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Process Modelling and Optimization of Styrene Polymerization

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Summary: Polystyrene is a common commodity with thin margin, it is desirable for industry to reduce the production cost by optimizing the process and producing polystyrene with desired properties. This paper has reviewed several commonly used process optimization policies from the literature. The kinetics of styrene polymerization with mono- or bifunctional initiator has also be described. It has been demonstrated that by using a temperature profile combined with selective mono- or bifunctional initiators, one can decrease bach time while still maintaining the desired molecular weight averages. The recently developed new tetra-functional initiator by Elf-Atochem provides a new tool for controlling/optimization purposes. Industrial process configurations of polystyrene production has also be discussed.

Keywords: bifunctional initiator; process optimization; process simulation; reaction kinetics; styrene production

1. Introduction

In polystyrene production, it is desirable to produce polystyrene with best properties at lower cost. In a batch process, the productivity can be increased by decreasing the batch time while still maintaining molecular weight distribution of the final polymer in a desired range. Optimization policies can be designed based on a good understanding of styrene reaction kinetics. Tieu et al.(1994)[1] have reviewed optimization policies for polymerization reactors. The surveyed papers cover batch, semi-batch and continuous reactors, and five typical case studies are discussed (temperature programming and initiator policies). Related numerical aspects of the optimization problem have been discussed in Tieu et al. (1995)[2].

Among optimization efforts in the last 20 years, noteworthy is the paper by Wu et al. (1982)[3]. They studied, both theoretically and experimentally, the bulk polymerization of styrene and derived optimal

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temperature policies which minimize the time to reach a desired final conversion and number average molecular weight. A time saving of about 18% was realized when compared to isothermal operation. The molecular weight and polydispersity of the polymer obtained during the experimental verification were in good agreement with the predictions of a mathematical model.

More recent literature efforts (primarily at the simulation level) on optimization of styrene-related systems include: Cavalcanti and Pinto (1997)[4], suspension reactor for styrene-acrylonitrile and Hwang et al. (1998)[5], thermal copolymerization in a continuously stirred tank reactor (CSTR).

In order to develop a sound optimization policy, a good understanding of styrene polymerization kinetics is necessary. In the following section the general kinetic scheme of styrene homopolymerization is introduced.

1.1 General Kinetic Scheme of Styrene Homopolymerization

The basic reaction scheme for free-radical bulk/solution styrene homopolymerization is described below. A complete description of copolymerization kinetics involving styrene is not given here, however, the homopolymerization kinetic scheme can be easily extended to describe copolymerization using the pseudokinetic rate constant method [6]. Such practice has been used by many research groups[7-10], and has been used extensively for modelling of copolymerization involving styrene by Gao and Penlidis (1998)[11]. In this section, all rate constants are defined as chemically controlled, i.e., they are only a function of temperature.

Initiation *(by monofunctional initiator)*

$$I \xrightarrow{kd} 2R_o\cdot \tag{1}$$

$$R_o\cdot + M \xrightarrow{kp} R\cdot \tag{2}$$

In the above reactions, I is the monofunctional chemical initiator, $R_o\cdot$ is the primary radical from initiator decomposition, M is the monomer and R· is a radical with a monomer unit attached. The rate of initiation through a monofunctional initiator R_{IM} (mol/L·sec) is,

$$R_{IM} = 2fk_d[I] \tag{3}$$

A distinctive characteristic of styrene polymerization is its thermal self-initiation at high temperatures (without the presence of a chemical initiator). The mechanism of styrene thermal initiation was first described by Mayo (1968)[12]. The kinetics of thermal initiation has been described by Weickert and Thiele (1983)[13] as a second order reaction, while Hui and Hamielec (1972)[14], Husain and Hamielec (1978)[15] and Ito (1986)[16] have proposed that the thermal initiation is a third order reaction which is more widely used today. The initiation rate is believed to be of third order with respect to monomer concentration. The kinetics of styrene thermal initiation is listed below,

