

A kinetic mathematical model for heterogeneous Ziegler–Natta copolymerization

A. B. de Carvalho

Research and Development Department, Polipropileno SA, Polo Petroquímico do Nordeste, Rua Hidrogenio, s/n, Camacari, Bahia, Brazil 42 810

P. E. Gloor and A. E. Hamielec*

McMaster Institute for Polymer Production Technology, Department of Chemical Engineering, McMaster University, Hamilton, Ontario, Canada L8S 4L7

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A kinetic model has been derived based upon multiple catalyst sites of differing reactivities for the Ziegler–Natta copolymerization of olefins. The kinetic scheme accounts for the formation, initiation and deactivation of active sites, as well as for spontaneous transfer and for transfer reactions to hydrogen, monomer and organometallics. The model predicts the rate of polymerization, the copolymer composition and the molecular-weight distribution of the polymer produced. The model accounts for the observed broad copolymer composition and molecular-weight distributions. A method for the estimation of the model parameters via temperature-rising elution fractionation, gel permeation chromatography and nuclear magnetic resonance is discussed. Some simple calculations are performed to demonstrate that the observed broad copolymer composition and molecular-weight distributions can be predicted by this model.

(Keywords: Ziegler–Natta catalysts; copolymerization; kinetics; multiple-site model; temperature-rising elution fractionation; gel permeation chromatography; nuclear magnetic resonance)

INTRODUCTION

Ever since their discovery, heterogeneous isospecific catalysts based on TiCl_3 and organometallic compounds have caused not only radical industrial innovations but also a great deal of scientific effort for better understanding of the fundamentals involved in this field. This research has covered a wide spectrum of subjects including polymerization kinetics and chemistry, catalyst synthesis, and the characterization of both homopolymers and copolymers. These attempts have resulted in several new developments, especially with regard to catalyst synthesis. For instance, the production of supported catalysts based on TiCl_4 and MgCl_2 has induced the appearance of new technologies such as gas-phase and bulk processes which are now replacing the old slurry plants. Unfortunately, much of the scientific information generated during the development of creating such processes is maintained in secrecy by the companies which have performed the studies. Even so, a large number of papers have been published, as well as some relevant books and theses.

Despite all of this research, many aspects related to the polymerization of olefins using heterogeneous Ziegler–Natta catalysts remain poorly understood and even matters of some controversy. One of the most important sources of controversy is the reason for the broad molecular-weight distribution (*MWD*) and for the compositional inhomogeneity of copolymers even if prepared with a constant monomer composition. Presently, there are two main theories which try to explain the observed phenomena: namely, either the

presence of a distribution of activities for the catalyst sites, or diffusional effects limiting the transport of reactants. The former assumes the existence of multiple catalyst sites of different activities, whereas the latter proposes the encapsulation of catalyst particles by the semicrystalline polymer, creating a diffusional barrier to monomer transport.

According to the first point of view, the different types of sites, related not only to the propagation rate but also to the decay rate and possibly to some transfer rates, account for both the broad *MWD* and the copolymer composition inhomogeneity. As for the second hypothesis, two consequences should occur: (i) the efficiency of the catalyst will drop as catalyst particles become more and more encapsulated; and (ii) active sites at different radial positions in the particle will have different levels of monomer available to them. Furthermore, different monomers will have different diffusion rates, resulting in the production of a spectrum of chain lengths and compositions.

Literature review

Boor¹ recognized that the reasons for the wide *MWD* in polymers prepared using Ziegler–Natta (ZN) catalysts were not well understood and presented five proposals covering both chemical and physical points of view. One of these was the existence of a multiple-site distribution related to the propagation rate constants, as had been proposed by Grievson²; whereas two others took into account diffusional limitations created by the encapsulation of the reactive sites by the growing polymer chains. In fact, many experimental results have been interpreted either by using a distribution of site

* To whom correspondence should be addressed

activities^{3–22} or by using the diffusional limitation approach^{23–37}.

Kissin³⁸ has pointed out some interesting evidence for the multiple-activity-site distribution hypothesis. After having discussed the inability of different diffusional models in the formulation of a coherent quantitative theory to explain the wide *MWD*, he presented strong evidence, based upon experimental work, to account for the existence of a distribution of rate constants. Considering the copolymer composition inhomogeneity, he stated that even for low monomer conversion, when diffusional effects should be minimized, it has been found that the copolymer composition is not homogeneous even for polymer produced at constant monomer composition.

A large number of physical models have been proposed in order to explain the wide *MWD* and the copolymer compositional inhomogeneity. Some of these have been described mathematically and applied for simulation purposes^{24,32,33,36,37,39,40}. Models have been developed in order to take into account the wide distribution of rate constants. Some attempts consider a small number (around 2) of different sites³⁹. The reasons for such a small number of sites seem to be that the added complexity of using more sites may limit the model's use for simulation purposes, and the estimation of the large number of kinetic parameters may be prohibitive. Bosworth⁴⁰ has made an attempt to use statistical distributions (normal and log-normal) for the propagation rate constants and has concluded that the variance of the distributions must be very large to explain the observed polydispersity. Bosworth considered this large variance to be improbable. Both authors^{39,40} eventually use a model that included diffusional aspects and a few types of active sites.

Why a multiple-active-site model

We believe that the existence of a distribution for the rate-constant values with respect to the catalyst sites constitutes the most probable hypothesis for explaining the broad molecular-weight, copolymer composition and stereoregularity distributions, for the following reasons.

(a) Kissin³⁸ states that fractions, separated based upon solubility, of homopolymer produced by heterogeneous ZN catalysts have a characteristic stereoregularity (as measured by melting points, n.m.r. and i.r.) and are not just a mixture of purely isotactic and atactic polymer. This suggests that there is a continuous distribution of values for the stereoreactivity ratios s^L and s^D , where:

$$s^D = k^{DD}/k^{DL} \quad s^L = k^{LL}/k^{LD}$$

Here DD and LL represent the two possibilities for isotactic linking between monomers and DL and LD represent the two possible syndiotactic linkings. Diffusional limitation models cannot account for this distribution of chains with regard to stereoregularity, but a multiple-site model, each class of sites having its characteristic s^D and s^L values, naturally accounts for this phenomenon.

(b) Usami⁴¹ has separated fractions of linear low-density polyethylene (LLDPE) using temperature-rising elution fractionation (TREF). Their TREF curve had two distinct peaks, representing distinct copolymer compositions. The reactivity ratios, as measured by ¹³C n.m.r., were different for each peak. They concluded that each peak was produced by a different kind of active site.

Based upon this evidence we believe that a valid model must include multiple sites for the Ziegler–Natta polymerization of olefins. Under certain conditions it may be necessary to include diffusional limitations for the reactions. This could be added later as necessary.

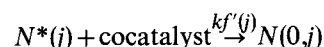
REACTION MECHANISM

The polymerization reactions occur at several reactive sites on the catalyst particle. In general, each class of sites (i.e. sites of type j) will have different reaction rates associated with it. The reactions listed below correspond to production of j -type sites and propagation, transfer and deactivation reactions on these. It is assumed that a terminal model is appropriate to model these reactions and thus penultimate effects are ignored.

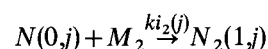
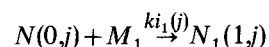
Initiation

We shall define any active site with a monomer molecule or growing polymer chain on it as a propagation site ($N(r,j)$ for $r=1,2,3,\dots$). Any active site without a monomer molecule or growing chain is an initiation site ($N(0,j)$, $N_H(0,j)$, $N_R(0,j)$). The number of active sites is the sum of the propagation sites and the initiation sites. A potential site ($N^*(j)$) is a site that may react via a formation reaction to form an active site. The number of sites is most likely proportional to the total surface area of the catalyst particles.

The formation of type- j propagation sites can be written as two reactions. First a potential site on the catalyst particle and the cocatalyst react to form an initiation site ($N(0,j)$). This site can then react with monomer i to produce a propagation site ($N_i(1,j)$) of unit length. The relative rates of these two reactions determine the extent of the acceleration stage in the polymerization³⁸. The reactions may be written as:



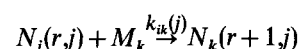
This initiation site can then react with monomer type 1 and monomer type 2 to form a propagation site:



The initiation sites $N_H(0,j)$ and $N_R(0,j)$ are formed by transfer to hydrogen and spontaneous transfer, and by transfer to organometallic reactions, as explained below.

Propagation

The propagation sites support growing polymer chains. These chains grow by the addition of either monomer type 1 or monomer type 2 to the chain at the point where the chain is attached to the catalyst site. The chain itself can end in either a monomer type 1 or type 2 group. Thus there are four propagation reactions: reactions between a chain r units long ending in a monomer type- i group and a monomer type- k molecule ($i=1,2$ and $k=1,2$):

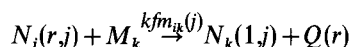


If one assumes a terminal-type model, then the propagation rate constants are not functions of the penultimate monomer type, but functions of temperature and site type only.

Transfer

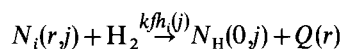
As well as undergoing propagation reactions, these sites can be involved in transfer reactions. These reactions involve the substitution of a small molecule on the active site, displacing the polymer chain. This chain becomes a dead polymer chain of length r ($Q(r)$) and is no longer involved in the polymerization. The active site with the small molecule attached can then undergo propagation reactions or initiation reactions to produce propagation sites. Thus one catalyst site can produce many polymer chains during the reaction.

Transfer to monomer. Reactions can occur between a chain r units long ending in a monomer type- i group and a monomer type- k molecule to form a site with a monomer k (i.e. a polymer chain of length 1) on it and a dead polymer chain of length r ending with a terminal double bond. This reaction can be expressed as:

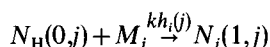


This site can then undergo propagation to become a long polymer chain.

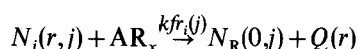
Transfer to hydrogen. Reactions can occur between a chain r units long ending in a monomer type- i group and a hydrogen molecule to form an initiation site with a hydrogen on it and a dead polymer chain of length r :



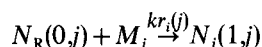
This site can then undergo an initiation reaction with monomer type i to become a growing polymer chain:



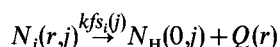
Transfer to organometallics. Reactions can occur between a chain r units long ending in a monomer type- i group and an organometallic molecule left over from the catalyst formation reactions:



The dead polymer chain has an end-group of type AR_{x-1} . This initiation site can then undergo an initiation-type reaction with monomer type i to become a growing polymer chain:



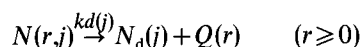
Spontaneous transfer. The propagation site may be able to lose its polymer chain, forming a site with a hydrogen on it and a dead polymer chain with a terminal double bond:



This site can undergo initiation reactions with monomer to become a growing chain as for transfer to hydrogen.

