A kinetic model for heterogeneous Ziegler–Natta (co)polymerization. Part 2: stereochemical sequence length distributions

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We have recently published a kinetic mathematical model, based upon multiple active site distribution approach, for olefins polymerized with heterogeneous Ziegler–Natta catalysts[1]. This model can be used to calculate not only production rates, but also both broad molecular weight and copolymer composition (temperature rising elution fractionation (TREF)) distributions. We now extend this model to account for both the stereo and the chemical sequence length distributions. We focus our analysis on α-olefin homopolymers and α-olefin–ethylene copolymers. The α-olefin must not be polymerizable by another mechanism (ionic or radical), so that styrene is not considered. Some simulations are carried out for typical productions of polypropylene and propylene-ethylene copolymer.

(Keywords: multiple active site model; fractionation; stereosequence length distribution; inhomogeneity)

INTRODUCTION

Several attempts have been made in the past to investigate Ziegler–Natta polymerization systems via digital simulation based on phenomenological mathematical modelling. Nevertheless, some problems have been encountered in trying to model these polymerizations. Polyethylene and poly-α-olefins produced with heterogeneous isospecific Ziegler–Natta (Ti-based) catalysts, possess a characteristically broad molecular weight distribution. The copolymers have, as well, a broad copolymer composition distribution. Furthermore, inhomogeneity with respect to both the chemical and the stereo sequence length distributions along the backbone of the chains has been found. These distributions cannot be explained by classical reaction modelling[1].

Two main hypotheses have been proposed in the literature to explain these observed wide and non-homogeneous distributions. Both hypotheses are controversial. One of them is based on physical criteria. It postulates that these particular characteristics result from the encapsulation of the catalyst particle by the polymer. This polymer layer is assumed to cause a spatially distributed spectrum of diffusional resistances to the diffusing monomer molecules. This implies that the propagation rate will decrease as the polymerization proceeds. The other adopts a chemical approach, whereby the surface of the catalyst particle is made up of centres with differing reactivity, each of them being responsible for the production of a particular fraction of polymer.

Although some models based on the former hypothesis

have recently been developed[64,65], and while some of them have been satisfactorily applied to predict the broad molecular weight distribution (MWD)[66,67], there is experimental evidence contradicting them. Firstly, polymers obtained under steady state conditions, and in the early stages of polymerization, when diffusional limitations are quite improbable, do have broad MW and chemical composition distributions, as well as chemical and stereo inhomogeneity[2].

Secondly, it has been proven that for stable catalysts of relatively low activity (e.g. $\alpha - TiCl_3$) the rate of polymerization remains virtually constant, independent of the amount of polymer produced[68,69]. Furthermore, even for highly active, unstable catalysts, for which a decrease in their activity by encapsulation is most probable, the rate of decay has been shown to be independent of the amount of polymer produced[70-72]. This conclusion should always be valid provided that effective mixing of the polymerization slurry is attained and the polymerization rate does not exceed the rate of gaseous monomer dissolution in the diluent[2]. Even more importantly, it has been demonstrated[63] that for polymerization with highly active catalyst under quasi-living conditions, the polydispersity remains constant throughout the run, so that the existence of thick polymer layers leading to diffusional limitation can not be the cause for the broadening of MWD.

Thirdly, very recent investigations have brought forward evidence that the reasons for the rate of decay are of a chemical nature[73]. Except for topological destruction of the active sites, the decaying process is most likely to be a reversible process in which hydrogen or a comonomer can temporarily restore the original propagation rate. In fact, it has been reported[74] that the $AlEtCl_2$, formed from the

equilibrium reaction with the co-catalyst, is mainly responsible for the rate decrease of the $TiCl_3 + AlEt_2Cl$ type catalyst.

Moreover, the main deficiency in the diffusional limitation theory is its inability to account for the stereo regularity distribution of polymers produced with moderately active and moderately stable catalyst, such as the $\delta - TiCl_3 + AlEt_2Cl/AlEt_3$.