$$M + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AH \tag{4}$$

$$M + AH \xrightarrow{ki} M\cdot\ (phCHCH_3\cdot) + A\cdot \tag{5}$$

$$M + M\cdot \xrightarrow{kp} R_1\cdot \tag{6}$$

$$M + A\cdot \xrightarrow{kp} R_1\cdot \tag{7}$$

$$M + AH \xrightarrow{ktr} Dimer \tag{8}$$

$$M + AH \xrightarrow{ktr} Trimer \tag{9}$$

In the above reactions, AH denotes the Diels-Alder adduct, M· and A· are initial monomeric and Diels-Alder adduct radicals generated in reaction 5, these radicals can further react with styrene monomer to start the polymer chain growth. The rate determining step in styrene thermal initiation is reaction 5. The rate of thermal initiation R_{IT} (mol/L·sec) is expressed as,

$$R_{IT} = 2\,k_i[M]^3 \tag{10}$$

The total rate of initiations R_I (mol/L·sec) is the summation of styrene thermal initiation and chemical initiator decomposition, i.e.,

$$R_I = 2fk_d[I] + 2k_i[M]^3 \tag{11}$$

It is worth noting that the dimer and trimer generated in reactions 8 and 9 can react with polymeric radicals as a chain transfer agent, therefore, their effect on the polymer molecular weight should not be neglected, the quantitative estimation of the concentration of these byproducts depends on the fact that whether the rate of thermal initiation is a second or third order reaction of monomer concentration. More kinetic information for such transfer reactions can be found in a number of publications [14-19]. Nevertheless detailed kinetic studies on such Diels-Alder byproducts remain scarce. Katzenmayer (1987)[20], Olaj et al.(1976, 1977)[21,22], Kirchner and Riederle (1985)[23] have published some quantitative results on this matter.

Initiation *(by bifunctional initiator)*

Bifunctional initiators have already been used in research laboratories and industrial production. They have the following general chemical structure: R_1-O-O-R_2-O-O-R_1, where R_1 and R_2 are hydrocarbon ligands. The oxygen bonds O-O, when heated, can thermally break up and generate two radicals:

$$R_1\text{-}OO\text{-}R_2\text{-}OO\text{-}R_1 \xrightarrow{k_{d1}} R_1\text{-}O\cdot + R_1\text{-}OO\text{-}R_2\text{-}O\cdot \tag{12}$$

The above reaction can be generalized as:

$$I \xrightarrow{k_{d1}} R_o\cdot + \tilde{R}_o\cdot \tag{13}$$

According to the bifunctional initiation mechanism, both decomposed initiator radical $R_o\cdot$ and undecomposed initiator radical $\tilde{R}_o\cdot$ are going to participate in the polymerization process. This means that each initial initiator radical $R_o\cdot$ or $\tilde{R}_o\cdot$ may generate a different polymer chain,

$$R_o\cdot + M \xrightarrow{k_p} R_1\cdot \tag{14}$$

$$\tilde{R}_o\cdot + M \xrightarrow{k_p} \tilde{R}_1\cdot \tag{15}$$

$\tilde{R}_1\cdot$ contains an undecomposed peroxide radical and is called 'macro' peroxide. It can further decompose like an initiator,

$$R_1\text{-}OO\text{-}R_2\text{-}O\cdot \xrightarrow{k_{d2}} R_1\text{-}O\cdot + \cdot O\text{-}R_2\text{-}O\cdot \tag{16}$$

If the macro peroxide radical terminates with another polymeric radical, it will generate a dead polymer chain which contains one undecomposed peroxide, $\tilde{P}_r$ (see reaction 24). If it terminates with another macro peroxide radical, a dead polymer with two undecomposed peroxides $\tilde{\tilde{P}}_r$ will be generated (see reaction 25). These two decomposable dead polymers can undergo decomposition to generate radicals, hence they should be included in the initiation step,

$$\tilde{P}_r \xrightarrow{k_{d2}} R_o\cdot + R_r\cdot \tag{17}$$

$$\tilde{\tilde{P}}_r \xrightarrow{2k_{d2}} R_o\cdot + \tilde{R}_r\cdot \tag{18}$$

The total rate of initiation (mol/L·sec) involving bifunctional initiator as well as styrene thermal initiation R_I can thus be expressed as,

$$R_I = 2k_i[M]^3 + 2fk_{d1}[I] + f'k_{d2}(\tilde{P}_r + 2\tilde{\tilde{P}}_r) \tag{19}$$

Early work by Prisyazhnyuk and Ivanchev (1970)[24] studied the fundamentals of the polymerization using bifunctional initiators. Recent studies on modelling and simulation can be found in a number of publications [25-30]. Model testing results of styrene homopolymerization using an extensive list of homo- and bifunctional initiators can be found in Dhib et al.(2000)[31].