Deactivation

It has been shown³⁸ that for some polymerizations the rate of reaction will decrease with time. This suggests a catalyst deactivation reaction of unstable centres. It has been found^{42–46} that the rate of deactivation does not depend upon either the amount or the type of monomer present. Thus the rate of deactivation can be considered to be independent of the polymerization process. The deactivation reaction is probably a complex series of reactions, but one may be able to approximate it by a first-order reaction of the form:



The deactivation reaction forms a dead polymer chain and a dead catalyst site. The rate of decay does not continue until all the catalyst sites are dead. It appears to level off after 1 or 2 h³⁸. This suggests that not all j sites have the same stability, and for some types of sites $kd(j)$ will be equal to zero.

MODEL DEVELOPMENT

A mathematical model based upon this kinetic scheme can be derived. This model will be essentially mass balances on the species present in the reactor and will be a series of algebraic and differential equations.

Formation of initiation and propagation sites

The rate of formation of active sites will be given by:

Rate of formation of type- j active sites = $kf'(j) \cdot [N^*(j)] \cdot [\text{cocat}] \cdot V$ (mol s⁻¹)

If the cocatalyst is added in excess then:

Rate of formation of type- j active sites = $kf(j) \cdot [N^*(j)] \cdot V$ (mol s⁻¹)

where $[X]$ denotes concentration of species X . The concentrations of sites are in moles per litre in the reactor, and all other concentrations of reactant species are moles adsorbed per unit of catalyst surface, multiplied by the total catalyst surface area per litre of reaction mixture. In this way all concentrations have units of moles per litre of reaction mixture, i.e.

$$\frac{\text{moles}}{\text{area}} \times \frac{\text{area}}{\text{litre}} = \frac{\text{moles}}{\text{litre}}$$

We shall assume that the concentrations of reactants available to each site are independent of the site type and location. It may be that local concentrations may vary, but we are neglecting this.

In the same manner one could define the concentration of sites as the moles of sites per unit catalyst surface area, multiplied by the total catalyst surface area per unit volume in the reactor. This gives the same result as saying moles of sites per unit volume. In a slurry reactor the volume of the reaction mixture is the volume of the

diluent phase, since there are no catalyst sites in the headspace.

$[N^*(j)]$ is the concentration (mol l^{-1}) of potential sites of type j in the reactor, and V is the reaction volume in litres. The units of the second-order rate constants are $\text{l mol}^{-1} \text{s}^{-1}$. The deactivation rate constant may not be a function of what type of chain is growing on the site or what type of molecule resides on the site but a function only of the site type.

The rate of deactivation of active sites will be given by:

$$\begin{aligned} \text{Rate of deactivation} \\ \text{of type-}j \text{ active sites} &= kd(j) \cdot [N_T(j)] \cdot V \quad (\text{mol s}^{-1}) \end{aligned}$$

Notice that the deactivation rate constant, $kd(j)$, will be zero for some values of j .

Since transfer and propagation reactions do not change the total number of active sites, one obtains a balance on the total number of type- j active sites in the reactor as:

$$\begin{aligned} dN_T(j)/dt &= kf(j) \cdot [N^*(j)] \cdot V - kd(j) \cdot [N_T(j)] \cdot V \\ &\quad + N_{T(j)\text{in}} - N_{T(j)\text{out}} \quad (\text{mol s}^{-1}) \end{aligned}$$

where

$$N_T(j) = \sum_{r=1}^{\infty} N(r,j) + N_H(0,j) + N_R(0,j) + N(0,j)$$

Notice that $kd(j)$ depends only on j , i.e. it has been assumed to be equal for every kind of site which constitutes $N_T(j)$.

The inflow and outflow will be determined by the type of process by which the polymer is made, i.e. batch, semibatch or continuous.

A balance on the total number of active sites, where the number of active sites can be written in terms of moles in the reactor (e.g. $[N(r,j)] \cdot V = N(r,j)$), is given by:

$$dN_T/dt = \bar{kf} \cdot N_T^* - \bar{kd} \cdot N_T + N_{T,\text{in}} - N_{T,\text{out}}$$

where

$$\begin{aligned} \sum_{j=1}^{\infty} N_T(j) &= N_T \\ \bar{kf} &= \sum_{j=1}^{\infty} [kf(j) \cdot \gamma(j)] \\ \bar{kd} &= \sum_{j=1}^{\infty} [kd(j) \cdot \gamma(j)] \end{aligned}$$

and the fraction of total active sites that are of type j is given by:

$$\gamma(j) = N(j)/N_T$$

The total number of potential sites is N_T^* .

One must also perform mass balances on the number of initiation sites in the reactor:

$$\begin{aligned} dN_H(0,j)/dt &= kfh(j) \cdot [H_2] \cdot Y_0(j) + kfs(j) \cdot Y_0(j) \\ &\quad - kh(j) \cdot N_H(0,j) \cdot [M] - kd(j) \cdot N_H(0,j) \\ &\quad + N_{H(0,j)\text{in}} - N_{H(0,j)\text{out}} \end{aligned}$$

$$\begin{aligned} dN_R(0,j)/dt &= kfr(j) \cdot [A] \cdot Y_0(j) - kr(j) \cdot N_R(0,j) \cdot [M] \\ &\quad - kd(j) \cdot N_R(0,j) + N_{R(0,j)\text{in}} - N_{R(0,j)\text{out}} \end{aligned}$$

$$\begin{aligned} dN(0,j)/dt &= kf(j) \cdot N^*(j) - ki(j) \cdot N(0,j) \cdot [M] - kd(j) \cdot N(0,j) \\ &\quad + N(0,j)\text{in} - N(0,j)\text{out} \end{aligned}$$

where $Y_0(j)$ is the zeroth moment of the live polymer distribution on type- j sites, or equivalently the moles of j -type propagation sites in the reactor. $[A]$ is the concentration of organometallics. The rate constants $kfr(j)$, $kfr_1(j)$, $kfr_2(j)$, $kfh(j)$, $kfh_1(j)$, $kfh_2(j)$, $kfs(j)$, $kfs_1(j)$, $kfs_2(j)$, $kr(j)$, $kr_1(j)$, $kr_2(j)$, $kh(j)$, $kh_1(j)$, $kh_2(j)$, $ki(j)$, $ki_1(j)$, $ki_2(j)$ and $kd(j)$ are pseudo rate constants that take into account the copolymer and comonomer composition, i.e.

$$kfr(j) = \phi_1(j) \cdot kfr_1(j) + \phi_2(j) \cdot kfr_2(j)$$

$$kfh(j) = \phi_1(j) \cdot kfh_1(j) + \phi_2(j) \cdot kfh_2(j)$$

$$kfs(j) = \phi_1(j) \cdot kfs_1(j) + \phi_2(j) \cdot kfs_2(j)$$

$$kr(j) = f_1 \cdot kr_1(j) + f_2 \cdot kr_2(j)$$

$$kh(j) = f_1 \cdot kh_1(j) + f_2 \cdot kh_2(j)$$

$$ki(j) = f_1 \cdot ki_1(j) + f_2 \cdot ki_2(j)$$

and $\phi_1(j)$ is the fraction of j -type sites that have a growing chain ending with a monomer 1-type unit and accounts for the copolymer composition. Finally f_1 is the mole fraction of monomer adsorbed onto the catalyst surface that is monomer type 1.

Rate of polymerization

The rate of polymerization can be found from the rate of monomer consumption. The total rate of monomer consumption is given by propagation, transfer and initiation reactions. If one assumes the long-chain approximation, then one can neglect the consumption of monomer due to the transfer and initiation reactions. The rate of polymerization of monomer type 1 is:

$$Rp_1 = \sum_{j=1}^{\infty} \{k_{11}(j) \cdot N_1(j) + k_{21}(j) \cdot N_2(j)\} [M_1] \quad (\text{mol s}^{-1})$$

where $[M_1]$ is the concentration of monomer on the surface of the catalyst and $N_i(j)$ is the moles of j -type sites having a growing chain that ends in a monomer type- i end-group. The rate of polymerization of monomer type 2 is given by:

$$Rp_2 = \sum_{j=1}^{\infty} \{k_{22}(j) \cdot N_2(j) + k_{12}(j) \cdot N_1(j)\} [M_2] \quad (\text{mol s}^{-1})$$

The rate of change of moles of total monomer in the reactor is given by:

$$dM/dt = \sum_{j=1}^{\infty} -\{kp(j) \cdot [M] \cdot N(j)\} + M_{\text{in}} - M_{\text{out}} \quad (\text{mol s}^{-1})$$

where M is the total moles of monomer,

$[M] = [M_1] + [M_2]$ is the concentration of total monomer on the surface of the catalyst, and $N(j) = N_1(j) + N_2(j)$ is the total moles of propagation sites of type j . The pseudo propagation rate constant is given by:

$$kp(j) = k_{11}(j) \cdot \phi_1(j) \cdot f_1 + k_{12}(j) \cdot \phi_1(j) \cdot f_2 + k_{21}(j) \cdot \phi_2(j) \cdot f_1 + k_{22}(j) \cdot \phi_2(j) \cdot f_2$$

If we define the fraction of propagation sites that are of type j as:

$$\eta(j) = N(j)/N_p$$

where N_p is the total number of propagation sites:

$$\begin{aligned} N_p &= \sum_{r=1}^{\infty} \sum_{j=1}^{\infty} N(r,j) \\ &= \sum_{j=1}^{\infty} \{N_T(j) - [N_R(0,j) + N_H(0,j) + N(0,j)]\} \\ &= \sum_{j=1}^{\infty} Y_0(j) \end{aligned}$$

then the mean propagation rate constant will be given by:

$$\overline{kp} = \sum_{j=1}^{\infty} kp(j) \cdot \eta(j)$$

and the rate of polymerization will be given by:

$$Rp = \overline{kp} \cdot [M] \cdot N_p \quad (\text{mol s}^{-1})$$

The instantaneous weight fraction of polymer made by each j site will be given by:

$$W(j) = \frac{\{m_1 \cdot F_{1,inst}(j) + m_2 \cdot [1 - F_{1,inst}(j)]\} \cdot kp(j) \cdot N(j)}{\sum_{j=1}^{\infty} \{m_1 \cdot F_{1,inst}(j) + m_2 \cdot [1 - F_{1,inst}(j)]\} \cdot kp(j) \cdot N(j)}$$

where m_1 and m_2 are the molecular weights of monomers 1 and 2 and $F_{1,inst}$ is the instantaneous copolymer composition (mole fraction of monomer 1-type units in the polymer).