Probably for these reasons, as well as to improve their capability to forecast the polymer microstructure, the multiple active site approach has been incorporated in the recent models based on diffusional limitation[66,67]. These models use only a small number of site types (around two), presumably due to the additional computational difficulties to make the model operational.

Investigations based on multiple active site models have been undertaken[60,61,75]. However, they consist of efforts to elucidate particular features of this vast field, so that no global derivation is available in the literature.

Thus, after having built a general kinetic model based upon catalyst sites of differing reactivity, and successfully applied it to predict MWD and temperature rising elution fractionation (TREF) chromatograms[1], we have decided to extend it so as to predict stereo and chemical sequence distributions along the backbone of the chain. An extensive literature review will be discussed while performing the developments.
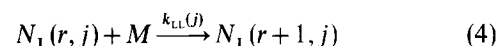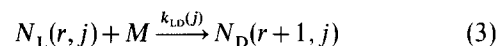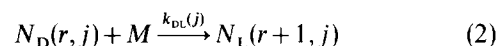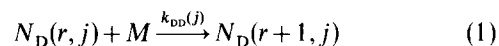
MODEL DEVELOPMENT

Homopolymer stereoregularity pattern

Throughout this development, it is assumed that the α-olefin units are regularly linked to each other according to a head-to-tail pattern. In fact, many spectroscopic estimations have shown that the percentage of inverted monomer units in polypropylene obtained with heterogeneous Ziegler–Natta catalysts (Ti-based and supported) is negligible[2]. As for the δ $TiCl_3 + AlEt_2Cl$, such a percentage is less than 1.5% for the unfractionated polymer sample[3] or less than 0.1% for the fraction insoluble in boiling heptane[2]. Significant amounts of inversion, accounted as percentage of head-to-head addition, have only been reported for V-based catalysts, mainly for the soluble ones[4,5].

There is strong evidence which supports the hypothesis that the stereo-regulating source is due neither to the chirality of the last unit attached to the site nor to the helix conformation induction, but mainly to the inherent asymmetric structure (chirality) of the isospecific catalyst centres. The different stereo-regulating power presented by catalysts prepared with different halogen organometallic compounds[6,7], as well as the drastic reduction of the amorphous fraction when the catalysts are modified by promotion with inorganic or organic substances[8-12], are important examples of such evidence. Several models describing the polymerization centre, its location on the catalyst surface, and the mechanism which determines its isospecific action have been proposed[13-20]. Presently, calculations in terms of nonbonded interactions have suggested that the chirality of the heterogeneous Ziegler–Natta catalyst centres depends not only on the arrangement of the metal and halogen atoms, but also on the orientation of either the growing polymer chain on the site[12] or the first C–C bond attached to the site[18-20]. Therefore, the mathematical structure to be derived must

take an inherent active site control mechanism into account.

To develop the multiple stereo activity site kinetic equations, the following mechanism for the homopolymer propagation will be adopted

$$N_D(r,j) + M \xrightarrow{k_{DD}(j)} N_D(r+1,j) \qquad (1)$$

$$N_D(r,j) + M \xrightarrow{k_{DL}(j)} N_L(r+1,j) \qquad (2)$$

$$N_L(r,j) + M \xrightarrow{k_{LD}(j)} N_D(r+1,j) \qquad (3)$$

$$N_L(r,j) + M \xrightarrow{k_{LL}(j)} N_L(r+1,j) \qquad (4)$$

The subscripts D and L denote the two possible spatial configurations of the tertiary carbon atoms along the backbone of the chain. The index j specifies the different classes of propagation sites with respect to their stereo-addition rate constants. It means that each j class is constituted with centres which possess the same particular values for the set of stereo addition rate constants. Therefore, a given j class must possess at least one of the stereo addition rate constants which is different from all the other classes. Thus, $N(j)$ represents a j type site or a class of j type sites. M is an α-olefin molecule.