Propagation

The general propagation reaction is,

$$R_r\cdot + M \xrightarrow{kp} R_{r+1}\cdot \tag{20}$$

The propagation reaction for a macro peroxide radical is,

$$\tilde{R}_r\cdot + M \xrightarrow{kp} \tilde{R}_{r+1}\cdot \tag{21}$$

$\tilde{R}_r\cdot$ is the macro polymeric radical with chain length *r* and $R_r\cdot$ is the polymeric radical of chain length *r*. When a bifunctional initiator is used, the rate of propagation, which is also the rate of polymerization Rp (mol/L·sec), is,

$$Rp = kp\ [M]\ ([\tilde{R}\cdot] + [R\cdot]). \tag{22}$$

Termination

As stated before, when bifunctional initiator is used, macro peroxide radical contains undecomposed peroxide is generated, this will lead to additional termination reactions 24 and 25, assuming styrene polymeric radicals terminate only through combination,

$$R_r\cdot + R_s\cdot \xrightarrow{kt} P_{r+s} \tag{23}$$

$$\tilde{R}_r\cdot + R_s\cdot \xrightarrow{kt} \tilde{P}_{r+s} \tag{24}$$

$$\tilde{R}_r\cdot + \tilde{R}_s\cdot \xrightarrow{kt} \tilde{\tilde{P}}_{r+s} \tag{25}$$

Termination step 23 is applicable to polymerization with no bifunctional initiator present. The value of k_t was recently measured by Buback et al.(2000)[32].

Chain Transfer Reactions

Transfer reactions to small molecules (T) including monomer, solvent, chain transfer agent (CTA), etc. are all very similar and are generalized below,

$$R_r\cdot + T \xrightarrow{k_{ft}} P_r + T\cdot \tag{26}$$

$$\tilde{R}_r\cdot + T \xrightarrow{k_{ft}} \tilde{P}_{r+1} + T\cdot \tag{27}$$

Reactions with Inhibition

$$R_r\cdot + Z \xrightarrow{k_z} P_r \tag{28}$$

$$\tilde{R}_r\cdot + Z \xrightarrow{k_z} \tilde{P}_r \tag{29}$$

where Z is a inhibitor.

Detailed equations describing rate of polymerization and molecular weight development can be found in Dhib et al.(2000)[31]. Yoon et al.(1998)[33] also calculated the molecular weight distribution in styrene batch thermal polymerization.

1.2 Treatment of Gel-Effect

Gel effect and limiting conversion are commonly observed in styrene homo-/copolymerization. Great advances have been made on polymerization kinetics at high conversion by different groups [34-39]. In a recent study by Vivaldo-Lima et al.(1994)[40], the models from Chiu et al.(1983)[39] and Marten and Hamielec (1982)[34] were compared. They concluded that the approach taken by Marten and Hamielec (1982)[34] based on free-volume theory seems to be able to describe the whole course of polymerization up to the limiting conversion successfully. Soh and Sundberg [35-38] also used and refined further the free-volume theory to investigate polymerization kinetics of styrene and obtained very good results. By using the free-volume theory, one[11,42] can successfully monitor the whole course of free-radical polymerization of many different homo-/copolymerization systems under a wide range of reaction conditions.

It must be stated that up to now models that can describe detailed styrene polymerization including all kinds of initiation step are rare. The work from Dhib et al.(2000)[31] is so far the most comprehensive in this aspect.

2 Process Simulation and Optimization of Styrene Homopolymerization

2.1 Using initiator combinations with designed temperature profile

There are several ways to minimize batch time. One can either raise the reaction temperature or simply add more initiator into the system. However, both methods will reduce the molecular weight. High levels of expensive initiators result in lower molecular weight and leave a larger amount of undecomposed initiator which is costly to be removed and also an environmental hazard. Using more initiators also increases the product cost. Thus it is preferable to run the reaction initiated by the right type of initiator or even multiple initiators at a temperature or a customized temperature profile to produce desired polymer at low cost.