Copolymer composition

The total moles of monomer type 1 bound as polymer (both living and dead) in the reactor is given by the solution to:

$$dP_1/dt = \sum_{j=1}^{\infty} \{[k_{11}(j) \cdot f_1 \cdot \phi_1(j) + k_{21}(j) \cdot \phi_2(j) \cdot f_1] \times N(j) \cdot [M]\}_j + P_{1,in} - P_{1,out} \quad (\text{mol s}^{-1})$$

A similar equation can be written for moles of monomer type 2 bound as polymer in the reactor. The copolymer composition of the polymer in the reactor is then given by:

$$F_1 = P_1/(P_1 + P_2)$$

and the instantaneous copolymer composition of the polymer made on a type- j site will be given by:

$$F_{1,inst}(j) = \frac{[r_1(j) - 1]f_1^2 + f_1}{[r_1(j) + r_2(j) - 2]f_1^2 + 2[1 - r_2(j)]f_1 + r_2(j)}$$

where the reactivity ratios for each type of site are given by:

$$r_1(j) = k_{11}(j)/k_{12}(j) \quad r_2(j) = k_{22}(j)/k_{21}(j)$$

The fraction of propagation sites that have a monomer type-1 end-group on it can be found by using the second long-chain approximation:

$$k_{12}(j) \cdot \phi_1(j) \cdot f_2 = k_{21}(j) \cdot \phi_2(j) \cdot f_1$$

and

$$\phi_2(j) = 1 - \phi_1(j)$$

to get:

$$\phi_1(j) = \frac{k_{21}(j) \cdot f_1}{k_{21}(j) \cdot f_1 + k_{12}(j) \cdot f_2}$$

Concentrations on the catalyst surface

To this point we have described the polymerization in terms of the concentrations of the species on the surface of the catalyst. Unfortunately, one knows not these concentrations but the bulk concentrations or partial pressures of the species in the reactor. For this reason one must consider expressions for the surface concentrations in terms of the bulk concentrations.

Any species in the reactor, except growing polymer chains, can in theory exist in four phases. These species may be (i) in the vapour phase in the headspace, (ii) dissolved in the diluent phase, (iii) in the swollen polymer phase surrounding a catalyst particle, and of course (iv) on the surface of the catalyst. Each species will have different affinities for each phase. There may be diffusion limitations between any two phases; for example, there may be resistance to diffusion from the vapour phase into the liquid phase^{47,48}, or a diffusion limitation from the diluent phase through a very viscous swollen polymer particle to the catalyst surface. These limitations may depend on the reactor type, and on the operating conditions.

One can find the equilibrium concentrations of the species in the diluent and the vapour phases by using some equation of state (e.g. the modified Benedict–Webb–Rubin equation⁴⁹) or phase-equilibrium constants⁵⁰ to relate the pressure of the reactor to the composition in the liquid phase.

To relate the surface concentrations to the surrounding concentrations one can use the Langmuir adsorption equation. The assumptions that must be valid to use this equation are⁴²: (i) adsorption of a molecule or atom takes place on an adsorption site, and only one molecule can be accepted by each site; (ii) the surface sites all have identical heats of adsorption; and (iii) there are no energy interactions between the adsorbed molecules. Then the fraction of adsorption sites on the catalyst surface that

have a species- k molecule adsorbed on them is given by:

$$\theta_k = \frac{K_k C_k}{1 + \sum_i K_i C_i}$$

Here k can be monomer, comonomer, organometallic or hydrogen, and the summation with respect to i includes all species that compete for adsorption sites on the catalyst surface including species k . In this expression, K_i is the adsorption equilibrium constant for species i and is a function of temperature:

$$K_i = (K_0)_i \exp(E_i/RT)$$

the activation energy E_i is of the order of 10 kcal mol⁻¹ (ref. 42), and C_i is the concentration of species i in the surrounding phase.

The total concentration of species k on the surface is given by:

$$[k] = \theta_k \theta_T \quad (\text{moles/volume})$$

where θ_T is the total number of adsorption sites on the catalyst surface per unit volume. This value is proportional to the total catalyst surface area divided by the volume of the reaction mixture.

For a diatomic molecule like H₂, which is adsorbed in the dissociated form, the term $K_{\text{H}C_{\text{H}}}$ is replaced by $(K_{\text{H}C_{\text{H}}})^{1/2}$.

Molecular-weight development

In order for the model to be useful, it must be able to predict the molecular weight of the polymer produced. The development of the molecular-weight equations is presented for the general case, and then a simplified development is derived. This simplified set of equations will be applicable under certain operating conditions and gives us a different insight into the factors that affect the molecular-weight distribution. The simplified equations should also be easier to solve.

General development. In general, both the molecular weight of the live and dead polymer are significant to the overall molecular weights. For this general case it would be difficult to solve for the molecular-weight distribution, but easy to solve for the leading moments of the distribution. From this one can obtain expressions for the number- and weight-average molecular weights and for the polydispersity of the distribution.

One considers a balance on the moles of growing chains of length r on a j -type site (for $r \geq 2$):

$$\begin{aligned} dN(r,j)/dt = & kp(j) \cdot [M] \cdot N(r-1,j) - kp(j) \cdot [M] \cdot N(r,j) \\ & - kt(j) \cdot N(r,j) - kfm(j) \cdot [M] \cdot N(r,j) - kd(j) \cdot N(r,j) \\ & + N(r,j)_{\text{in}} - N(r,j)_{\text{out}} \end{aligned}$$

where

$$kt(j) = kfs(j) + kfh(j) \cdot [H_2] + kfr(j) \cdot [A]$$

All of the rate constants presented here are pseudo rate constants that take into account the comonomer and copolymer composition.

A balance on propagation sites of type j of unit length yields:

$$\begin{aligned} dN(1,j)/dt = & kfm(j) \cdot [M] \cdot Y_0(j) + kI(j) \cdot [M] - kd(j) \cdot N(1,j) \\ & - kt(j) \cdot N(1,j) - kp(j) \cdot [M] \cdot N(1,j) - kfm(j) \cdot [M] \cdot N(1,j) \\ & + N(1,j)_{\text{in}} - N(1,j)_{\text{out}} \end{aligned}$$

where

$$kI(j) = kr(j) \cdot N_{\text{R}}(0,j) + kh(j) \cdot N_{\text{H}}(0,j) + ki(j) \cdot N(0,j)$$

and $Y_0(j)$ is the zeroth moment of the live polymer distribution on the site type j . The consumption of $N(1,j)$ by transfer to monomer term appears because we have included $N(1,j)$ in the generation of $N(1,j)$ by transfer to monomer (in $Y_0(j)$).

The definition of the n th moment of the live polymer distribution is:

$$Y_n(j) = \sum_{r=0}^{\infty} r^n \cdot N(r,j)$$

and notice that $N(0,j)$ (i.e. $r=0$) is not considered live polymer, so the summation may start at $r=1$ instead of $r=0$. To find this moment we must simply multiply the equation for $N(r,j)$ by r^n and sum it from $r=2 \rightarrow \infty$, then add the equation for $N(1,j)$ to complete the sum from $r=1 \rightarrow \infty$.

Setting $n=0$ and noting that:

$$\sum_{r=2}^{\infty} N(r-1,j) = \sum_{r=1}^{\infty} N(r,j) = Y_0(j)$$

one gets:

$$\begin{aligned} dY_0(j)/dt = & kI(j) \cdot [M] - kt(j) \cdot Y_0(j) - kd(j) \cdot Y_0(j) \\ & + Y_0(j)_{\text{in}} - Y_0(j)_{\text{out}} \end{aligned}$$

Repeating this procedure for $n=1$ and noting that:

$$\sum_{r=2}^{\infty} r \cdot N(r-1,j) = \sum_{r=1}^{\infty} (r+1) \cdot N(r,j) = Y_1(j) + Y_0(j)$$

and that:

$$Y_2(j) \gg Y_1(j) \gg Y_0(j)$$

one gets:

$$\begin{aligned} dY_1(j)/dt = & kp(j) \cdot [M] \cdot Y_0(j) + kI(j) \cdot [M] \\ & - kfm(j) \cdot [M] \cdot Y_1(j) - kt(j) \cdot Y_1(j) - kd(j) \cdot Y_1(j) \\ & + Y_1(j)_{\text{in}} - Y_1(j)_{\text{out}} \end{aligned}$$

And repeating this procedure for $n=2$ and noting that:

$$\sum_{r=2}^{\infty} r^2 \cdot N(r-1,j) = \sum_{r=1}^{\infty} (r+1)^2 \cdot N(r,j) = Y_2(j) + 2Y_1(j) + Y_0(j)$$

one gets:

$$dY_2(j)/dt = kp(j) \cdot [M] \cdot 2Y_1(j) + kI(j) \cdot [M] - kfm(j) \cdot [M] \cdot Y_2(j) - kt(j) \cdot Y_2(j) - kd(j) \cdot Y_2(j) + Y_2(j)_{in} - Y_2(j)_{out}$$

Now one must account for the dead polymer produced by the transfer and deactivation reactions. A balance on dead polymer of chain length r produced by a j -type site gives (for $r \geq 2$):

$$dQ(r,j)/dt = kt(j) \cdot N(r,j) + kfm(j) \cdot [M] \cdot N(r,j) + kd(j) \cdot N(r,j) + Q(r,j)_{in} - Q(r,j)_{out}$$

Since $Q(1,j)$ is not considered dead polymer $Q(1,j) = 0$.

Let the n th moment of the dead polymer distribution produced by a type- j site be given by:

$$X_n(j) = \sum_{r=1}^{\infty} r^n \cdot Q(r,j)$$

The $N(1,j)$ term must be subtracted since the transfer reactions with $N(1,j)$ do not produce polymer but:

$$X_2(j) \gg X_1(j) \gg X_0(j) \gg N(1,j)$$

The moments of the dead polymer distribution produced by site j are given by:

$$dX_0(j)/dt = \{kt(j) + kfm(j) \cdot [M] + kd(j)\} \cdot Y_0(j) + X_0(j)_{in} - X_0(j)_{out}$$

$$dX_1(j)/dt = \{kt(j) + kfm(j) \cdot [M] + kd(j)\} \cdot Y_1(j) + X_1(j)_{in} - X_1(j)_{out}$$

$$dX_2(j)/dt = \{kt(j) + kfm(j) \cdot [M] + kd(j)\} \cdot Y_2(j) + X_2(j)_{in} - X_2(j)_{out}$$

Now having the moments of the live and dead polymer distribution one can find the accumulated number- and weight-average chain lengths:

$$\overline{rn} = \frac{\sum_{j=1}^{\infty} [Y_1(j) + X_1(j)]}{\sum_{j=1}^{\infty} [Y_0(j) + X_0(j)]}$$

$$\overline{rw} = \frac{\sum_{j=1}^{\infty} [Y_2(j) + X_2(j)]}{\sum_{j=1}^{\infty} [Y_1(j) + X_1(j)]}$$

and the polydispersity is given by $\overline{rw}/\overline{rn}$.