The overall propagation rate for such a mechanism is given by[1]

$$R(j) = k(j)MN(j) = k(j)M\eta(j)N \quad \text{mol/l s} \qquad (5)$$

where M is the concentration of monomer on the catalyst surface (mole/l), which is assumed to be independent of j, and $N(j)$ is the concentration of the j type propagation sites (mol-sites/l). Notice that $\eta(j)$ should be defined as the fraction of sites that are type j, since N represents the total concentration of propagation sites, i.e.

$$\eta(j) = N(j)/N \qquad (6)$$

$$N = \sum_j N(j) \qquad (7)$$

$k(j)$ is the global propagation rate constant (l/mol-sites s).
Recognizing that

$$N(j) = N_D(j) + N_L(j) \qquad (8)$$

the following fractions of j-type sites can be defined

$$\phi_D(j) = 1 - \phi_L(j) = N_D(j)/N(j) \qquad (9)$$

Therefore, $k(j)$ can be expressed in terms of the individual stereo addition rate constants as follows

$$k(j) = (k_{DD}(j) + k_{DL}(j))\phi_D(j) + (k_{LD}(j) + k_{LL}(j))\phi_L(j) \qquad (10)$$

Equations (5)–(10) are valid for each j class of sites separately. For the polymer as a whole, it can be stated that[1]

$$R = \sum_j R(j) = \bar{k}MN \qquad (11)$$

where

$$\bar{k} = \sum_j k(j)\eta(j) \qquad (12)$$

The last term in equation (11) has been widely applied to calculate the propagation rate of Ziegler–Natta polymerizations. Nevertheless, this analysis shows that when multiple sites are present, which generally occurs with heterogeneous Ziegler–Natta catalysts, the propagation

rate constant is an average value, as given by equation (12). In practice, such expressions will be valid as long as the monomer concentration is moderate or high. Otherwise, a second order (with respect to monomer) rate expression has been found, possibly because in this case the initiation process is slow[2,17].

Considering that

$$k_{DL}(j)\phi_D(j) = k_{LD}(j)\phi_L(j)$$
$$\phi_D(j) = 1 - \phi_L(j) = k_{LD}(j)/[k_{DL}(j) + k_{LD}(j)] \tag{13}$$

are valid for all j, one obtains the expression for the instantaneous polymer stereocomposition (as moles of units having D configuration in the polymer produced on both the D and the L attached j-type sites)

$$F_D(j) = 1 - F_L(j) = [k_{DD}(j)\phi_D(j) + k_{LD}(j)\phi_L(j)]/k(j)$$
$$= [S_D(j) + 1]/[(S_D + 1) + (S_L(j) + 1)] \tag{14}$$

where

$$S_D(j) = k_{DD}(j)/k_{DL}(j)$$
$$S_L(j) = k_{LL}(j)/k_{LD}(j) \tag{15}$$

are the stereo reactivity ratios.

Notice that it is not impossible that two or more classes of sites have the same values for the stereo reactivity ratios and thus produce polymer with the same stereo composition.

The probabilities for D and L configurations are given by combination of the respective dyad probabilities, i.e.

$$F_D(j) = d_{DD}(j) + \tfrac{1}{2}(d_{LD}(j) + d_{DL}(j))$$
$$F_L(j) = d_{LL}(j) + \tfrac{1}{2}(d_{DL}(j) + d_{LD}(j)) \tag{16}$$

where the probabilities for the specific dyads are given by

$$d_{DD}(j) = k_{DD}(j)\phi_D(j)/k(j)$$
$$= S_D(j)/[(S_D(j) + 1) + (S_L(j) + 1)]$$
$$d_{DL}(j) + d_{LD}(j) = 2/[S_D(j) + 1) + (S_L(j) + 1)] \tag{17}$$
$$d_{LL}(j) = S_L(j)/[(S_D(j) + 1) + (S_L(j) + 1)]$$