Butala et al.(1992)[41] have applied optimization techniques to styrene polymerization initiated by BPO (di-benzoyl peroxide,1 hour half-life time, 91°C) and TBPB (*tert*-butyl perbenzoate, 1 hour half-life time, 124°C). As mentioned before, batch time can be minimized using non-isothermal temperature profiles. Three independent runs with different optimization policies were performed. The detailed control policies are listed in Table 1 below.

Table 1 **Optimization policies of styrene homopolymerization**

	Policy 1	Policy 2	Policy 3
BPO (mol%)	80	69.2	39.4
TBPB (mol%)	20	30.8	60.6
Temperature (°C)	87-103	94-107	119-133
Batch Time (hr)	6.04	5.13	3.04
Conversion	98.4	98.5	98.4
Xn	780	782	930
residual initiator (ppm)	680	660	8

It can be seen from the results listed in Table 1 that by using the right combination of initiators combined with a rising temperature profile, one can reduce the batch time significantly while at the same time increase the molecular weight (comparison of policy 3 and policy 1). The final residual initiator amount is also greatly reduced. Their experimental results confirm that the optimization goal was achieved by employing the proper control policy.

2.2 Using Bifunctional Initiators

The success of polystyrene products by free radical processes is affected to a significant extent by the quality and performance of initiators. Monofunctional initiators such as benzoyl peroxide or azo-bis-iso-butyronitrile have been utilized in bulk and solution polymerizations for theoretical studies and practical applications. Gao and Penlidis (1996)[42] have recently reviewed the wide range of research carried out on polymerization of various monomers including styrene. They have incorporated most previous work on monofunctionally initiated free radical polymerization in a comprehensive simulation package.

The market requirements regarding the properties and varieties of polymer grades are very specific. Consequently, there is a growing need to produce polymers with certain quality and to seek processes with high rates of polymerization and controlled polymer molecular weights. Organic peroxides, existing in a large number, are widely used in polymerization industries. It has been demonstrated that peroxides play a major role in controlling molecular weights, polymer properties and rate of polymerization[43]. For economical and safety reasons, the selection of the appropriate (initiator) peroxide is of great importance. Polystyrene reactors are usually designed for producing polystyrene in the temperature range of 90-180°C. If the peroxide decomposes at a very slow rate, the overall reactor efficiency becomes poor, and undecomposed peroxides may exit the reactor. Recycling impurities to the reactor causes operation problems not easy to overcome even by means of good control schemes. On the other hand, if the decomposition is very fast, a runaway polymerization is likely to occur.

The increase of polymerization rate observed when using bifunctional initiators is one of the main motivations for both industry and academia to better understand peroxide chemistry. In general, an increase in reaction temperature for boosting productivity lowers polymer molecular weights. This problem of obtaining lower molecular weight averages can be circumvented by the use of a proper bifunctional initiator. An extensive review of bulk/solution polymerization of styrene with both mono- and bi-functional initiators, with literature and industrial (Elf Atochem) data, was recently given by Dhib et al. (2000)[31]. Over 80 polystyrene-related references were discussed along with a general and flexible mathematical model. Additional recent literature sources can be found in Krispin et al.(1995)[44] and Cavin et al.(2000 a)[45].

An optimization exercise, similar to that of Wu et al. (1982)[3], but now with a bifunctional initiator Luperox 101 (2,5-dimethyl-2,5 bis (*t*-butylperoxy) hexane, 0.002 mol/L), would yield similar beneficial results from temperature programming. One can obtain shorter batch times (productivity enhancements, see figure 2) and stable molecular weight averages (product quality improvements, see figure 3), compared to typical isothermal operation. The designed temperature programming profile is displayed in figure 1.