Simplified analysis. This simplified analysis depends upon making some assumptions about the operating conditions in the reactor. This analysis allows one to find a simple expression for the instantaneous molecular-weight distribution and expressions for the number- and weight-average molecular weights as well as for the polydispersity. We shall introduce these assumptions at the points where they are needed in the derivation.

First, the stationary-state hypothesis (SSH) for

growing chains of length r will be assumed. This assumption involves the supposition that most of the polymer in the reactor is dead polymer, and the lifetime of the growing polymer is short with respect to the total polymerization time. This assumption should be valid for cases where the hydrogen concentration in the reactor is high enough for large transfer rates. Secondly, it will be assumed that the inflows and outflows of live polymer chains are negligible. If the concentration of live polymer in the reactor is small, then this should be valid. Furthermore, the deactivation rate will be considered to be negligible. Therefore, the moles of growing chains on type- j sites with a chain length of 2 or greater will be given by:

$$N(r,j) = \frac{kp(j) \cdot [M] \cdot N(r-1,j)}{kp(j) \cdot [M] + kt(j) + kfm(j) \cdot [M]} \quad (\text{moles})$$

If we let:

$$\begin{aligned} \tau(j) &= \frac{kt(j)}{kp(j) \cdot [M]} + \frac{kfm(j)}{kp(j)} \\ &= \frac{kfs(j) + kfh(j) \cdot [H_2] + kfr(j) \cdot [A]}{kp(j) \cdot [M]} + \frac{kfm(j)}{kp(j)} \end{aligned}$$

where it may be that only transfer to hydrogen is important, our equation for $N(r,j)$ becomes:

$$\begin{aligned} N(r,j) &= \left(\frac{1}{1 + \tau(j)} \right) \cdot N(r-1,j) \\ &= \left(\frac{1}{1 + \tau(j)} \right)^{r-1} \cdot N(1,j) \end{aligned}$$

Considering chains of unit length, the application of both the SSH and the assumption of a negligible amount of these species in the stream, as was made above, leads to:

$$\begin{aligned} N(1,j) &= \frac{kfm(j) \cdot [M] \cdot Y_0(j) + kI(j) \cdot [M]}{kp(j) \cdot [M] + kt(j) + kfm(j) \cdot [M]} \\ &= \frac{(kfm(j)/kp(j))Y_0(j) + (kI(j)/kp(j))}{1 + \tau(j)} \quad (\text{moles}) \end{aligned}$$

Now, repeating the same procedure for the initiation-type sites, one gets:

$$N_H(0,j) = \frac{[kfh(j) + kfs(j)] \cdot Y_0(j)}{kh(j) \cdot [M]} \quad (\text{moles})$$

$$N_R(0,j) = \frac{kfr(j) \cdot Y_0(j)}{kr(j) \cdot [M]} \quad (\text{moles})$$

$$N(0,j) = \frac{kf(j) \cdot N^*(j)}{ki(j) \cdot [M]} \quad (\text{moles})$$

Substituting these into the balance for $N(1,j)$ and dividing both top and bottom by $kp(j)[M]$ one gets:

$$N(1,j) = \frac{\tau(j) \cdot Y_0(j) + (kf(j)N^*(j)/kp(j))[M]}{1 + \tau(j)}$$

Let:

$$\beta(j) = \frac{kf(j) \cdot N^*(j)}{kp(j) \cdot [M]}$$

Thus:

$$N(r, j) = \left(\frac{1}{1 + \tau(j)} \right)^r [\beta(j) + \tau(j) \cdot Y_0(j)]$$

The instantaneous weight fraction of dead polymer produced on a *j*-type site that is length *r* is given by:

$$Wd(r, j) = \frac{\{kfm(j) \cdot [M] + kfh(j) \cdot [H_2] + kfr(j) \cdot [A] + kfs(j)\} N(r, j) \cdot r}{kp(j) \cdot [M] \cdot Y_0(j)}$$

$$= \tau(j) \cdot r \cdot \left(\frac{N(r, j)}{Y_0(j)} \right)$$

$$Wd(r, j) = \left(\frac{1}{1 + \tau(j)} \right)^r \cdot r \cdot [\tau(j) \cdot \beta(j) + \tau(j)^2]$$

If we assume that all the active sites are formed before flowing into the reactor then $\beta(j) = 0$ and we define:

$$\psi(j) = 1/[1 + \tau(j)]$$

Then:

$$Wd(r, j) = \tau(j)^2 \cdot r \cdot \psi(j)^r$$

Up to this point we have assumed that both the formation and the deactivation of active sites are negligible during the polymerization. This means that the number of active sites remains constant throughout the polymerization.

The instantaneous weight fraction of polymer produced by a type-*j* site is given by:

$$W(j) = \frac{kp(j) \cdot Y_0(j)}{kp \cdot N_p}$$

The overall dead polymer instantaneous molecular-weight distribution is given by:

$$Wd(r) = \sum_{j=1}^{\infty} W(j) \cdot \tau(j)^2 \cdot r \cdot \psi(j)^r$$

$$= \sum_{j=1}^{\infty} \frac{kp(j) \cdot Y_0(j)}{kp \cdot N_p} \cdot \tau(j)^2 \cdot r \cdot \psi(j)^r$$

The instantaneous weight-average chain length is given by:

$$rw = \sum_{r=1}^{\infty} [r \cdot Wd(r)]$$

$$= \sum_{j=1}^{\infty} \left(W(j) \cdot \tau(j)^2 \cdot \sum_{r=1}^{\infty} r^2 \cdot \psi(j)^r \right)$$

Notice that:

$$\sum_{r=1}^{\infty} [r^2 \cdot \psi(j)^{r-1}] = \frac{1 + \psi(j)}{[1 - \psi(j)]^3}$$

Then:

$$rw = \sum_{j=1}^{\infty} W(j) \cdot \tau(j)^2 \cdot \psi(j) \left(\frac{1 + \psi(j)}{[1 - \psi(j)]^3} \right)$$

If $\tau(j) \ll 1$ (as it should be since it is the ratio of transfer reactions to propagation reactions) then:

$$\psi(j) \approx 1$$

and

$$1 - \psi(j) = 1 - \left(\frac{1}{1 + \tau(j)} \right) = \frac{\tau(j)}{1 + \tau(j)} \sim \tau(j)$$

Then:

$$rw \approx 2 \sum_{j=1}^{\infty} [W(j)/\tau(j)]$$

Replacing *W*(*j*) we find that:

$$rw = \frac{2}{kp} \sum_{j=1}^{\infty} \frac{kp(j)^2 \cdot \eta(j)}{\lambda(j)}$$

where

$$\lambda(j) = kfm(j) + \frac{kfs(j)}{[M]} + \frac{kfr(j) \cdot [A]}{[M]} + \frac{kfh(j) \cdot [H_2]}{[M]}$$

Thus the instantaneous weight-average chain length for the polymer produced by a type-*j* site is given by:

$$rw(j) = 2/\tau(j)$$

The instantaneous number-average chain length is given by:

$$rn = \frac{1}{\sum_{r=1}^{\infty} [Wd(r)/r]}$$

$$\frac{1}{rn} = \sum_{j=1}^{\infty} \left(W(j) \cdot \tau(j)^2 \sum_{r=1}^{\infty} \psi(j)^r \right)$$

Since:

$$\sum_{r=1}^{\infty} \psi(j)^{r-1} = 1/[1 - \psi(j)]$$

therefore:

$$\frac{1}{rn} = \sum_{j=1}^{\infty} \left(W(j) \cdot \tau(j)^2 \cdot \frac{\psi(j)}{1 - \psi(j)} \right)$$

$$= \frac{1}{kp} \sum_{j=1}^{\infty} \eta(j) \cdot \lambda(j)$$

Also notice that the number-average molecular weight of the polymer produced by a type-*j* site is given by:

$$rn(j) = 1/\tau(j)$$

If we assume that the transfer reactions are not functions of the type of reactive site, then $\lambda(j)$ is not a function of j . It may quite well be valid if the rate of transfer to hydrogen dominates the transfer process. Hydrogen is a small molecule and may therefore have a transfer rate that is independent of the site type. Thus, the instantaneous polydispersity is given by:

$$\frac{rw}{rn} = 2 \left(1 + \frac{\sigma^2}{kp^2} \right)$$

where σ^2 is the variance of the distribution of propagation rate constants:

$$\sigma^2 = \sum_{j=1}^{\infty} \eta(j) \cdot [kp(j) - \bar{kp}]^2$$

We have derived an expression for the instantaneous polydispersity that uses only the mean propagation rate constant and the variance of the $kp(j)$ values. The instantaneous molecular-weight distribution for each j site is the most probable ($rw(j)/rn(j)=2$) and varies from the most probable for the entire polymer produced by the ratio of the variance of the $kp(j)$ values to the mean kp value. Nevertheless, this expression should be seen as an approximation which will only be valid if all the assumptions made during its derivation are fulfilled. As we have pointed out above, the *MWD* for a copolymer produced with heterogeneous ZN catalyst is broad even if the polymerization is carried out under steady-state conditions at constant monomer ratio. In that case, this equation is actually not able to predict a broad molecular-weight distribution when some of the most common statistical distributions are adopted for the propagation rate constant, $kp(j)$. For instance, if the propagation rate constant is assumed to be exponentially distributed, this equation will give a small value (equal to 4) for the polydispersity. In addition, if a normal distribution is assumed, one may have to consider negative values for the rate constant in order to achieve the usual large values for the polydispersity. Consequently, in order to explain the wide molecular-weight distribution by using this equation, one must adopt a skewed distribution for the propagation rate constant, such as the log-normal distribution. Even so, the value for the variance may be excessively large in order to achieve the observed large polydispersity.

To find the accumulated number- and weight-average molecular weights and polydispersity (rn , rw , rw/rn) we must find the weighted averages of the instantaneous values (rn , rw , rw/rn) and the inflows and outflows. To find the accumulated weight-average chain length we must take a mass-weighted average of rw , i.e. we must weight the instantaneous rw by the mass of polymer that is that rw . Mp is the mass of polymer in the reactor and m is the effective molecular weight per repeat unit. The subscripts 'in' and 'out' denote inflowing and outflowing quantities:

$$dMp \cdot \overline{rw} / dt = \overline{rw}_{in} \cdot Mp_{in} + rw \cdot m \cdot \overline{kp} \cdot N_p \cdot [M] - \overline{rw}_{out} \cdot Mp_{out}$$

$$dMp / dt = Mp_{in} + m \cdot \overline{kp} \cdot N_p \cdot [M] - Mp_{out}$$

and the accumulated weight-average molecular weight of

the polymer in the reactor is given by the ratio of the solutions to the two equations above, i.e.

$$\overline{rw} = Mp \cdot \overline{rw} / Mp$$

For an ideal continuously stirred tank reactor (CSTR) the properties of the outflowing polymer are the accumulated properties in the reactor, i.e. $rw_{out} = rw$.

