtaining the complete MWD, but had limited validity when considering polymerization temperatures higher than 130°C.

This works deals with the experimental and theoretical study of the bulk polymerization of St using DEKTP at temperatures of 150 to 200°C, where initiator decomposition consists of two parallel decomposition reactions (sequential and total decomposition), as previously stated. A mathematical model is developed, based on an extended kinetic mechanism considering both decomposition reactions, allowing the prediction of the evolution of the reacting species' concentration, monomer conversion and detailed polymer molecular structure. The effect of reaction temperature on process productivity and final product molecular characteristics is investigated.

EXPERIMENTAL WORK

The experimental work consisted on initiator synthesis and bulk polymerizations of St using DEKTP at different reaction
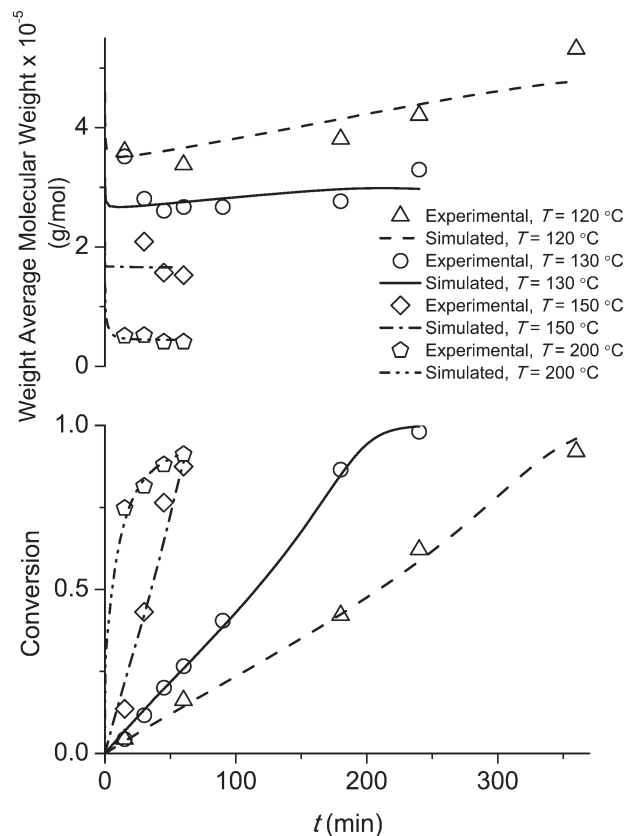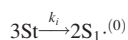

FIG. 2. Conversion and weight-average molecular weight as a function of time for $T = 120°$, $T = 130°C$, $T = 150°C$, and $T = 200°C$.

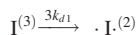temperatures. In both cases, similar procedures to the ones described in Berkenwald et al. [21] were used.

The selected polymerization temperatures were 150°C, and 200°C. Initiator concentration was 0.01 mol/L, previously found to be the optimal initiator concentration for bulk polymerization of St using DEKTP [21]. Monomer conversion was determined gravimetrically and molecular weights by gel permeation chromatography (GPC) at different reaction times. For molar mass measurements, a Hewlett-Packard HPLC 1050 with software from Polymer Laboratories for Chemstation, equipped with Refraction Index and UV detectors, with ultrastyragel columns (10^5, 10^4, 10^3, A) was used. Polystyrene standards (580–3,900,000 g/mol) were used, at ambient temperature. To measure conversion, the obtained polymer was directly precipitated in methanol (volume ratio 1:10), filtered and dried under vacuum until constant weight (approximately 24 h). The experimental determination of conversion and molar masses were duplicated and the experimental error was limited to approximately 5%.

The experimental results are presented in Fig. 2. Results for temperatures of 120 to 130°C were previously reported in Berkenwald et al. [21] and are included for comparison purposes. As stated in this previous work, it can be observed that initiation by DEKTP allows for high reaction rates and high average molecular weights simultaneously at a polymerization temperature of 120 to 130°C. For polymerization temperatures of 150 and 200°C, polymerization rates are higher, but the produced average molecular weights are lower. The polydispersity of the obtained product is approximately 2, which is expected for these types of initiators at temperatures higher than 130°C [13]. On the other hand, an
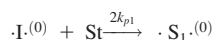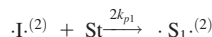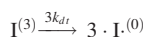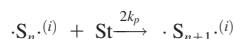
TABLE 1. Adopted Kinetic Mechanism

Initiation

Thermal initiation

$3St \xrightarrow{k_i} 2S_1 \cdot^{(0)}$

Chemical initiation

    by sequential decomposition

    $I^{(3)} \xrightarrow{3k_{d1}} \cdot I \cdot^{(2)}$

    by total decomposition

    $I^{(3)} \xrightarrow{3k_{dt}} 3 \cdot I \cdot^{(0)}$

$\cdot I \cdot^{(2)} + St \xrightarrow{2k_{p1}} \cdot S_1 \cdot^{(2)}$

$\cdot I \cdot^{(0)} + St \xrightarrow{2k_{p1}} \cdot S_1 \cdot^{(0)}$

Propagation ($n = 1, 2, 3, \ldots;\ i = 0, 1, 2 \ldots$)

$S_n \cdot^{(i)} + St \xrightarrow{k_p} S_{n+1} \cdot^{(i)}$

$\cdot S_n \cdot^{(i)} + St \xrightarrow{2k_p} \cdot S_{n+1} \cdot^{(i)}$

Transfer to Monomer ($n = 1, 2, 3, \ldots;\ i = 0, 1, 2 \ldots$)

$S_n \cdot^{(i)} + St \xrightarrow{k_{fM}} S_n^{(i)} + S_1 \cdot^{(0)}$

$\cdot S_n \cdot^{(i)} + St \xrightarrow{2k_{fM}} S_n \cdot^{(i)} + S_1 \cdot^{(0)}$

Re-initiation ($n = 2, 3, \ldots;\ m = 1, 2, \ldots, n-1;\ i = 1, 2, \ldots;\ j = 0, 1, 2 \ldots i$)

    by sequential decomposition

    $S_n^{(i)} \xrightarrow{ik_{d2}} S_{n-m} \cdot^{(i-j)} + S_m \cdot^{(j-1)}$

    by total decomposition

    $S_n^{(i)} \xrightarrow{ik_{dt}} \sum_{I=1}^{n-1} \alpha_I S_I \cdot^{(0)} + \sum_{k=1}^{n-1} \beta_{ik} \cdot S_k \cdot^{(0)}$

    where $\alpha_I = 1, 2$ and $\beta_{ik} = 1, 2, \ldots i-1$ with $\sum_{k=1}^{\infty} \beta_{ik} = i-1$

Combination Termination ($n, m = 1, 2, 3, \ldots;\ i, j = 0, 1, 2 \ldots$)

$\cdot S_n \cdot^{(i)} + \cdot S_m \cdot^{(j)} \xrightarrow{4k_{tc}} \cdot S_{n+m} \cdot^{(i+j)}$

$\cdot S_n \cdot^{(i)} + S_m \cdot^{(j)} \xrightarrow{2k_{tc}} S_{n+m} \cdot^{(i+j)}$