Notice that the dyad probabilities are related to the stereo composition by means of the following conditional relationships

$$d_{DD}(j) = p_{DD}(j)F_D(j)$$
$$d_{DL}(j) = p_{DL}(j)F_D(j)$$
$$d_{LD}(j) = p_{LD}(j)F_L(j) \tag{18}$$
$$d_{LL}(j) = p_{LL}(j)F_L(j)$$

where $p_{LD}(j)$ means, for example, the probability that an existing L-attached j-type site has inserted another monomer unit to the chain in the D configuration. These conditional probabilities are such that

$$p_{DD}(j) + p_{DL}(j) = 1 \tag{19}$$

for the D-attached type site;

$$p_{LL}(j) + p_{LD}(j) = 1 \tag{20}$$

for the L-attached type site.

In order to evaluate them for isotactic (DD and LL), hereafter denoted as (*i*), and syndiotactic (DL and LD), hereafter denoted as (*s*), placements, it is necessary to account for both the D and the L-attached j-type sites, by

means of

$$p_i(j) = p_{DD}(j) + p_{LL}(j)$$
$$p_s(j) = p_{DL}(j) + p_{LD}(j) \tag{21}$$

For the D-attached j-type sites it can be stated that

$$p_{DD}(j) = \frac{k_{DD}(j)}{k_{DD}(j) + k_{DL}(j)} = \frac{d_{DD}(j)}{F_D(j)} = \frac{S_D(j)}{S_D(j) + 1}$$
$$p_{DL}(j) = 1 - p_{DD}(j) = \frac{1}{S_D(j) + 1} \tag{22}$$

whereas for the L-attached j-type sites it follows that

$$p_{LL}(j) = S_L(j)/[S_L(j) + 1]$$
$$p_{LD}(j) = 1/[S_L(j) + 1] \tag{23}$$

The equations developed so far can be significantly simplified if the stereo addition rate constants are related to each other by means of a stereo control mechanism. Basically, two kinds of stereo defects can be envisaged[2], each one being based upon a specific control mechanism. That which is the change of the monomer unit chirality, (...DDDDLLLL...) or (...LLLLDDDD...), and that which is represented by (...DDDDLDDDD...) or (...LLLLDLLLL...).

The former is associated with the idea of polymer growing chain end control, according to which the stereo regularity of monomer addition to a growing polymer chain is governed by electronic and/or steric interactions between the approaching unit and the last unit of the growing chain. In this case, a consistent control mechanism should be

$$k_{DD}(j) = k_{LL}(j)$$
$$k_{DL}(j) = k_{LD}(j) \tag{24}$$

respectively, for isotactic and syndiotactic placements. Consequently

$$S_D(j) = S_L(j) = S(j)$$
$$F_D(j) = F_L(j) = 0.50 \tag{25}$$

The latter is connected with the idea of enantiomorphous control of the chain growth, by which the stereo regularity is controlled by the steric structures of the centres. This error occurs when a centre normally producing a given isotactic chain makes a single error and then merely corrects itself.

Several spectroscopic data indicate, as amply discussed by Kissin[2] and elaborately shown by Pavan et al.[3], that the stereo defects presented by the highly isotactic fractions of polymers, produced with isospecific heterogeneous Ziegler–Natta catalysts, are those predicted by the enantiomorphous control mechanism.

Therefore, an enantiomorphous control mechanism, instead of an end chain one, ought to be adopted. It is made through the assumption that the catalyst contains equal numbers of D and L-preferring centres[2,21]. Furthermore, to account for the multiple active site distribution, we shall assume that all D- and L-type sites are equally composed of the same j-type classes of sites. Thus, the following relationships are valid

For D-preferring centres

$$k_{DD}(j) = k_{LD}(j) \gg k_{LL}(j) = k_{DL}(j)$$
$$S_D(j) = 1/S_L(j) > 1 \tag{26}$$

and consequently the fraction of D-attached centres, $\phi_D(j)$, is close to one.