To find the accumulated number-average chain length we must find the number-weighted average of rn , i.e. we must weight the instantaneous rn by the number of moles of polymer that is that rn , i.e. $Mp/(m \cdot rn)$:

$$\frac{d}{dt} \left(\frac{Mp}{m \cdot rn} \right) = \frac{Mp_{in}}{m \cdot rn_{in}} + \frac{\overline{kp} \cdot N_p \cdot [M]}{rn} - \frac{Mp_{out}}{m \cdot rn_{out}}$$

The number-average chain length is then given by dividing the mass of polymer in the reactor by the solution to the above equation, i.e.

$$\overline{rn} = \left(\frac{1}{m} \right) \cdot \left(\frac{Mp}{Mp/(m \cdot rn)} \right)$$

and the accumulated polydispersity is given by the ratio of the accumulated averages.

The accumulated molecular-weight distribution is given by weighting the mass of the fraction of polymer of chain length r by the mass of polymer in exactly the same manner as we found the accumulated weight-average molecular weight:

$$dMp \cdot \overline{Wd}(r) / dt = \overline{Wd}(r)_{in} \cdot Mp_{in} + \sum_{j=1}^{\infty} \{ Wd(r, j) \cdot m \cdot kp(j) \cdot Y_0(j) \cdot [M] \} - \overline{Wd}(r)_{out} \cdot Mp_{out}$$

and

$$\overline{Wd}(r) = Mp \cdot \overline{Wd}(r) / Mp$$

We now have expressions for the accumulated number- and weight-average molecular weights. But more importantly we now have a simple expression for the instantaneous molecular-weight distribution. From this we can calculate the weight fraction of polymer of any chain length and not just the averages.

ESTIMATION OF PARAMETERS

Possibly, the major difficulty associated with a model which takes into account a multiple-activity-site distribution is the large number of parameters to be estimated. Cozewith^{1,2} has shown that if N multiple sites are present, the reactivity ratios estimated from the conventional copolymerization equation (r_1 and r_2) should be seen as average values. Following our nomenclature, these averages can be expressed as:

$$r_k = \frac{\sum_{j=1}^N [r_k(j) \cdot k_{ki}(j) \cdot \phi_k(j) \cdot \eta(j)]}{\sum_{j=1}^N [k_{ki}(j) \cdot \phi_k(j) \cdot \eta(j)]}$$

where $k, i = 1, 2; k \neq i$.

Analysing a two-species system, he has concluded that the product of these average values falls between the reactivity ratio products of the individual j sites. Moreover, the application of the average $r_1 \cdot r_2$ values and the average copolymer composition to predict the propagation probability underestimates the amount of material in longer sequences.

Many attempts have been made to calculate the reactivity ratios for whole insoluble samples of copolymers produced with heterogeneous Ziegler–Natta catalysts. Some of them have brought about the hypothesis of multiple sites because these copolymers have failed the first-order Markov process. ^{13}C n.m.r. has been applied as a powerful technique to calculate reactivity ratios and the chemical composition distribution^{51,52}. Analysing propylene/ethylene copolymer produced with TiCl_3 , Kakugo⁵¹ has interpreted discrepancies for ethylene-centred triads, determined with basis on r_k , as though they were caused by at least two different kind of sites. Ross^{34,52} and very recently Cozewith⁵³ have discussed Kakugo's data. The former has derived equations for dyad and triad distributions with regard to multiple sites, each site having random character. This model fits Doi's¹³ and Kakugo's⁵¹ data much better than the first-order Markov approach. As for Cozewith, he has analysed the suitability of three different models (single site; multiple sites with $r_1 \cdot r_2 = 1$; and two sites also having random character) to fit data generated not only by Kakugo but also by Ray⁵⁴, Doi¹³ and himself⁵³. He concluded that multiple catalyst species were present in all cases, in general more than two. According to his estimates, the reactivity ratio products for the individual sites lie between 0.5 and 3.0. Even so, the two-random-site model was appropriate for many cases.

As has been pointed out above, the reactivity ratios calculated with basis on a sample of the whole insoluble copolymer are averages of the individual reactivity ratios. Therefore, in order to determine the individual reactivity ratios it is necessary to perform n.m.r. in each copolymer fraction produced by each j -type site.

We shall point out how to estimate the main parameters of the model presented in the previous sections, without assuming any particular character for the j sites.

A conceptual approach

Considering a copolymer produced using a heterogeneous Ziegler–Natta catalyst, one should identify three main sources of heterogeneity:

- (a) that caused by differing mean chain lengths for each site, leading to the broad molecular-weight distribution;
- (b) that caused by differing mean chemical composition for each site, resulting in the existence of a broad comonomer sequence distribution; and
- (c) that caused by differing mean stereoregularities for each site, bringing about the existence of a broad stereosequence distribution.

The ideal approach would consist of an effective technique which was capable of either separating fractions according to their chemical composition independent of both MW and stereoregularity distributions, or fractionating the copolymer in terms of its stereoregularity independent of MW and chemical composition distributions. Furthermore, it would be

strictly necessary that these two processes of separation were not influenced by the presence or absence of other macromolecules.

If such a procedure were to exist, one could develop the following conceptual model: each fraction obtained by this procedure would be generated by an individual type of site, having as its characteristic parameters the rate constants for formation, initiation, transfer, deactivation and propagation reactions. Therefore, by analysing each fraction, one could determine, for each type of site, the main parameters associated with MW , chemical composition and stereoregularity distributions, which are functions of the rate constants.

As this ideal technique does not exist, we will develop a realistic approach to estimate, as well as possible, the parameters for our model by using TREF, n.m.r. and g.p.c. techniques, while maintaining the conceptual basis for the existence of individual sites which produce particular fractions.

A realistic approach

Attempts have been made to achieve compositional separation by using fractionation based upon crystallizability, via either isothermal crystallization at successively lower temperatures^{55,56} or isothermal dissolution at a series of rising temperatures^{57,58}.

Recently, Wild⁵⁹ has reported an improved temperature-rising elution fractionation (TREF) system capable of segregating a copolymer according to its chemical composition without being influenced to a great extent by either molecular-weight distribution or cocrystallization effects between unlike macromolecule species. In this work Wild used mainly polyethylene and copolymers of polyethylene produced by a high-temperature process to draw his conclusions, so that branching constituted the main source of copolymer inhomogeneity. At that time Wild suggested the possibility of performing joint TREF and size exclusion chromatography (s.e.c.) analysis in order to characterize copolymers.

Following Wild's ideas, Nakano⁶⁰ has developed an automatic cross-fractionation technique which combined both crystallizability and molecular-weight fractionations. Nevertheless, Nakano was more concerned with the technique itself than with the interpretation of copolymer structure.

Subsequently, Wild also reported the analysis of cross-fractionation data⁶¹ in which fractions obtained by TREF were subjected to s.e.c. measurements. By following such a methodology he has obtained three-dimensional plots for characterizing not only HD–LDPE but also LLDPE polymers. According to their plots, HP–LDPE presents a unimodal bivariate distribution whereas LLDPE has a bimodal one.

In 1986, Usami⁴¹ reported an attempt to characterize TREF fractions of copolymers (LLDPE) produced with heterogeneous Ziegler–Natta catalysts. Analysing LLDPE samples from four different continuous processes (gas-phase, bulk, solution and slurry), he found bimodal TREF distributions for all of them, confirming Wild's observations. As the hypothesis for the existence of a common discontinuous change in monomer concentration in the four processes seemed to be quite improbable, he assumed that the cause of the bimodal distribution should be associated with the existence of at

least two types of sites each having its characteristic reactivity ratio product. After having obtained six fractions of a sample from the gas-phase process, he observed sharp d.s.c. thermograms for each one, indicating that the TREF performed well. He also obtained three more fractions on the same sample by adopting only three elution temperatures instead of the previous six. For five of the first six fractions, as well as for the last three, the reactivity ratio products were determined through ^{13}C n.m.r. In general, the values were different for each fraction, varying from 0.49 to 1.00. He concluded that the two peaks on the TREF curves were caused by two different types of sites, one having an alternating character, $r_1(1) \cdot r_2(1) = 0.50$ to 0.60 , and the other having random character, $r_1(2) \cdot r_2(2) = 1.00$. The *MWD* measurements allowed him also to state that the sites with alternating character produce lower-molecular-weight polymer whereas the sites with random character give the higher-molecular-weight polymer.

The methodology of the work described above constitutes the most advanced tool for estimation of the parameters of a multiple-site model available at this time. It is a practical attempt to carry out the ideal approach that we have presented above. However, as will be shown, extensive analysis of TREF fractions is able to estimate directly only those parameters which lead to monomer reaction rates, chemical composition and *MWD*. Even if an enantiomorphous control mechanism is adopted, the stereoregularity parameters for each kind of site cannot be estimated in this manner because four different rate constants for isotactic and syndiotactic addition are included in each rate constant for propagation. Moreover, even though the TREF fractionation is not strongly influenced by *MWD* and cocrystallization between unlike chains, it seems improbable that fractionation should be independent of stereoregularity. Therefore, unless the amount of atactic and stereo-block polymer can be neglected, an overlap between chemical and configurational compositions should be expected when performing fractionation based on crystallizability. Otherwise, previous segregation of the polymer into atactic (that fraction soluble in cold solvent), stereo-block (that fraction soluble in boiling solvent) and isotactic (that insoluble fraction) polymer should be performed before the TREF analysis in order to reduce the effect due to stereo-inhomogeneity.

Mathematical treatment. Having obtained a TREF curve by analysing a copolymer sample produced with constant monomer composition, one can, using a calibration curve, generate a plot between the weight per cent of copolymer and the copolymer composition. Then, following our conceptual model, each discretized coordinate on the TREF curve can be seen as a particular point which corresponds to an individual type of site. Evidently, in a practical sense one has to select the significant coordinates through a careful analysis of the TREF pattern and operational conditions. Nevertheless, the TREF curve is not sufficient by itself to allow the estimation of parameters because the copolymer composition equation:

$$F_{k,\text{inst}}(j) = \frac{\{r_k(j) \cdot [f_k/(1-f_k)] + 1\}}{\{r_1(j) \cdot [f_1/(1-f_1)] + 1\} + \{r_2(j) \cdot [(1-f_1)/f_1] + 1\}}$$

where $k = 1, 2$, cannot be solved for both $r_1(j)$ and $r_2(j)$

because they are not independent equations. Thus, each chosen fraction ought to be subjected to extensive characterization.