$S_n \cdot^{(i)} + \cdot S_m \cdot^{(j)} \xrightarrow{k_{tc}} S_{n+m}^{(i+j)}$

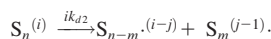|	
St	Styrene.
$I^{(3)}$	Trifunctional initiator (DEKTP).
$\cdot I \cdot^{(2)}$	Initiator diradical with 2 undecomposed peroxide groups generated by sequential decomposition.
$\cdot I \cdot^{(0)}$	Initiator diradical without undecomposed peroxide groups generated by total decomposition.
$\cdot S_1 \cdot^{(2)}$	Monomer diradical with two undecomposed peroxide groups.
$\cdot S_1 \cdot^{(0)}$	Monomer diradical without undecomposed peroxide groups.
$S_1 \cdot^{(0)}$	Monomer monoradical without undecomposed peroxide groups.
$S_n \cdot^{(i)}$	PS monoradical of chain length n containing i undecomposed peroxide groups.
$\cdot S_n \cdot^{(i)}$	PS diradical of chain length n containing i undecomposed peroxide groups.
$S_n^{(i)}$	Polymer with n repetitive units of St and i undecomposed peroxide groups.
α_n	Stoichiometric coefficient corresponding to a PS monoradical of chain length n generated by total decomposition of a polymer with undecomposed peroxide groups.
β_n	Stoichiometric coefficient corresponding to a PS diradical of chain length n generated by total decomposition of a polymer with undecomposed peroxide groups.

The following has been assumed: (a) intramolecular termination is neglected; (b) disproportionation termination is negligible; (c) all peroxide groups present in the trifunctional intiator and in the accumulated polymer exhibit the same thermal stability; (d) due to the short life time of radicals, decomposition of undecomposed peroxide groups cannot occur in radical molecules; (e) propagation and transfer reactions are unaffected by chain length or conversion; and (f) degradation reactions are negligible.

Note the following: (i) when two monoradicals with i and j undecomposed peroxide groups terminate, the formed polymer will contain $i+j$ undecomposed peroxide groups; (ii) diradicals only have an even number of peroxide groups, as they are generated only by propagation of the initiator diradical (with only two peroxide groups), and by combination termination of other diradicals, all of which have an even number of peroxide groups or no peroxide groups; (iii) due to assumption (c), polymeric chains may suffer both sequential decomposition reactions or total decompositions reactions. In the former, two monoradicals which may contain undecomposed peroxide groups are generated. In the latter, the chain may fragment itself in both monoradicals and di-radicals (depending on the position of the peroxide groups within the chains) without undecomposed peroxide groups; (iv) due to the molecular structure of the DEKTP molecule, only linear di- and mono radicals and linear polymer chains can be formed in the reaction system.

Homogeneous Model

From the kinetics of Table 1 and assuming homogeneous bulk polymerization, the mathematical model of Appendices A and B was developed. The Basic Module of Appendix A allows the prediction of global chemical species' evolution along the reaction (total mono- and diradicals, total polymer). The Distributions Module of Appendix B allows simulation of the evolution of all chemical species characterized by their chain length and their number of undecomposed peroxide groups, and allows the estimation of the evolution of the molecular weight distribution (MWD) of each species and the number of undecomposed peroxide groups.

increase in the rate of polymerization is observed as temperature increases from 120, 130, to 150°C. At 200°C, the rate of polymerization is high at the beginning of the reaction, but it becomes lower than the one at 150°C after a short period of time (about 30 min). Molecular weights increase along the reaction for polymerization temperatures of 120 to 130°C. Meanwhile at higher temperatures, molecular weights remain relatively constant (150°C) or decrease along the reaction (200°C).

MATHEMATICAL MODEL

Kinetic Mechanism

The proposed kinetics involves initiation via a symmetrical cyclic trifunctional initiator by sequential and total decomposition reactions, thermal initiation, propagation, transfer to the monomer, combination termination and re-initiation. Consider the global kinetic mechanism presented in Table 1, which is an extension of the kinetic mechanism from Berkenwald et al. [21] The following nomenclature is adopted:

TABLE 2. Theoretical study of the effect of temperature on average rates of polymerization up to 90% conversion.

T (°C)	$\overline{R}_{p0,9}$ (mol $\cdot$ L^{-1} min^{-1})
130	0.0401
150	0.131
170	0.673
180	1.030
185	0.140
190	0.125
200	0.149

The proposed model considers constant temperature, assuming that the reactor cooling/heating system is ideal in the sense that it is capable of providing/removing the exact amount of heat in order to keep the temperature constant. However, it is possible to simulate reactions at different temperatures through the use of Arrhenius expressions for the kinetic constants. The gel effect was indirectly considered by appropriately reducing the value of the termination kinetic constant with increasing conversion [22].

The equations for solving the Basic Module are equations *A1, A2, A5, A12, A13, A17, A24*, and *A26*. For the Distributions Module, equations *B1, B2, A14*, and *A15* are solved, using the results of the Basic Module.

The Basic Module is solved by a standard stiff differential equation numerical method based on a modified Rosenbrock formula of order 2. In the Distributions Module, a large number of equations (more than 250,000) must be integrated. For this reason, an explicit forward Euler method was used, using the time intervals obtained from resolution of the Basic Module. A typical simulation requires less than 1 second for the Basic Module and about 10 min for the Distribution Module using an Intel Core i3 based processor at 2.93 GHz.

Simulation Results

The adopted kinetic parameters used for the simulation are presented in Table 3.

The adjusted parameters correspond to initiator decomposition (k_{d1}, k_{d2} and k_{dt}) and transfer to monomer reactions (k_{fM}). Since all peroxide groups (in the initiator or in the polymer chains) were assumed to have the same thermal stability, $k_{d1} = k_{d2}$. All other kinetic parameters were taken from the literature and are valid in a temperature range of 100 to 230°C [22]. The Basic Module allowed the adjustment for k_{d1} and k_{dt} from the estimation of the monomer conversion and k_{fM} from the estimation of average molecular weights. A sensitivity analysis was performed by decreasing and increasing the adjusted values for the kinetic parameters and checking that the model's response is within the acceptable range for this type of system.

The model was used to simulate the experiments described in the previous section. Simulated results are compared with experimental measurements in Fig. 2. Note that experiments with data taken from Berkenwald et al. [21] (120–130°C), were resimulated using the extended model. As expected, theoretical predictions for these experiments are very similar to those reported in this previous work.