For L-preferring centres

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

$$S_L(j) = 1/S_D(j) > 1 \tag{27}$$

and consequently the fraction of L-attached centres, $\phi_L(j)$, is close to one.

Since both D and L-preferring centres are assumed to exist in equal amount and to have the same j distribution, the stereo regulating power of each j site can be represented by a single stereo reactivity ratio parameter, expressed in terms of isotactic and syndiotactic placements

$$S(j) = \frac{k_i(j)}{k_s(j)} = \left(\frac{k_{DD}(j)}{k_{DL}(j)}\right)_D = \left(\frac{k_{LL}(j)}{k_{LD}(j)}\right)_L \tag{28}$$

Shelden[21] has pointed out that the enantiomorphic site model based on a single parameter will be suitable even for unfractionated polymers produced by stereo specific heterogeneous Ziegler–Natta catalyst provided that it is applicable for each site separately. Notice that such a prediction is in accordance with the assumptions for the j distribution.

Accordingly, both the global propagation rate constant and the statistical expressions previously derived for macromolecules produced on one kind of preferring centre (D or L) are also applicable to the whole polymer. The new set of simplified equations then becomes

For the propagation rate constant:

$$k(j) = (k_{DD}(j) + k_{DL}(j))_D$$
$$= (k_{LL}(j) + k_{LD}(j))_L$$
$$= k_i(j)(1 + 1/S(j)) \tag{29}$$

For the stereo composition

$$(F_D(j))_D = (F_L(j))_L = S(j)/[S(j) + 1]$$
$$(F_L(j))_D = (F_D(j))_L = 1/[S(j) + 1] \tag{30}$$

For the dyads

$$(d_{DD}(j))_D = (d_{LL}(j))_L = (S(j))^2/(S(j) + 1)^2$$
$$(d_{LL}(j))_D = (d_{DD}(j))_L = 1/(S(j) + 1)^2 \tag{31}$$
$$(d_{DL}(j) + d_{LD}(j))_D = (d_{DL}(j) + d_{LD}(j))_L = 2S(j)/(S(j) + 1)^2$$

For the probabilities of isotactic and syndiotactic placements

$$(p_{DD}(j))_D = (p_{LL}(j))_L = S(j)/[S(j) + 1]$$
$$(p_{DL}(j))_D = (p_{LD}(j))_L = 1/[S(j) + 1]$$
$$(p_{LL}(j))_D = (p_{DD}(j))_L = 1/[S(j) + 1] \tag{32}$$
$$(p_{LD}(j))_D = (p_{DL}(j))_L = S(j)/[S(j) + 1]$$

As it will be shown later, these probabilities can be related to spectroscopic (n.m.r. and i.r.) and melting point data, making the estimation of $S(j)$ possible.

GUIDELINES FOR ESTIMATION OF PARAMETERS

Difficulties

It should be recognized that equations (29)–(32) are based upon the enantiomorphous control mechanism

adopted, so that they are strictly valid only for those j centres which are isospecific to a great extent, i.e., which possess $S(j) \gg 1$. Actually, significant deviations from the enantiomorphous propagation model have been found for the moderately isotactic fractions of polypropylene[3,22]. For this reason, the index j must now be restricted to that category of sites which produces the highly isotactic fraction of poly-α-olefin.

In the ideal case, one would like to fractionate the polymer so as to obtain fractions having their unique $S(j)$ and $k(j)$ values. Unfortunately, there is no method available for this fine fractionation.

The number of centre categories can be chosen somewhat arbitrarily in terms of the standard methodology of polypropylene fractionation based on solubility. Thus, three categories are to be considered

1. That which produces the highly isotactic fraction of polymer, insoluble in boiling solvent (usually n-heptane).
2. That which brings about the moderately isotactic fraction, insoluble in cold solvent ($20°C$), but soluble in hot solvent, the so-called stereo block polymer containing relatively short isotactic blocks separated by atactic or syndiotactic sequences.
3. That which gives rise to the amorphous (atactic) polymer, soluble in cold solvent.