As for the chemical composition, each fraction of copolymer taken from the elected TREF coordinates will consist of chains which are constituted by four kinds of dyad sequences, namely:

$$d_{ij}(j) \quad \text{for } M_k \text{ units added to the } N_i(j) \text{ sites}$$

where $i, k = 1, 2$. Each of these dyad compositions is produced by its corresponding propagation equation. Therefore, in terms of instantaneity, they can be derived from:

$$d_{ik,\text{inst}}(j) = \frac{k_{ik}(j) \cdot \phi_i(j) \cdot f_k}{kp(j)}$$

If one considers both the first and the second long-chain approximations, and if in addition the copolymer comes from a steady-state process in which not only the monomer composition but also the reactor volume and streams are constant throughout the copolymerization, one's equations for these four dyad compositions can be reduced to:

$$d_{11}(j) = \frac{r_1(j) \cdot [f_1/(1-f_1)]}{\{r_1(j) \cdot [f_1/(1-f_1)] + 1\} + \{r_2(j) \cdot [(1-f_1)/f_1] + 1\}}$$

$$d_{12}(j) = d_{21}(j) = \frac{1}{\{r_1(j) \cdot [f_1/(1-f_1)] + 1\} + \{r_2(j) \cdot [(1-f_1)/f_1] + 1\}}$$

$$d_{22}(j) = \frac{r_2(j) \cdot [(1-f_1)/f_1]}{\{r_1(j) \cdot [f_1/(1-f_1)] + 1\} + \{r_2(j) \cdot [(1-f_1)/f_1] + 1\}}$$

Now it follows that:

$$F_k(j) = [d_{ik}(j)]_{i=k} + [d_{ik}(j)]_{i \neq k}$$

and therefore the reactivity ratios can be expressed as:

$$r_k(j) = \frac{[d_{ik}(j)]_{i=k} \cdot (1-f_k)}{\{F_k(j) - [d_{ik}(j)]_{i=k}\} \cdot f_k}$$

It should be recognized that both $F_k(j)$ and $d_{ik}(j)$ can be interpreted in terms of probability. The former represents the probability of a k monomer addition to any site whereas the latter means the probability of a k monomer addition to an i site, producing a specific ik dyad. Note that one can also define the following conditional probabilities from the dyads and copolymer composition, for the formation of a new i site from a given k site, as:

$$p_{ki}(j) = d_{ik}(j)/F_k(j)$$

or, in kinetic terms:

$$p_{ki}(j) = \frac{k_{ki}(j) \cdot \phi_k \cdot f_i}{\sum_{i=1}^2 [k_{ki}(j) \cdot \phi_k \cdot f_i]}$$

For a given k , these conditional probabilities are such that:

$$\sum_{i=1}^2 p_{ki}(j) = 1$$

Therefore, the reactivity ratios can be calculated via:

$$r_k(j) = \frac{p_{(kk)}(j) \cdot (1 - f_k)}{p_{(ki)}(j) \cdot f_k}$$

And by handling ^{13}C n.m.r. data from each TREF fraction, those conditional probabilities can be determined, providing estimation for each j set of reactivity ratios.

Furthermore, the main parameters associated with the propagation rate can be estimated from the weight fraction of the copolymer, as follows. The weight of the copolymer sample subjected to TREF is given by:

$$S_w = \sum_{j=1}^{\infty} \{m_1 \cdot F_1(j) + m_2 \cdot [1 - F_1(j)]\} \cdot kp(j) \cdot \eta(j) \cdot \Delta t$$

where Δt is some small interval of reaction time. Also, the weight of each selected TREF fraction is given by:

$$S_w(j) = \{m_1 \cdot F_1(j) + m_2 \cdot [1 - F_1(j)]\} \cdot kp(j) \cdot \eta(j) \cdot \Delta t$$

Thus, the weight fraction of copolymer for each j fraction can be split for both $k=1$ and $k=2$ monomers according to:

$$W_k(j) = F_k(j) \cdot W(j)$$

where

$$W(j) = S_w(j) / S_w$$

This provides the following pair of equations ($k=1,2$) for each j fraction:

$$W_k(j) = \left(\frac{m_k \cdot F_k(j) \cdot \eta(j)}{S_w} \right) \cdot \left[k_{11}(j) \cdot \phi_1(j) \cdot \left(f_1 + \frac{f_2}{r_1(j)} \right) + k_{22}(j) \cdot \phi_2(j) \cdot \left(\frac{f_1}{r_2(j)} + f_2 \right) \right]$$

and from the second long-chain approximation, as before:

$$\phi_1(j) = \frac{[k_{22}(j)/r_2(j)] \cdot f_1}{[k_{22}(j)/r_2(j)] \cdot f_1 + [k_{11}(j)/r_1(j)] \cdot f_2}$$

$$\phi_2(j) = 1 - \phi_1(j)$$

Therefore, these equations can be solved for the propagation rate parameters, namely:

$$k_{ik}(j) \cdot \eta(j)$$

As we have stated above, the estimation of the stereoregularity parameters involves additional difficulties. If one neglects penultimate and higher-order effects, each of the four propagation equations can be written in terms of four other propagation equations which take into account isotactic and syndiotactic additions. Therefore, the mechanism of copolymerization will comprise 16 equations, so that the pseudo propagation rate constants for each j site will be expressed as:

$$k_{ik}(j) \cdot \phi_i(j) \cdot f_k = \{ [k_{ik}^{\text{DD}}(j) + k_{ik}^{\text{DL}}(j)] \cdot \phi_i^{\text{D}}(j) + [k_{ik}^{\text{LD}}(j) + k_{ik}^{\text{LL}}(j)] \cdot \phi_i^{\text{L}}(j) \} \cdot f_k$$

This system of four equations contains 16 unknowns, which are the rate constants for stereo-additions. Even if an enantiomorphous control mechanism is assumed, for example:

$$k_{ik}^{\text{DD}}(j) = k_{ik}^{\text{LD}}(j) \gg k_{ik}^{\text{LL}}(j) = k_{ik}^{\text{DL}}(j)$$

i.e.

$$s_{ik}^{\text{D}}(j) \gg s_{ik}^{\text{L}}(j)$$

one would still have two unknowns per equation, as well as two stereoreactivity ratios to be estimated as:

$$s_{ik}^{\text{D}}(j) = k_{ik}^{\text{DD}}(j) / k_{ik}^{\text{DL}}(j)$$

In order to complete the estimation process, g.p.c. analysis carried out in each TREF fraction provides estimations for $Mn(j)$ and $Mw(j)$. Thus, $\tau(j)$ can also be evaluated, making the determination of the total transfer rate constant possible.

COMPUTER CALCULATIONS

We shall use this model to perform some simple calculations to generate TREF and MW plots. It will be shown that this model is able to predict, even for a copolymer produced under steady-state conditions, broad chemical composition and molecular-weight distributions. If the model is able to predict TREF and MW plots then it is possible to estimate model parameters from actual TREF and MW measurements.

For illustrational purposes we shall arbitrarily choose a distribution for the propagation rate constant, which has mean values roughly corresponding to literature values for the copolymerization of propylene (1) and ethylene (2) with titanium trichloride and aluminium alkyl as active catalyst.

Thus, the propagation rate constant for the monomer 1 addition to the sites which are linked to monomer 1 units (k_{11}) will be assumed to be distributed between two extreme values ($k_{11}^{\text{min}} = 0.5$ and $k_{11}^{\text{max}} = 500.01 \text{ mol}^{-1} \text{ s}^{-1}$). Two cases will be considered: case 1, in which k_{11} has a slight positively skewed unimodal distribution, having expected value about 9.071 mol s^{-1} ; case 2, in which the distribution for k_{11} is strongly skewed and slightly bimodal, having mean about $25.61 \text{ mol}^{-1} \text{ s}^{-1}$. *Figure 1* shows both the distributions, as the fraction of propagation sites $\eta(j)$ versus $k_{11}(j)$. Although presented as continuous curves, they are actually discrete distributions:

$$k_{11}(j+1) = k_{11}(j) + \delta$$

where

$$\delta = (k_{11}^{\text{max}} - k_{11}^{\text{min}}) / 500$$

Notice that for case 1 the $k_{11}(j)$ values greater than 30.0 are associated with negligible fractions of sites, whereas for case 2 the fraction of sites becomes negligible only from values greater than 100.0.

We shall also assume that for each distribution case the four propagation rate constants are related to each other by means of a specific chemical control mechanism. Thus,

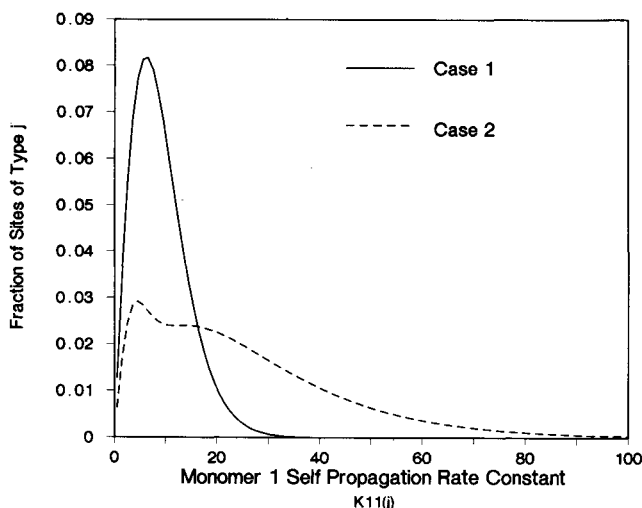


Figure 1 The $k_{11}(j)$ distributions for case 1 and case 2

for case 1 we shall assume that:

$$k_{21}(j) = k_{11}(j)$$

$$k_{12}(j) = k_{22}(j) = 120.0$$

and for case 2 that:

$$k_{21}(j) = k_{11}(j)$$

$$k_{12}(j) = k_{22}(j) = 80.0$$

Both the control mechanisms are simple ones which take into account the existence of multiple active sites only for the monomer 1 addition, each site having random character. We are therefore using a conservative approach to perform the calculations.

Simulated TREF curves

The normalized TREF curves are presented as the number of methyl groups per thousand carbon atoms (SCB) versus the differential weight fraction of polymer (W'). As the weight fraction of copolymer is naturally normalized on j , but not on the copolymer composition, a transformation of variables was performed through the following equalities:

$$W(j) \cdot dj = \hat{W}(F_1) \cdot dF_1$$

$$dF_1 = F_1(j) - F_1(j-1)$$

and recognizing that:

$$SCB = 500F_1 \quad W' = \hat{W}/500$$

Figure 2 shows TREF plots for both the cases at monomer composition equal to 0.50. Notice that the broader the k_{11} the broader the TREF. Also notice that the TREF curve has only one peak for case 1, whereas it is bimodal for case 2.