In addition, a very good agreement between predicted and measured values for high temperature experiments (150–200°C)

is observed. Figure 2 shows the simulation results corresponding to the evolution of conversion and average molecular weights. The simulated polydispersity of the formed polymer is around 2, in agreement with the experimental value. As stated in Berkenwald et al. [21], the change of the slope in the conversion curve in Fig. 2 at approximately 200 min at 120°C and 150 min at 130°C, is due to the combined effect of thermal and chemical initiation, which includes initiator decomposition and decomposition of unreacted peroxide groups within the polymer chains, together with the gel effect, globally producing an increase in the rate of polymerization. The re-initiation reactions within the polymer chains are also responsible for the high molecular weights observed experimentally and predicted by the model at temperatures of 120 to 130°C, where initiator decomposition is mostly sequential. The change of the slope in the conversion curves at 150°C is less noticeable. At this temperature, the molecular weights are lower than in the previous temperature, and do not significantly increase along the reaction. At 200°C, initiator decomposition is completely total, and its behavior is similar to the one of a classic monofunctional initiator, rather than a multifunctional initiator. The slope of the conversion curve decreases with reaction time, as the initiator is fully consumed after approximately 1 min, with the remaining initiation reactions exclusively due to thermal initiation. At this polymerization temperature, simulation results predict the existence of a limiting conversion which may be lower than unity, indicating a polymerization mechanism corresponding to a "dead-end" polymerization [23, 24], where radicals are rapidly consumed by termination and transfer reactions, resulting in short polymer chains. This behavior and its relation to the initiator decomposition reaction will be discussed in detail below. At 150°C, both decomposition mechanisms coexist, but the total decomposition of the initiator does not generate polymer chains with undecomposed peroxide groups, therefore reducing the amount of re-initiation reactions that contribute to the increase of the rate of polymerization. As expected, thermal initiation at these high temperatures accounts for 80 to 100% of total initiation (thermal and chemical), depending on the system temperature and reaction time.

Aside from the prediction of experimental results presented in Fig. 2, the model was used to simulate other variables. Other model predictions are shown in Figs. 3–6.

Figure 3 represents the evolution of the concentration of the peroxide groups within the polymer chains for different reaction temperatures. For a polymerization temperature of 130°C, sequential decomposition of the initiator generates polymeric chains with undecomposed peroxide groups. As initiator decomposition is relatively slow, there is initiator left in the system throughout the polymerization reaction. For this reason, the rate of generation of peroxide groups within the polymer chains exceeds their rate of decomposition, resulting in an increasing function of time until the end of the polymerization reaction. Note that peroxide groups within the polymer chains still decompose and generate long chain monoradicals, which result in high average molecular weights predicted by the model for temperatures of 120 to 130°C. If temperature is increased above 130°C, initiator decomposition increases due to both thermal activation and total decomposition. In this case, the concentration of peroxide groups in the polymer might decrease with time in the course of the polymerization reaction. Total
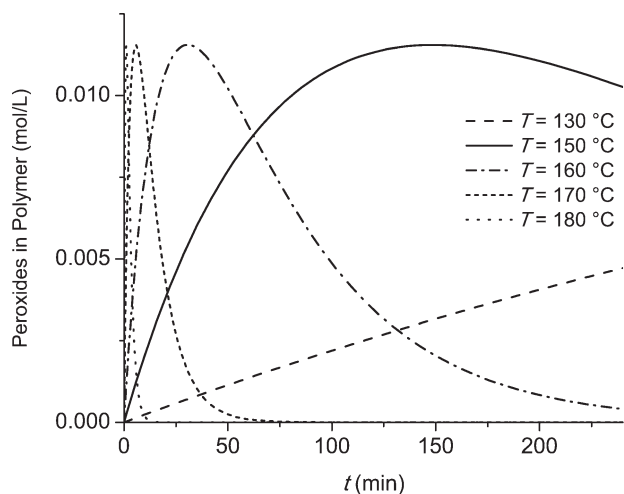
FIG. 3. Evolution of peroxide groups in polymer for different reaction temperatures.

FIG. 5. Theoretical MWD of the polymeric species at the end of polymerization for: a) $T = 130°C$, b) $T = 150°C$, and c) $T = 200°C$.

decomposition of the initiator molecule becomes comparable with the sequential decomposition at temperatures of approximately 150°C. For this reason, even though the obtained R_ps are high, the obtained molecular weights are low and do not increase along the reaction, as opposed to the case in the previous temperature range of 120 to 130°C. At higher temperatures (170, 180°C), initiator decomposition becomes very rapid, with a small contribution of sequential decomposition. This contribution increases the concentration of peroxides in polymer, which then decreases as a result of the decomposition undecomposed peroxide groups in polymer chains. At a temperature of 200°C, initiator decomposition is mostly total and the concentration of peroxide groups in the polymer becomes zero almost instantaneously after the beginning of the reaction. These groups decompose so rapidly that the effect on molecular weights and average rate of polymerization is negligible. For this reason, at temperatures of 200°C, the initiator behaves as a regular monofunctional initiator, and while high R_ps are obtained, high average molecular weights might be difficult to achieve.

Comparing the conversion curves for 150 and 200°C in Fig. 2, it can be observed that the slope of the conversion curve (related to the rate of polymerization) is almost constant at
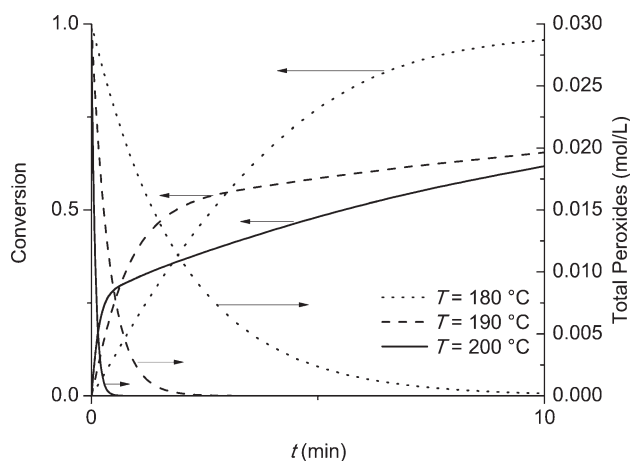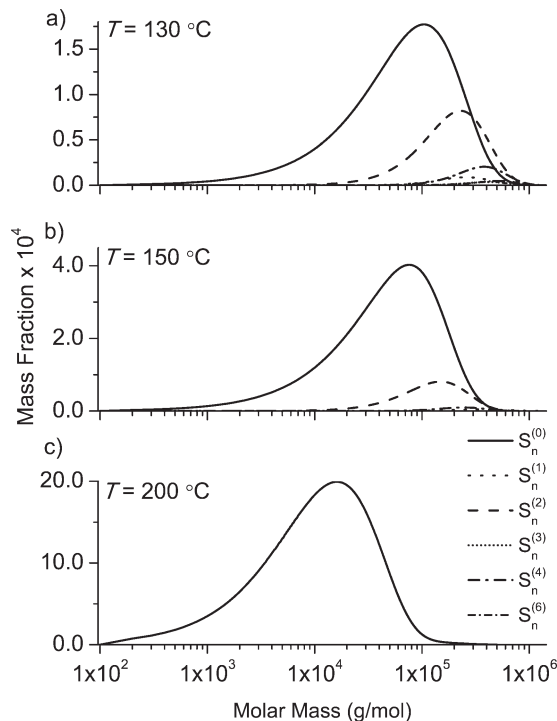
150°C, whereas at 200°C, conversion reaches a high value in a short period of time, and the slope of the curve largely decreases after said period. This behavior is common to "dead-end" polymerization, which is caused by an extremely rapid consumption of the initiator [23, 24]. In this system, such behavior arises due to the total decomposition mechanism, which has a high activation energy and becomes important at high temperatures.