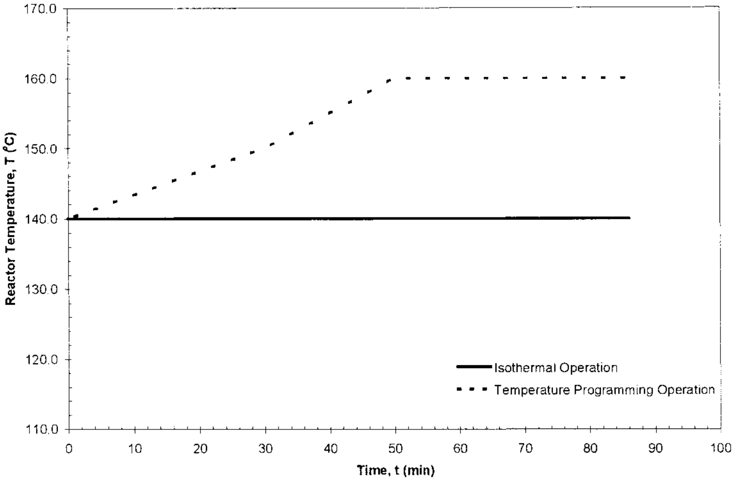

Figure 1 Reactor temperature profile for the bulk polymerization of styrene initiated b Luperox 101 (0.002 M) for isothermal and temperature programming operation

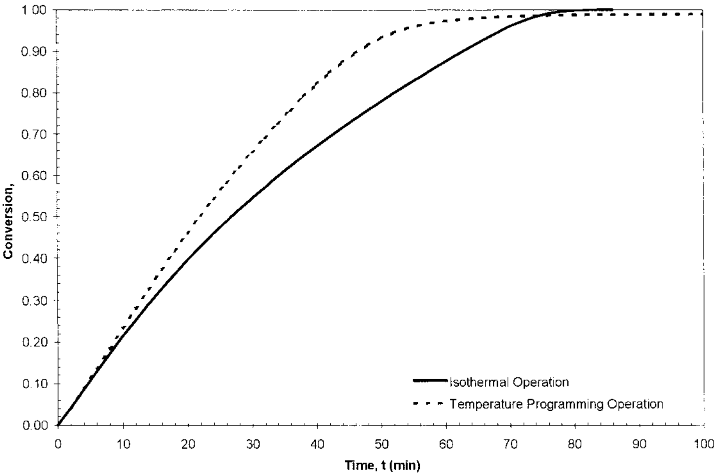

Figure 2 Conversion as a function of time for the bulk polymerization of styrene initiated by Luperox 101 (0.002 M) for isothermal operation at 140 °C and temperature programming operation

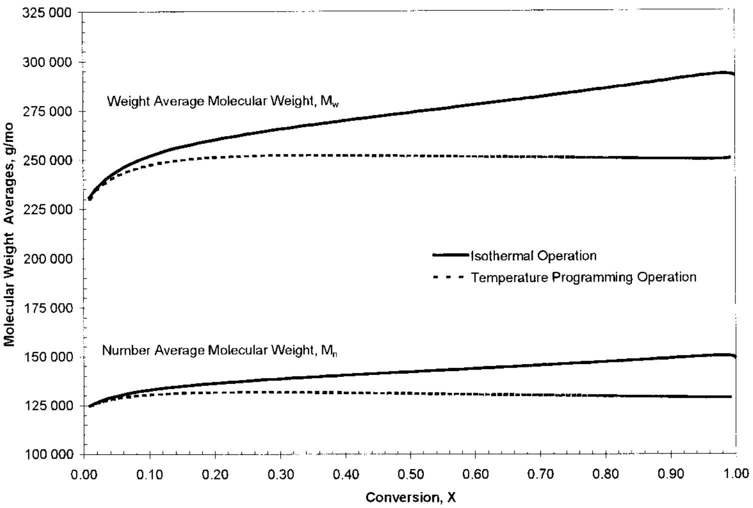

Figure 3 Molecular weight averages for the bulk polymerization of styrene initaited by Luperox 101 (0.002M) for isothermal operation at 140°C and temperature programming operation.

Recently, tetra-functional initiators have also been introduced for styrenics. In 2001, Atofina Chemicals introduced a novel tetra-functional initiator, Luperox JWEB50, developed specifically for the styrenics industry to produce high molecular weight, high-heat, crystal polystyrene at improved productivity in a cost-effective manner. JWEB50 is a room temperature stable, liquid peroxide with a half-life similar to currently used cyclic perketals, appropriate for use in mass polystyrene processes. A unique aspect of JWEB50 is its ability to produce long chain branching, in addition to providing higher molecular weight resins than those obtainable from a bi-functional initiator alone. Krupinski (2000)[46] used a combination of thermal and tetra-functional peroxide initiation to produce polystyrenics with improved melt strength. An extensive (and the first academic) kinetic evaluation of JWEB50 (with studies of temperature, initiator concentration and initiator functionality effects) is given by Fityani-Trimm and Penlidis (2001)[47].