Figure 3 compares TREF plots for case 2 at different values (0.20, 0.50 and 0.80) of monomer composition. As f_1 is increased the width of the TREF curve increases. This behaviour is expected because only the rate constant for the monomer 1 addition is distributed. Furthermore, the

TREF is bimodal for small values of f_1 and becomes less bimodal as f_1 increases. This means that the TREF pattern depends not only on the distributions for the propagation rate constants but also on the relative amount of monomers. Moreover, the existence of more than one peak does not necessarily indicate that different reactivity ratio products are present.

As these figures demonstrate, the copolymer produced with multiple-active-site catalysts has a wide chemical composition, even for constant monomer composition.

Simulated molecular-weight distributions

By using the simplified analysis for the molecular weight one can calculate the molecular-weight distribution. If we consider the expression for $\lambda(j)$ and assume that transfer to hydrogen is the only significant reaction controlling molecular weight, one can say that:

$$\lambda(j) = kfh(j) \cdot [H]/[M]$$

If we use the Langmuir equation to relate the surface concentrations to the bulk concentration, and note that:

$$K_H C_H \ll 1 + K_M C_M$$

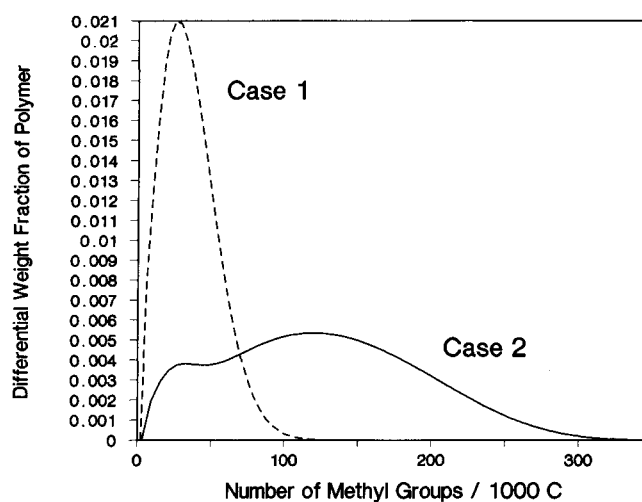


Figure 2 Simulated TREF curves for copolymer produced using catalysts with case 1 and case 2 distributions for $k_{11}(j)$. Comonomer composition $f_1 = 0.5$

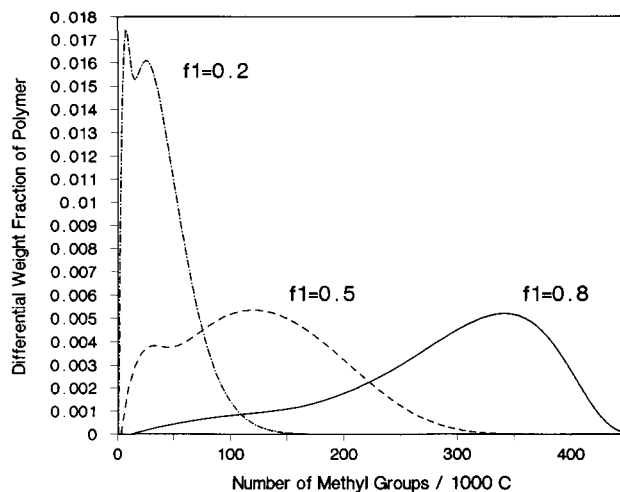


Figure 3 The effect of comonomer composition f_1 on simulated TREF curves. Case 2 distribution

then one can say:

$$\lambda(j) \approx K(j)(C_H)^{0.5}/C_M$$

where $K(j)$ is a grouping of constant values for each site. We can choose arbitrary distributions for $K(j)$ to test the effect of a $\lambda(j)$ that is either independent of or is a function of j . The mean value of $K(j)$ should be the same for both distributions in order to compare the MWD results. The distributions for $K(j)$ are:

constant $\lambda(j)$

$$K(j) = 19.716$$

non-constant $\lambda(j)$

$$K(j) = 0.5 \bar{k}_{11} \cdot (k_{21} \cdot k_{11})^{1/2}$$

Figure 4 shows the $\lambda(j)$ vs. $k_{11}(j)$ curve for:

$$\frac{C_H^{0.5}}{C_M} = \frac{(0.007)^{0.5}}{25} = 3.33 \times 10^{-3}$$

We can evaluate $Wd(r)$ at several r values to generate the chain length distribution and we can also calculate the

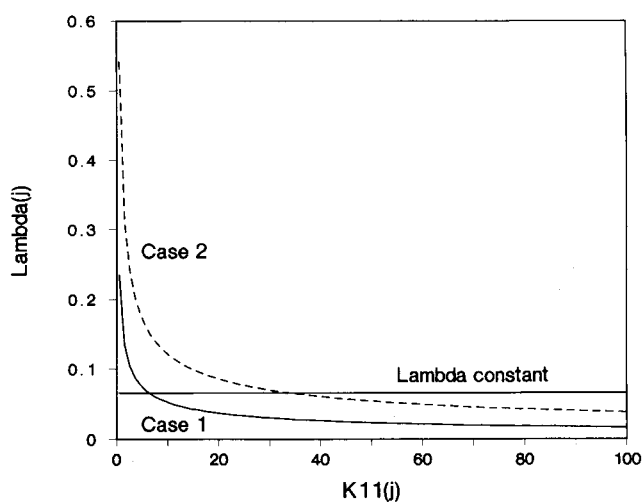


Figure 4 The chosen $\lambda(j)$ distributions for case 1, case 2 and for constant $\lambda(j) = \bar{\lambda}$. $C_M = 25.0$; $C_H = 0.007$

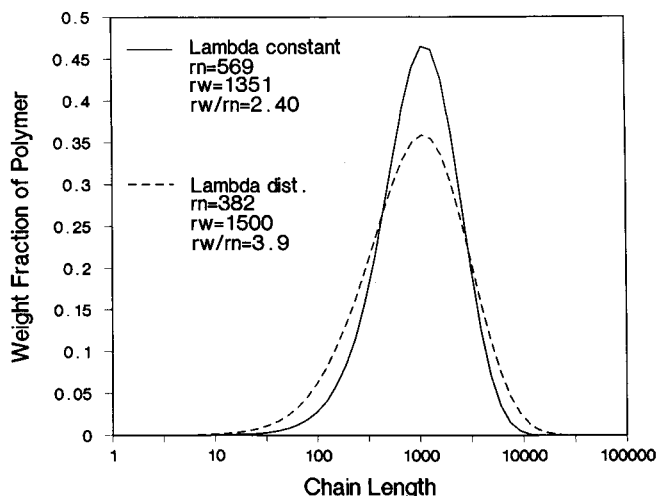


Figure 5 The effect of the $\lambda(j)$ distribution on the simulated MWD . Case 2 distribution; $f_1 = 0.8$; $C_M = 25.0$; $C_H = 0.007$

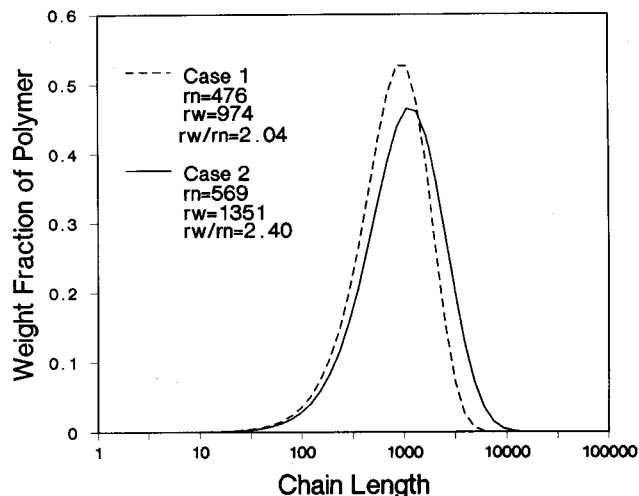


Figure 6 The effect of the $k_{11}(j)$ distribution on the simulated MWD . Case 1 and case 2 distributions; $f_1 = 0.8$; $C_M = 25.0$; $C_H = 0.007$; constant λ

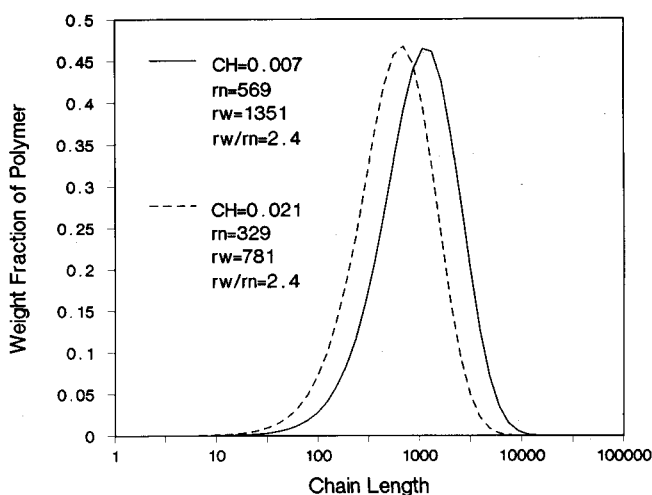


Figure 7 The effect of the bulk hydrogen concentration on the simulated MWD for constant λ . Case 2 distribution; $f_1 = 0.8$; $C_M = 25.0$; $C_H = 0.007, 0.021$

instantaneous number- and weight-average chain lengths. The normalized MW plots are presented as $Wd(r) \cdot r$ versus r in logarithmic scale.

Considering case 2 at $f_1 = 0.80$, Figure 5 shows how having a distribution for $\lambda(j)$ broadens the chain length distribution. The polydispersity increases from 2.4 to 3.9 when $\lambda(j)$ is allowed to vary from site to site.

The molecular-weight distribution is certainly affected by the distribution of propagation rate constants. Figure 6 shows, for λ constant, how the chain length distribution changes from case 1 to case 2. A broader k_{11} distribution gives rise to a broader MWD .