From the experimental and theoretical results, it can be seen that both systems (150 and 200°C) reach about 90% conversion in about the same period of time, despite their large temperature difference (50°C). This indicates a similar average rate of
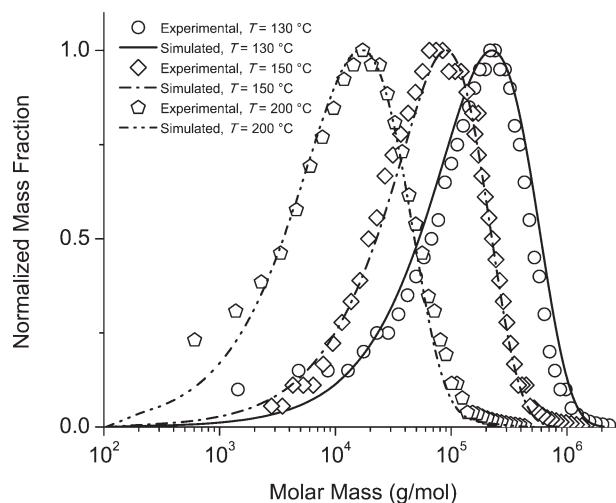

FIG. 4. Theoretical conversion and evolution of total peroxide groups for $T = 180°C$, $T = 190°C$ and $T = 200°C$.

FIG. 6. Experimental and theoretical MWDs of the total polymer for $T = 130°C$, $T = 150°C$, and $T = 200°C$.

polymerization. The average rate of polymerization to attain a given conversion value can be theoretically calculated using *Eq. A28*, for different reaction temperatures.

Table 2 shows the average rates of polymerization predicted by the model for different reaction temperatures for a conversion value of 90%. It can be seen that the average rate of polymerization increases with temperature up to a temperature of 180°C. At 185°C, a drastic decrease in the average rate of polymerization is observed. The rapid decomposition of the initiator and the lack of peroxide groups in polymer chains to re-initiate the reaction (due to total decomposition), generate a decrease in the polymerization rate. This decrease is not compensated by the increase in thermal initiation of styrene. For temperatures higher than 190°C, a slight increase in polymerization rate can be observed, because of the increase in the thermal initiation of styrene, which is the main radical generation mechanism at 190°C and higher temperatures, with almost no contribution from peroxide groups.

To better illustrate the change in rate of polymerization, the conversion curves corresponding to 180, 190 and 200°C at short polymerization times are represented in Fig. 4, together with the evolution of total peroxide groups. It can be observed that the decrease between the rate of polymerization at 180°C and the rate of polymerization at 190°C is due to the rapid decomposition of total peroxide groups, generating a large number of radicals at very short reaction times. For a temperature of 190°C, the system becomes exclusively thermally activated for a time of around 7 min, in agreement with the time in which peroxide groups throughout the system are totally consumed. For a lower temperature of 180°C, the total peroxides are not fully consumed within the time at which the reaction reaches full conversion, the polymerization rate is almost constant up to high conversion values.

Figure 5 shows the theoretical MWDs of all formed polymer species at the end of the polymerization reaction. Only MWDs of a few polymeric species are represented in order to keep the picture clear but still representative. The polymeric species are characterized by both their chain length and number of undecomposed peroxide groups, as calculated by the distributions modules of the mathematical model. When the polymerization temperature is such that the initiator decomposition is mostly sequential (130°C), polymeric chains with undecomposed peroxide groups remain in the obtained product. Polymers with two undecomposed peroxide groups have higher concentration than polymers with a higher number of undecomposed peroxide groups, because these are the main products of an initiator diradical[1] that propagated and terminated to form a polymeric chain. As the reaction temperature increases the fraction of polymers with undecomposed peroxide groups decreases. When the polymerization temperature is such that the initiator is consumed by both sequential and total decomposition (150°C) this fraction is lowered, and when the polymerization temperature is such that initiator decomposition is mostly total (200°C), there are no polymeric species with undecomposed peroxide groups at the end of the polymerization reaction. In this case, the simulated molecular structure of the obtained product is analogous to the one obtained in the bulk polymerization of St using a traditional monofunctional initiator. It can be seen that polymers with undecomposed peroxide groups have longer chains than the polymer with no undecomposed peroxide groups for a tempera-
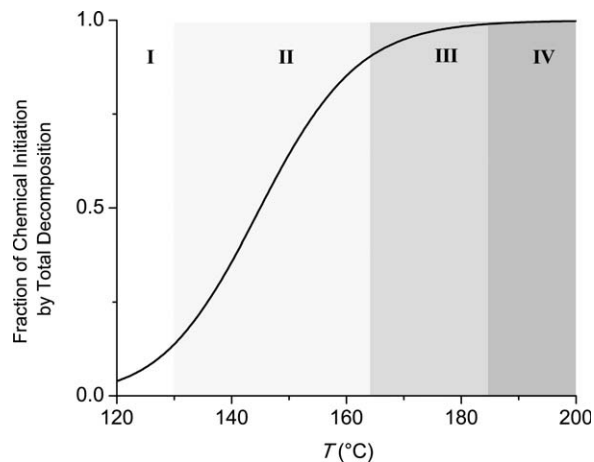

FIG. 7. Fraction of chemical initiation by total decomposition of DEKTP and working zones as functions of temperature.

ture of 130°C (sequential decomposition). This is not the case for a temperature of 150°C, due to the coexistence of both decomposition mechanisms.

Figure 6 shows the comparison between experimental and simulated normalized MWDs of the total polymer (i.e. the sum of all polymeric species) at the end of the polymerization reaction for different reaction temperatures. The mass fraction is normalized by dividing by the maximum mass fraction in order to represent the MWDs for temperatures of 130, 150, and 200°C in the same figure. A good agreement between experimental and simulated values is observed.

The experimental and theoretical results for the bulk polymerization of St using DEKTP indicate that the initiator decomposition reaction can determine the behavior of the polymerization system, in terms of rates of polymerization and final properties of the obtained polymer (average molecular weight, presence of undecomposed peroxide groups). The different behaviors can be related to the reaction temperature.

Figure 7 shows the fraction of the rate of chemical initiation by total decomposition as a function of temperature. This fraction can be defined by *Eq. A30* which involves the kinetic parameters for sequential (k_{d1}) and total decomposition (k_{dt}). Figure 7 consists of four different "working zones", each of them determined by the polymerization temperature. For each of these working zones, the polymerization system has different characteristics.

In Zone I (120–130°C), initiator decomposition is mostly sequential, since the value for k_{d1} is about one order of magnitude greater than the one for k_{dt} (about 3 to 10% chemical initiation by total decomposition). In this region, high rates of polymerization (0.024–0.040 mol·L^{-1} min^{-1}) and high molecular weights (450,000–297,000 g/mol) are simultaneously obtained. Average molecular weights increase along the reaction, and the final product is a polymer containing undecomposed peroxide groups.

In Zone II (130–165°C), initiator decomposition consists of both sequential and total decomposition mechanism, since both kinetic parameters have values in the same order of magnitude. This zone covers a wide range of temperatures for which the fraction of chemical initiation by total decomposition ranges from 10 to about 90%. In this working zone, polymerization

rates are high (0.040–0.440 mol $\cdot$ L^{-1} min^{-1}), but the obtained molecular weights are significantly lower than those obtained in Zone I ($297{,}000$–$77{,}000$ g/mol), and it is observed that the average molecular weights remain constant or decrease along the reaction. Simulation results also show that polymers containing undecomposed peroxide groups might be obtained when the system reaches full conversion up to a temperature of 160°C.