2.3 Using Reactor Combination

It is known that general purpose polystyrene (GPPS) can be produced in a CSTR reactor. However, due to the limitation of mixing and heat removal capacity of a CSTR, polystyrene can only be produced at relative low temperatures and conversion levels. Effort has been made for many years to increase the heat removal capacity, e.g. use of additional cooling coil, however such apparatus together with a predetermined temperature profile may lead to undesired product properties. The high viscosity of polystyrene also presents a processing problem for a CSTR reactor. Even though it is of common industrial practise to add a small percentage of solvent like toluene or ethyl benzene into the reaction mixture, polystyrene still can not be produced in a CSTR up to high conversion. In order to increase productivity and reduce residual monomer, it is highly desired to achieve high conversion. An alternative is to combine the CSTR with a plug flow reactor or, sometimes called, a tower reactor. CSTR is suitable for polymerization at low conversion level where the viscosity is relatively low. The reaction mixture is subsequently transferred to a plug flow reactor. The unagitated plug flow reactor can have several temperature zones and additional reactant can be added into each zone. This provides greater flexibility in comparison to a CSTR. It is also common to use a loop reactor with a static mixer instead of a CSTR reactor. Such loop reactor has better mixing for more viscous reaction mixture. A pilot plant which is similar to the process described above was used by Cavin et al.(2000 b, c)[48-49] in their work on online conversion monitoring using an ultrasound velocity measuring device. Figure 4 displays a sketch of such a pilot plant.

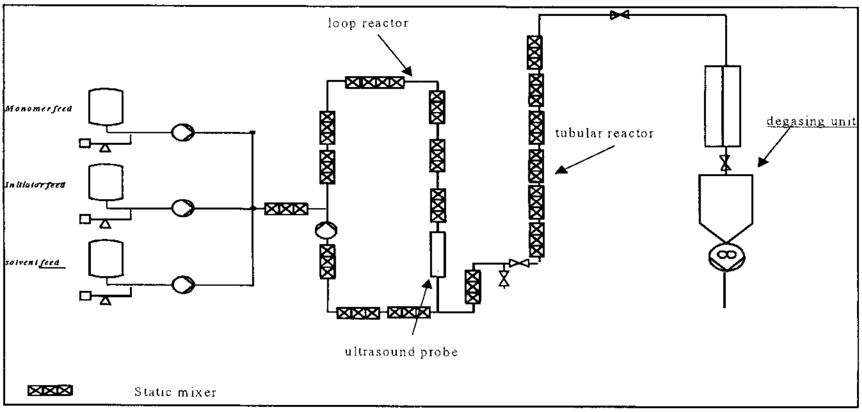

Figure 4 Pilot plant (a loop reactor and a plug flow reactor) for styrene polymerization

3. Conclusion

It has been known that for a commodity product like polystyrene, the production cost can be reduced by optimizing the process and polystyrene with desired properties can be produced by regulating the reaction conditions. This paper has discussed briefly the kinetics of styrene polymerization and several commonly used process optimization policies. It has been demonstrated that by using a temperature profile combined with selective mono- or bifunctional initiators one can decrease bach time while still maintaining the desired molecular weight averages. The more recently developed new tetra-functional initiator by Elf-Atochem provides a new tool for controlling/optimization purposes. Additional optimization methods not discussed in this paper are related to advanced online control theory combined with a kinetic model to control the polystyrene process. Mankar et al. (1998)[50] gave a review of on-line optimizing control of polymerization reactors.

Nomenclature

f = initiator decomposition efficiency
f' = bifunctional initiator decomposition efficiency
k_d = rate constant for decomposition (1/sec)
k_{d1} = rate constant for decomposition of bifunctional initiator (1/sec)
k_{d2} = rate constant for decomposition of macro peroxide initiator (1/sec)
k_i = thermal initiation efficiency (L^3/mol^{3}ßsec)
k_p = diffusion controlled rate constant for propagation (L/mol_sec)
k_t = diffusion controlled rate constant for termination (L/mol_sec)
k_{ft} = rate constant for chain transfer (L/molßsec)
k_z = rate constant for inhibition (L/molßsec)
T = reaction temperature

$[j]$ = concentration of species j (mol/L)

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