Since transfer to hydrogen is assumed to control the molecular weight, a change in the bulk hydrogen concentration should shift the chain length distribution. Figures 7 and 8 show, for case 2 and $f_1 = 0.80$, the shift in the MWD when the hydrogen to monomer ratio was increased by three times. Figure 7 shows that for λ constant, a change in C_H only shifts the MWD curve and does not change the polydispersity. Notice that the number-average chain length decreased from 569 to 329

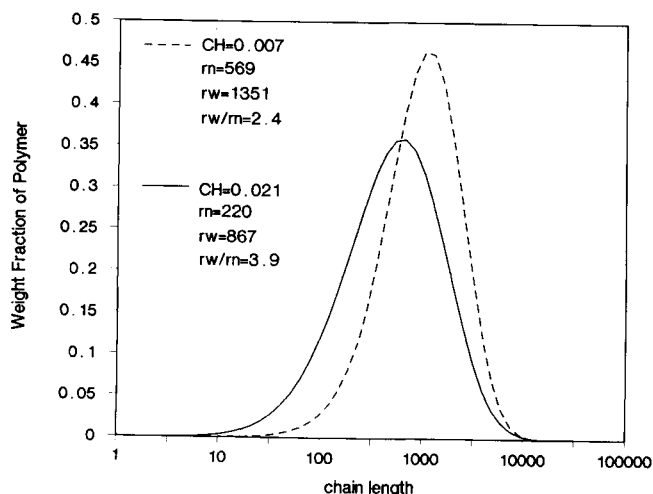


Figure 8 The effect of the bulk hydrogen concentration on the simulated *MWD* for distributed $\lambda(j)$. Case 2 distribution; $f_1=0.8$; $C_M=25.0$; $C_H=0.007, 0.021$

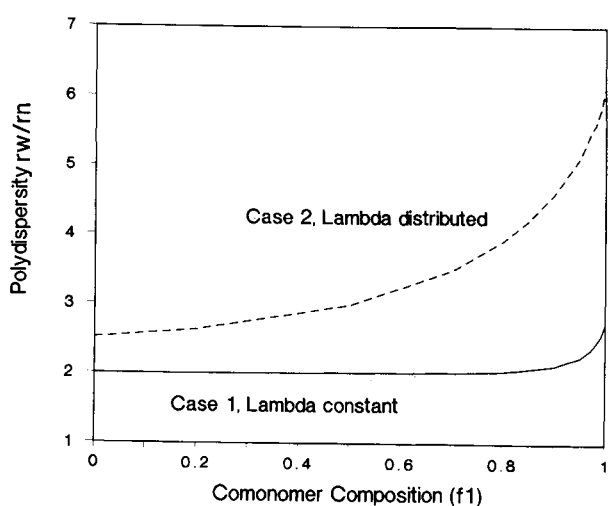


Figure 9 The effect of comonomer composition on the width of the *MWD* (polydispersity) for case 1 and λ constant, and case 2 and $\lambda(j)$ distributed

or:

$$329/569 = 0.577 = 3^{-0.5}$$

and thus we see that rn is proportional to $C_H^{-0.5}$. This has been observed in actual practice³⁹. Figure 8 shows that for a distributed λ a change in C_H not only shifts the *MWD* curve, but also changes the polydispersity.

We suggest an experiment where C_H would be varied and the polydispersity measured. If the polydispersity remains constant then λ can be a constant for all j for that catalyst type. Hydrogen has been observed to increase the polydispersity for a commercial Stauffer type AA $TiCl_3 \cdot \frac{1}{3}AlCl_3$ with DEAC cocatalyst⁶².

Only k_{11} and k_{21} change from site to site. Therefore, as the concentration of monomer 1 is increased, the importance of $k_{11}(j)$ and $k_{21}(j)$ to the overall pseudo propagation rate constant is increased. Therefore, the variance of the distribution of $kp(j)$ increased as f_1 is increased, giving rise to an increased polydispersity. Figure 9 shows how the polydispersity increased with increasing monomer 1, even though $\lambda(j)$ is independent of

j . Notice that for case 1 and λ constant the polydispersity changes from 2 (ethylene homopolymer) to 2.73 (propylene homopolymer), whereas for case 2 and λ distributed the polydispersity varies between the homopolymer extremes from 2.51 to 6.14.

SUMMARY

A multiple-site model is necessary in order to account for the properties of polymer produced by heterogeneous Ziegler–Natta catalysts. These properties include broad molecular-weight copolymer composition and stereoregularity distributions. A kinetic model has been derived, based upon multiple catalyst sites of differing reactivities, for the ZN copolymerization of olefins. The kinetic scheme accounts for the formation, initiation and deactivation of active sites, as well as for spontaneous transfer and transfer reactions to hydrogen, monomer and organometallics. The model predicts the rate of polymerization, the copolymer composition and the molecular-weight distribution of the polymer produced as well as accounting for the observed broad copolymer composition and molecular-weight distributions.

A generalized molecular-weight development has been derived by calculating the leading moments of the live and dead polymer chain length distributions for each type of active site. A simplified method was also proposed, which would be valid under certain operating conditions and would give some insight into the factors influencing the *MWD*. From this analysis, an equation for instantaneous molecular-weight distribution (not just the leading moments) was found. The instantaneous *MWD* for each site would be the most probable distribution (polydispersity = 2) and the instantaneous polydispersity for the entire amount of polymer produced would deviate from 2 by the ratio of the variance of the propagation rate constants to the mean propagation rate constant.

Guidelines are given for the estimation of the model parameters based upon a conceptual approach, according to which each fraction segregated on the basis of crystallizability can be seen as if it came from a particular type of site. The technique of temperature-rising elution fractionation (TREF) is presented as the best available method of separating fractions based on crystallizability. Following this point of view, it is shown that n.m.r. and g.p.c. analysis on each selected TREF fraction allows the estimation of the parameters associated with the propagation and transfer rates, the chemical composition, as well as the molecular-weight distribution, separately, for each type of site. It is not possible to estimate the stereoregularity ratios via this technique.

Some computer simulations were made to demonstrate the ability of the model to predict broad chemical composition and molecular-weight distributions.

NOMENCLATURE

r	Chain length
j	Active or potential site type
$N^*(j)$	Moles of potential sites of type j . Potential sites are catalyst sites that do not facilitate polymerization, but may react, via formation reactions, to form active sites that do facilitate polymerization

$N(r, j), N(j)$	Moles of propagation sites of type j with growing chain of length r , and total moles of propagation sites of type j	p_{ik}	The conditional probability that an i -type monomer adds onto a growing chain given that a k -type monomer unit was added immediately before, or equivalently, the probability of adding a monomer type i to a growing chain ending in monomer type k
$N(0, j), N_H(0, j), N_R(0, j)$	Moles of initiation sites of type j produced by formation, by transfer to hydrogen or spontaneous transfer, and by transfer to organometallics	$S_w, S_w(j)$	The total sample mass for TREF and the mass of the j fraction
$N_T(j), N_T$	Moles of active sites of type j (sum of initiation sites and propagation sites of type j) and total number of active sites	property	Any quantity that is an accumulated property (as opposed to an instantaneous property)
$N_p(j), N_p$	Moles of propagation sites of type j , and total moles of propagation sites	<i>Greek letters</i>	
$N_i(r, j), N_i(j)$	Moles of active sites with polymer of chain length r ending in a monomer type- i group, and total moles of active sites having a chain ending in a monomer type- i group	$\gamma(j)$	The fraction of the total active sites that are of type j
$Q(r, j), Q(j)$	Moles of dead polymer of chain length r produced by type- j sites and moles of dead polymer of all chain lengths produced by type- j sites	$\eta(j)$	The fraction of the propagation sites that are type j
M_i, M	Moles of monomer type i and total monomer	$\phi_i(j)$	The fraction of j -type sites that have a growing chain ending in a monomer type- i unit
M_p	Mass of polymer in the reactor (or inflowing and outflowing if the subscripts 'in' or 'out' are present)	$\tau(j)$	The ratio of the transfer rates to the propagation rates for type- j sites
m_1, m_2, m	The molecular weights of monomers 1 and 2 and the effective molecular weight per repeat unit	$\psi(j)$	A grouping of constants related to $\tau(j)$
A	Moles of organometallic	$\lambda(j)$	A grouping of transfer constants
H_2	Moles of hydrogen	σ^2	The variance of the propagation rate constants about the mean propagation rate constant
V	Reaction volume	θ_k	The fraction of adsorption sites on the catalyst surface that are occupied by a k -type molecule ($k = \text{hydrogen, monomer, organometallic}$)
t	Time	θ_T	The total moles of adsorption sites on the catalyst surface per unit volume of reaction mixture (mol l^{-1})
f_i	Mole fraction of adsorbed monomer that is type i (monomer composition)	<i>Subscripts/superscripts</i>	
$F_i, F_{i, \text{inst}}$	Accumulated and instantaneous mole fractions of monomer type i bound as polymer (copolymer composition)	1, 2	Pertaining to monomer types 1 and 2
P_i	Total moles of monomer type i bound as polymer	H, R, S; h, r, s	Pertaining to reactions with hydrogen and organometallic and spontaneous reactions
R_p	Rate of polymerization	T	Denotes total quantities
$W(j)$	Instantaneous mass fraction of polymer produced by j -type sites	in, out	Denote flows into and out of the reactor
$Wd(r, j), Wd(r)$	The instantaneous weight fractions of dead polymer that is chain length r produced by type- j sites, and by all sites	inst	Denotes an instantaneous value
W' and \hat{W}	The differential weight fraction of polymer in terms of short-chain branching and mole fraction of monomer 1 bound as polymer	D, L	Denote the stereo-regular orientation of the monomer
$Y_n(j)$	The n th moment of the live polymer chain length distribution produced by j -type sites	<i>Kinetic rate constants</i>	
$X_n(j)$	The n th moment of the dead polymer chain length distribution produced by j -type sites	Rate constants with (j) denote reactions with type- j sites. The subscripts i, k denote monomer types, and if the rate constant has no i, k subscript they are pseudo rate constants that take into account the copolymer and monomer compositions. First-order rate constants will have units of reciprocal time, and second-order rate constants will have units of litre/moles time.	
$\overline{m}, \overline{r_w}, m, r_w$	The accumulated number- and weight-average chain lengths, and the instantaneous number- and weight-average chain lengths	$k_f(j), k_f'(j)$	Pertaining to formation of active catalyst sites (type j) from potential sites
$[X]$	Denotes concentrations of species X either on the catalyst surface or in the reactor (mol l^{-1})	$ki(j)$	Pertaining to formation of propagation sites from initiation sites (initiation reactions)
C_i	Denotes the bulk concentrations of species i in the reactor (mol l^{-1})	$kh(j), kr(j)$	Pertaining to formation of propagation sites from initiation sites that have been formed by transfer to a hydrogen or organometallic reaction (initiation reactions)
K_i	The equilibrium constant for adsorption of species i on the catalyst surface	$k_{ik}(j), kp(j)$	Pertaining to propagation reactions
s^D, s^L	Stereoreactivity ratios. The ratio of the rate constant for isotactic addition of monomer to syndiotactic addition of monomer	$kfm(j), kfh(j), kfr(j), kfs(j)$	Pertaining to transfer to monomer, transfer to hydrogen, transfer to organometallic and spontaneous transfer reactions
d_{ik}	Probability of forming a dyad with monomers i and k		

$kd(j)$ Deactivation reactions
 k_p, kd, kf Mean propagation, deactivation and formation rate constants
 $k_{ik}^{DL}(j)$ The propagation rate constant for the addition of k -type monomer with L configuration to a growing chain ending in an i -type monomer in the D configuration on a j -type site

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