In Zone III (165–185°C), the dominant decomposition mechanism is the total decomposition, as the value for k_{d1} is about one order of magnitude lower than the one for k_{dt} (90–95% chemical initiation by total decomposition). In this region, rates of polymerization are very high (0.44–0.14 mol $\cdot$ L^{-1} min^{-1}), but the average molecular weights are low ($77{,}000$–$48{,}000$ g/mol) and decrease along the reaction. No polymers with undecomposed peroxide groups are obtained at the end of the reaction.

In Zone IV (185–200°C), initiator decomposition is mainly total (more than 95% chemical initiation by total decomposition) and so rapid that the system behaves as a "dead-end" polymerization system, and exhibits a limiting value for conversion which can be lower than unity. In this region, the rates of polymerizations can be lower than those of Zone III (0.14–0.15 mol $\cdot$ L^{-1} min^{-1}) and the obtained molecular weights are very low ($48{,}000$–$44{,}000$ g/mol).

Zone I is therefore the zone of technological interest, in which high polymerization rates and high average molecular weights can be obtained simultaneously. However, in industrial polystyrene processes where the final stages are carried out at high temperatures (above 180°C), the effect of the decomposition of the undecomposed peroxide groups remaining within the polymer, and their effect on average molecular weights must be evaluated. In order to preliminarily estimate this effect, simulations were carried out considering only peroxide group decomposition at high temperatures. Simulations results show a decrease of about 30 to 40% in average molecular weight. Nevertheless, the obtained molecular weights are still comparable to those obtained in traditional radical styrene polymerization using monofunctional initiators, but the polymerization rates are higher, resulting in a better overall process productivity.

The working zones defined in this analysis can be directly related to the values of the kinetic parameters of the initiator decomposition reaction. This type of analysis can be performed for another multifunctional initiator, once the model parameters have been validated with experimental data, in order to find the zone of technological interest, once the reaction conditions and desired physical properties are specified.

CONCLUSIONS

The bulk polymerization of St in the presence of DEKTP at temperatures of 150 and 200°C was experimentally and theoretically investigated.

A mathematical model was developed, considering two simultaneous initiator decomposition mechanisms: sequential and total decomposition of DEKTP. The model allows the prediction of the evolution of the reacting species' concentration, monomer conversion and detailed polymer molecular structure.

The mathematical model can be applied to simulate polymerizations in a wide temperature range (120–200°C), where exper-

imental information shows that both decomposition mechanisms can be present.

Chemical initiation by DEKTP can be modeled as a set of two parallel reactions for temperatures of 120 to 200°C. Experimental and theoretical results indicate a strong dependence of initiator decomposition kinetics with polymerization temperature. For polymerization temperatures of 120 to 130°C, initiator decomposition is mostly sequential, resulting in high R_{p}s and high molecular weights simultaneously. For polymerization temperatures of 130 to 160°C, where both decomposition mechanisms are present, higher rates of polymerization can be obtained, at the cost of reducing the average molecular weight of the final product. For polymerization temperatures higher than 160°C, initiator decomposition is mostly total. The obtained polymers exhibit low molecular weights. In addition, no undecomposed peroxide groups remain within the polymer chains at these reaction temperatures. For temperatures higher than 185°C, the system can behave as a "dead-end" polymerization system, with low average rates of polymerization and low molecular weights.

The mathematical model can be applied to choose the operating conditions in order to obtain a good balance between process productivity and quality of the obtained product.

Finally, this approach could be extended to other multifunctional initiators or other polymers obtained via radical polymerization, as a tool for understanding the process kinetics and their interrelation with reaction conditions.

APPENDIX A: BASIC MODULE

Balances for the Nonpolymeric Reagents and Products

Initiator (DEKTP).

$$\frac{d}{dt}([\mathrm{I}^{(3)}]V) = -3(k_{d1}+k_{dt})[\mathrm{I}^{(3)}]V \tag{A1}$$

Monomer. Assuming the "long chain approximation" (by which propagation is the only monomer-consuming reaction), one can write:

$$\frac{d}{dt}([\mathrm{St}]V) = -R_{p}V = -k_{p}[\mathrm{St}]([\mathrm{R}\cdot]+2[\cdot\mathrm{R}\cdot])V \tag{A2}$$

where R_{p} is the global St polymerization rate, and

$$[\mathrm{R}\cdot] = \sum_{i=0}^{\infty}\sum_{n=1}^{\infty}[\mathrm{S}_{n}\cdot^{(i)}] \tag{A3}$$

$$[\cdot\mathrm{R}\cdot] = \sum_{i=0}^{\infty}\sum_{n=1}^{\infty}[\cdot\mathrm{S}_{n}\cdot^{(i)}] \tag{A4}$$

represent the total concentrations of mono- and diradicals respectively.

Radical Species. Consider the mass balances of all free radical appearing in the global kinetics. Such balances provide:

$$\frac{d}{dt}([\cdot\mathrm{I}\cdot^{(2)}]V) = (3f_{1}k_{d1}[\mathrm{I}^{(3)}]-2k_{p1}[\cdot\mathrm{I}\cdot^{(2)}][\mathrm{St}])V \tag{A5}$$

Kinetic parameter	Units	Arrhenius expression	References
$k_{\mathrm{d}}, k_{\mathrm{d2}}$	[s^{-1}]	$1.87\times10^{8}e^{-25,500/RT}$	Adjusted in this work
$k_{\mathrm{d}t}$	[s^{-1}]	$1.53\times10^{30}e^{-67,549/RT}$	Adjusted in this work
k_{i}	L^2 mol^{-2} s^{-1}	$2.19\times10^{5}e^{-27,340/RT}$	Hui and Hamielec (1972) [22]
$k_{\mathrm{p1}}, k_{\mathrm{p}}$	L mol^{-1} s^{-1}	$1.051\times10^{7}e^{-7082/RT}$	Hui and Hamielec (1972) [22]
k_{fM}	L mol^{-1} s^{-1}	$3.84\times10^{9}e^{-17,836/RT}$	Adjusted in this work
k_{tc}	L mol^{-1} s^{-1}	$1.255\times10^{9}e^{-(1667.3/RT)-2(C_1x+C_2x^2+C_3x^3)\mathrm{a}}$	Hui and Hamielec (1972) [22]
f		0.98	Cerna et al. (2002) [13]

$^{\mathrm{a}}C_1=2.57-0.00505T$; $C_2=9.56-0.0176T$; $C_3=-3.03+0.00785T$, with x monomer conversion.
R = 1986 cal/mol K.

$$\frac{d}{dt}([\cdot\mathrm{I}.^{(0)}]V)=(6f_2k_{\mathrm{d}t}[\mathrm{I}^{(3)}]-2k_{\mathrm{p1}}[\cdot\mathrm{I}.^{(0)}][\mathrm{St}])V \qquad (A6)$$

$$\frac{d}{dt}([\mathrm{S}_1.^{(0)}]V)=\{2k_i[\mathrm{St}]^3-(k_{\mathrm{p}}[\mathrm{S}_1.^{(0)}]-k_{\mathrm{fM}}([\mathrm{R}\cdot]+2[\cdot\mathrm{R}\cdot])$$
$$+k_{\mathrm{fM}}[\mathrm{S}_1.^{(0)}])[\mathrm{St}]-k_{\mathrm{tc}}[\mathrm{S}_1.^{(0)}]([\mathrm{R}\cdot]+2[\cdot\mathrm{R}\cdot])\}V \qquad (A7a)$$

$$\frac{d}{dt}([\cdot\mathrm{S}_1.^{(2)}]V)=\{(2k_{\mathrm{p1}}[\cdot\mathrm{I}.^{(2)}]-2k_{\mathrm{p}}[\cdot\mathrm{S}_1.^{(2)}]-2k_{\mathrm{fM}}[\cdot\mathrm{S}_1.^{(2)}])[\mathrm{St}]$$
$$-2k_{\mathrm{tc}}[\cdot\mathrm{S}_1.^{(2)}]([\mathrm{R}\cdot]+2[\cdot\mathrm{R}\cdot])\}V \qquad (A7b)$$

$$\frac{d}{dt}([\cdot\mathrm{S}_1.^{(0)}]V)=\{(2k_{\mathrm{p1}}[\cdot\mathrm{I}.^{(0)}]-2k_{\mathrm{p}}[\cdot\mathrm{S}_1.^{(0)}]-2k_{\mathrm{fM}}[\cdot\mathrm{S}_1.^{(0)}])[\mathrm{St}]$$
$$-2k_{\mathrm{tc}}[\cdot\mathrm{S}_1.^{(0)}]([\mathrm{R}\cdot]+2[\cdot\mathrm{R}\cdot])\}V \qquad (A8)$$

$$\frac{d}{dt}([\cdot\mathrm{S}_n.^{(i)}]V)=\{2k_{\mathrm{p}}[\mathrm{St}]([\cdot\mathrm{S}_{n-1}.^{(i)}]-[\cdot\mathrm{S}_n.^{(i)}])-2k_{\mathrm{fM}}[\mathrm{St}][\cdot\mathrm{S}_n.^{(i)}]$$
$$-2k_{\mathrm{tc}}([\mathrm{R}\cdot]+2[\cdot\mathrm{R}\cdot])[\cdot\mathrm{S}_n.^{(i)}]+2k_{\mathrm{tc}}\sum_{j=0}^{i}\sum_{m=1}^{n-1}[\cdot\mathrm{S}_{n-m}.^{(i-j)}][\cdot\mathrm{S}_m.^{(j)}]\}V$$
$$(n\geq 2,\ i=2,4,6,\ldots) \qquad (A9)$$

$$\frac{d}{dt}([\mathrm{S}_n.^{(i)}]V)=\{(k_{\mathrm{p}}([\mathrm{S}_{n-1}.^{(i)}]-[\mathrm{S}_n.^{(i)}])$$
$$+k_{\mathrm{fM}}(2[\cdot\mathrm{S}_n.^{(i)}]-[\mathrm{S}_n.^{(i)}]))[\mathrm{St}]\ -k_{\mathrm{tc}}([\mathrm{R}\cdot]+2[\cdot\mathrm{R}\cdot])[\mathrm{S}_n.^{(i)}]$$
$$+2k_{\mathrm{tc}}\sum_{j=0}^{i}\sum_{m=1}^{n-1}[\cdot\mathrm{S}_{n-m}.^{(i-j)}][\mathrm{S}_m.^{(j)}]\ +k_{\mathrm{d2}}\sum_{j=i+1}^{\infty}\sum_{m=n+1}^{\infty}p_{mj}(n,i)j[\mathrm{S}_m^{(j)}]$$
$$+\delta_{i0}k_{\mathrm{d}t}\sum_{j=i+1}^{\infty}\sum_{m=n+1}^{\infty}p'_{mj}(n,0)j[\mathrm{S}_m^{(j)}]\}V$$
$$(n\geq 2,\ i=0,1,2,3,\ldots) \qquad (A10)$$

In *Eq. A10* $p_{mj}(n,i)$ is the probability that a scission of a chain of dead polymer of length m and j peroxide groups yields a monoradical of chain length n with i peroxide groups. Adding this probability over all i s and n s, the following can be proven:

$$\sum_{i=1}^{\infty}\sum_{n=1}^{\infty}\sum_{j=i+1}^{\infty}\sum_{m=n+1}^{\infty}p_{mj}(n,i)j[\mathrm{S}_m^{(j)}]=2\sum_{i=1}^{\infty}\sum_{n=1}^{\infty}i[\mathrm{S}_n^{(i)}]=2[\mathrm{Pe_P}]$$
$$(A11a)$$

where [Pe$_P$] is the concentration of peroxide groups in the polymer chains. The 2 in *Eq. A10* arises from the fact that the scission of any polymer chain with peroxide groups produces two monoradicals.

Similarly, $p'_{mj}(n,0)$ in *Eq. A10* is the probability that a scission of a chain of dead polymer of length m and j peroxide groups yields a monoradical of chain length n without peroxide groups, due to a total decomposition reaction. It is assumed that total decomposition reactions generate monoradicals without undecomposed peroxide groups. Actually, di-radicals would also expected to be generated when a polymeric chain with undecomposed peroxide groups suffers a total decomposition reaction. These probability coefficients will be related to the stoichiometric coefficients α_n and β_n in the kinetic mechanism of Table 3. However, this is expected to have little or no effect on the detailed polymer MWD, as polymeric chains with undecomposed peroxide groups in systems in which initiator decomposition is mostly total are expected to have very low concentrations, because in these systems the behavior of the initiator is close to the one of a traditional monofunctional initiator, and the MWD for temperatures at which initiator decomposition is not exclusively sequential is controlled by transfer to monomer reactions.

The generation of monoradicals from decomposition of peroxide groups within polymeric chains due to total decomposition must be considered solely for monoradicals without undecomposed peroxide groups ($i = 0$), where δ_{i0} (Kronecker delta) is included, with a value of unity if $i = 0$, and equal to zero if $i \neq 0$.

The following assumption will be made

$$\sum_{i=0}^{\infty}\sum_{n=1}^{\infty}\sum_{j=i+1}^{\infty}\sum_{m=n+1}^{\infty}\delta_{i0}p'_{mj}(n,0)j[\mathrm{S}_m^{(j)}]\approx 2[\mathrm{Pe_P}] \qquad (A11b)$$

which is equivalent to asserting that the total decomposition of any polymer chain with undecomposed peroxide groups (without characterizing it by chain length) generates two monoradicals (which contain no undecomposed peroxide groups), which is in turn equivalent to stating that the polymer chains may have only one undecomposed peroxide group. This is a simplification since the total decomposition of a polymer chain generates as many radicals as undecomposed peroxide groups were within the chain, and the number of peroxide groups within the chains is a variable.

However, it allows for a much more simple form for the equations in the Basic Module, and simulations show that, in the simulated conditions, this assumption has little effect on the values of the theoretical predictions that are of interest.

From *Eqs. A6* through *A10* the total concentration of mono- and diradicals may be obtained:

$$\frac{d}{dt}([R\cdot]V)=\{2k_i[St]^3+4k_{fM}[St][\cdot R\cdot]-k_{tc}[R\cdot]^2+2(k_{d2}+k_{dt})[Pe_P]\}V$$
(A12)

$$\frac{d}{dt}([\cdot R\cdot]V)=\{(2k_{p1}([\cdot I\cdot^{(2)}]+[\cdot I\cdot^{(0)}])-2k_{fM}[\cdot R\cdot])[St]$$
$$-2k_{tc}[\cdot R\cdot]([R\cdot]+2[\cdot R\cdot])+2k_{tc}[\cdot R\cdot]^2\}V$$
(A13)

Balances for the Polymeric Species

Polymer without peroxide groups ($i=0$)

$$\frac{d}{dt}([S_n^{(0)}]V)$$
$$=\left\{k_{fM}[St][S_n\cdot^{(0)}]+\frac{k_{tc}}{2}\sum_{m=1}^{n-1}[S_{n-m}\cdot^{(0)}][S_m\cdot^{(0)}]\right\}V \quad (n\geq 2)$$
(A14)

Polymer with peroxide groups ($i\neq 0$)

$$\frac{d}{dt}([S_n^{(i)}]V)=\{k_{fM}[St][S_n\cdot^{(i)}]+\frac{k_{tc}}{2}\sum_{j=0}^{i}\sum_{m=1}^{n-1}[S_{n-m}\cdot^{(i-j)}][S_m\cdot^{(j)}]$$
$$-(k_{d2}+k_{dt})i[S_n^{(i)}]\}V \quad (n\geq 2,\ i=1,2,3,\ldots)$$
(A15)

The concentration of the polymer with i undecomposed peroxide groups can be defined as

$$[P^{(i)}]=\sum_{n=1}^{\infty}[S_n^{(i)}]$$
(A16)

Let us define the total polymer concentration $[P]$

$$[P]=\sum_{i=0}^{\infty}[P^{(i)}]=\sum_{i=0}^{\infty}\sum_{n=1}^{\infty}[S_n^{(i)}]$$
(A17)

By adding up *Eq. A13* over all n s and *A14* over all n s and all i s, the balance for the molar concentration of polymer can be written:

$$\frac{d}{dt}([P]V)=\left\{k_{fM}[St][R\cdot]+\frac{k_{tc}}{2}[R\cdot]^2-k_{d2}[Pe_P]\right\}V$$
(A18)

Peroxide Groups

The total concentration of peroxide groups is

$$[Pe]=3[I^{(3)}]+2[\cdot I\cdot^{(2)}]+[Pe_{R\cdot}]+[Pe_{\cdot R\cdot}]+[Pe_P]$$
(A19)

with

$$[Pe_{R\cdot}]=\sum_{i=1}^{\infty}\sum_{n=1}^{\infty}i[S_n\cdot^{(i)}]$$
(A20)

$$[Pe_{\cdot R\cdot}]=\sum_{i=1}^{\infty}\sum_{n=1}^{\infty}i[\cdot S_n\cdot^{(i)}]$$
(A21)

$$[Pe_P]=\sum_{i=1}^{\infty}\sum_{n=1}^{\infty}i[S_n^{(i)}]$$
(A22)

where $[Pe_{R\cdot}]$, $[Pe_{\cdot R\cdot}]$, and $[Pe_P]$ respectively represent the molar concentration of peroxide groups accumulated in monoradicals, diradicals, and polymer species. From *Eq. A19* and assuming pseudosteady-state for radical species (by which all time derivatives may be set to 0), it can be written:

$$\frac{d[Pe]}{dt}=3\frac{d[I^{(3)}]}{dt}+\frac{d[Pe_P]}{dt}$$
(A23)

Peroxide groups are consumed only by decomposition reactions in the initiator and the polymer chains. Therefore:

$$\frac{d[Pe]}{dt}=-3(k_{d1}+k_{dt})[I^{(3)}]-(k_{d2}+k_{dt})[Pe_P]$$
(A24)

By considering *Eqs. A1* and *A24* and from *Eq. A23*, the total peroxide groups contained in the polymer chains can be calculated from the following equation:

$$\frac{d[Pe_P]}{dt}=6(k_{d1}+k_{dt})[I^{(3)}]-(k_{d2}+k_{dt})[Pe_P]$$
(A25)

Conversion

The monomer conversion can be calculated from

$$x=\frac{[St]^0V^0-[St]V}{[St]^0V^0}$$
(A26)

where the superscript "0" indicates initial conditions. In this model the effect of volume contraction was neglected and therefore

$$x=\frac{[St]^0-[St]}{[St]^0}$$
(A27)

Equations A1, *A2*, *A5*, *A12*, *A13*, *A18*, *A25*, *A27* can be simultaneously solved to find the evolutions of $[I]$, $[\cdot I\cdot^{(2)}]$, $[St]$, $[R\cdot]$, $[\cdot R\cdot]$, $[P]$, $[Pe_P]$, and x.

Average Rate of Polymerization

The average rate of polymerization can be defined, for a given value of conversion x as

$$\overline{R}_{px}=\frac{1}{t_x}\int_0^{t_x}R_p dt$$
(A28)

where t_x is the time at which value for conversion is x. In view of Eq. *A2*, it may be written

$$\overline{R}_{px} = -\frac{1}{t_x}\int_0^{t_x}\frac{1}{V}d([\mathrm{St}]V) = \frac{1}{t_x}([\mathrm{St}]_0 - [\mathrm{St}]_{t_x})$$

where constant volume is assumed. Considering the definition of conversion of (A27), the average rate of polymerization may be calculated as

$$\overline{R}_{px} = \frac{[\mathrm{St}]_0 x}{t_x} \tag{A29}$$

The fraction of chemical initiation by total decomposition can be defined as

$$f_{td} = \frac{-3k_{dt}[\mathrm{I}^{(3)}]}{-3(k_{d1}+k_{dt})[\mathrm{I}^{(3)}]} = \frac{k_{dt}}{k_{d1}+k_{dt}} \tag{A30}$$

The Number Chain Length Distribution (NCLD) for the PS species can then be found by integrating *Eqs. A13* and *A14* with the expressions found for $[\mathrm{S}_n^{(i)}\cdot]$.

The maximum chain length (maximum value of n) and number of peroxide groups (maximum value of i) simulated by resolution of the model are determined as follows: simulations are carried out with a large number for maximum undecomposed peroxide groups within the polymer chains (up to 30) and a very large number for maximum chain length (up to 25,000 monomer units). The maximum chain length and number of peroxide groups simulated is then adapted in order to ensure that the system simulates the species that determine the molecular structure of the polymer and the average molecular weights values, and at the same time, minimize the time required for the simulations.

In order to account for the formation of monoradicals from random scission of the polymer chains containing peroxide groups in a sequential decomposition, consider a polymer chain with length n and i peroxide groups, all of which have the same thermal stability. Let m be a uniformly distributed random variable whose value ranges from 1 to $n-1$. The polymer chain may form two monoradicals, one with length m, and the other one with length $n-m$. These chains will have $i-j$ and $j-1$ undecomposed peroxide groups respectively.

If the peroxide groups are uniformly distributed in the formed monoradicals, the following relation must hold:

APPENDIX B: DISTRIBUTIONS MODULE

Consider *Eqs. A8* and *A9*. Assuming pseudosteady-state, all time derivatives may be set to zero and the following recurrence formulas can be obtained:

$$[\cdot\mathrm{S}_n^{(i)}] = \frac{k_p[\mathrm{St}][\cdot\mathrm{S}_{n-1}^{(i)}] + k_{tc}\sum_{j=1}^{i}\sum_{m=1}^{n-1}[\cdot\mathrm{S}_{n-m}^{(i-j)}][\mathrm{S}_m^{(j)}]}{k_p[\mathrm{St}] + k_{fM}[\mathrm{St}] + k_{tc}([\mathrm{R}\cdot] + 2[\cdot\mathrm{R}\cdot])}$$
$$(n \geq 2,\ i = 2,4,6,\ldots) \tag{B1}$$

$$[\mathrm{S}_n^{(i)}\cdot] = \frac{(k_p[\mathrm{S}_{n-1}^{(i)}] + 2k_{fM}[\cdot\mathrm{S}_n^{(i)}])[\mathrm{St}] + 2k_{tc}\sum_{j=0}^{i}\sum_{m=1}^{n-1}[\cdot\mathrm{S}_{n-m}^{(i-j)}][\mathrm{S}_m^{(j)}]}{k_p[\mathrm{St}] + k_{fM}[\mathrm{St}] + k_{tc}([\mathrm{R}\cdot] + 2[\cdot\mathrm{R}\cdot])}$$
$$+ \frac{k_{d2}\sum_{j=i+1}^{\infty}\sum_{m=n+1}^{\infty}p_{mj}(n,i)j[\mathrm{S}_m^{(j)}] + \delta_{i0}k_{dt}\sum_{j=i+1}^{\infty}\sum_{m=n+1}^{\infty}p'_{mj}(n,0)j[\mathrm{S}_m^{(j)}]}{k_p[\mathrm{St}] + k_{fM}[\mathrm{St}] + k_{tc}([\mathrm{R}\cdot] + 2[\cdot\mathrm{R}\cdot])} \quad (n \geq 2,\ i = 0,1,2,3,\ldots) \tag{B2}$$

$$\frac{j-1}{n-m} = \frac{i-j}{m} \tag{B3}$$

Therefore,

$$j = \left[\frac{i(n-m)+m}{n}\right] \tag{B4}$$

where the brackets indicate the integer part of the expression.

The scission has then generated two monoradicals, one with length m and $i-j$ peroxide groups, the other one with length $n-m$ and $j-1$ peroxide groups.

This scission must be performed for all polymer chains whose peroxide group number is greater than 0.

For the case of a total decomposition, it is assumed that the scission of a polymer with chain length n and i undecomposed peroxide groups may generate $(i + 1)$ monoradicals, each with a chain length

$$m = \left[\frac{n}{i+1}\right] \tag{B5}$$

Average Molecular Weights

The number average molecular weight may be calculated with:

$$\overline{M}_n = M_{\mathrm{St}}\frac{\sum_{i=0}^{\infty}\sum_{n=2}^{\infty}n[\mathrm{S}_n^{(i)}]}{\sum_{i=0}^{\infty}\sum_{n=2}^{\infty}[\mathrm{S}_n^{(i)}]} \tag{B6}$$

and the weight average molecular weight with:

$$\overline{M}_w = M_{\mathrm{St}}\frac{\sum_{i=0}^{\infty}\sum_{n=2}^{\infty}n^2[\mathrm{S}_n^{(i)}]}{\sum_{i=0}^{\infty}\sum_{n=2}^{\infty}n[\mathrm{S}_n^{(i)}]} \tag{B7}$$

REFERENCES

1. K. Y. Choi and G. D. Lei, *AIChE J.*, **33**(12), 2067 (1987).

2. D. A. Estenoz, G. P. Leal, Y. R. López, H. M. Oliva, and G. R. Meira, *J. Appl. Polym. Sci.*, **62**, 917 (1996).

3. J. Kim, W. Liang, and K. Choi, *Ind. Eng. Chem. Res.*, **28**, 131 (1989).

4. D. B. Priddy, Polymer Synthesis. *Recent Advances in Styrene Polymerization*. Advances in Polymer Science, Springer Berlin Heidelberg, Vol. 111, pp. 67–114 (1994).

5. I. M. González, G. R. Meira, and H. Oliva, *J. Appl. Polym. Sci.*, **59**, 6 (1996).

6. W. J. Yoon and K. Y. Choi, *J. Appl. Polym. Sci.*, **46**, 1353 (1992).

7. W. J. Yoon and K. Y. Choi, *Polymer*, **33**, 4582 (1992).

8. M. A. Villalobos, A. E. Hamielec, and P. E. Wood, *J. Appl. Polym. Sci.*, **42**, 629 (1991).

9. K. Y. Choi, W. R. Liang, and G. D. Lei, *J. Appl. Polym. Sci.*, **35**, 1547 (1988).

10. M. Benbachir and D. Benjelloun, *Polymer*, **42**, 7727 (2001).

11. D. A. Estenoz, G. P. Leal, Y. R. López, H. M. Oliva, and G. R. Meira, *J. Appl. Polym. Sci.*, **62**, 917 (1996).

12. J. Cerna, G. Morales, G. N. Eyler, and A. I. Canizo, *J. Appl. Polym. Sci.*, **83**, 1 (2002).

13. J. Cerna, "*Uso de Peróxidos Cíclicos Multifuncionales como Iniciadores de la Polimerización de estireno a alta tempertur con un enfoque de aplicación industrial*", Doctoral Thesis, CIQA (2002).

14. L. Cavin, A. Rouge, T. Meyer, and T. Renken, *Polymer*, **41**, 3925 (2000).

15. C. M. Mateo, G. N. Eyler, E. E. Alvarez, and A. I. Cañizo, *Inform. Tecnol.*, **9**(2), 19 (1998).

16. W. C. Sheng, J. Y. Wu, G. R. Shan, Z. M. Huang, and Z. X. Weng, *J. Appl. Polym. Sci.*, **94**(3), 1035 (2004).

17. M. J. Scorah, *Doctoral Thesis*, University of Waterloo, Canada (2005).

18. M. J. Scorah, R. Dhib, and A. Penlidis, *Chem. Eng. Sci.*, **61**, 4827 (2006).

19. M. J. Scorah, R. Dhib, and A. Penlidis, *Macromol. React. Eng.*, **1**(2), 209 (2007).

20. P. Acuña, G. Morales, and R. Díaz de León, *J. Appl. Polym. Sci.*, **114**, 3198 (2009).

21. E. Berkenwald, C. Spies J. R. Cerna Cortez, G. Morales, and D. Estenoz, *J. Appl. Polym. Sci.*, **128**(1), 776 (2013).

22. A. W. Hui and W. Hamielec, *J. Appl. Polym. Sci.*, **16**, 749 (1972).

23. A. V. Tobolsky, *J. Am. Chem. Soc.*, **80**(1), 5927 (1958).

24. A. V. Tobolsky, C. E. Rogers, and R. D. Brickman, *J. Process Control*, **82**(1), 1277 (1960).