Therefore, for the highly isotactic polymer it can be established that

$$R_i(i) = k_i(i)(1 + 1/S(i))M\eta_i(i)N \tag{33}$$

where

$$\eta_i(i) = N_i(i)/N \tag{34}$$

Notice that in these expressions the index i refers only to that category of sites which produces the highly isotactic polymer. For the overall propagation rate, considered for all i, the last term in equation (11) remains valid, where

$$\bar{k}_i = \sum_i k_i(i)(1 + 1/S(i))\eta_i(i) \tag{35}$$

As can be seen, the last term in equation (11) is an approximation of equation (33) when $S(i)$ is considered to be infinity for all i.

Considering propagation rate expressions for both the stereo block and the amorphous (atactic) polymers, one can observe some complex features.

As far as the stereo block polymer is concerned, three main features should be emphasized. Firstly, these fractions could be further fractionated by using different solvents and temperature levels, as in references 2 and 3.

Secondly, each one of these subfractions presents stereo defects which are not expected by the single parameter enantiomorphic site model[3,22], i.e., short isotactic and syndiotactic stereo blocks. Doi[35] has proposed a model to explain the stereo regularity pattern presented by the stereo-irregular fraction (soluble in boiling solvent) of polypropylene produced with six different Ti-based catalysts at $41°C$. He has envisaged the existence of two sites. Site A, which would produce the highly isotactic polypropylene fraction, and site B, which would be responsible for the production of the stereo-irregular fraction (or fractions). The former would be that on which the surface metal (Ti, or Mg, if the catalyst is supported) binding to the active titanium complex was coordinatively saturated.

The latter would possess the surface metal coordinately unsaturated with one vacancy, so that it would be liable to assume two structures. The first is structure B1, equal to that presented by site A, in which two chlorine atoms of the alkyl aluminium compound would be coordinated with the active titanium atom (hexacoordinated titanium site). This structure would then produce isotactic polymer. The other, structure B2, in which one of the chlorine atoms of the alkyl aluminium compound would be coordinated with the active titanium atom and the other chlorine atom would be coordinated with the surface metal (pentacoordinated titanium site). This structure would produce syndiotactic polymer. In addition, both the B1 and the B2 structures would exist in equilibrium, because the migration of the alkyl aluminium would be reversible. Therefore, during the course of the polymerization the B type site would give rise to isotactic and syndiotactic stereo blocks. By assuming that the single parameter enantiomorphic site model is applicable to the B hexacoordinated titanium site and that the Bernoullian model is applicable to the B pentacoordinated titanium site, Doi[23] has determined the conditional probabilities (of a D unit configuration taking place on a D-preferring site and of a syndiotactic placement) which best fit the observed pentad sequence distributions.

Thirdly, the amount of head-to-head and tail-to-tail additions presented by the stereo-irregular fractions is larger than that presented by the highly stereo regular fraction[3,5,23]. Doi[23] has also discussed quantitatively the inversion of propylene units in the stereo-irregular fractions. According to his conclusions, the regioselectivity of an inserting propylene seems to depend not only on the polarity of the active carbon–titanium bond but also on the steric effects of the last propylene unit of a growing chain.

With regard to the atactic polymer, defined as the most amorphous of the fractions, it is not reasonable to presume that it is composed of purely atactic polymer chains, produced on centres which possess equal stereo-addition rate constants. In other words, the following control mechanism does not prevail

$$k_a = k_{DD} = k_{DL} = k_{LD} = k_{LL}$$
$$S_a = 1 \tag{36}$$

and therefore the atactic propagation rate is not given by

$$R_a = k_a M \eta_a N$$
$$\eta_a = N_a / N \tag{37}$$

Notice that in these equations the subscript a refers to the sites which produce the most amorphous of the fractions.

Suter[24,25] has obtained amorphous polypropylene through the epimerization of the highly isotactic fraction to stereo chemical equilibrium. Even though such an atactic polymer has not exactly presented a Bernoullian distribution for the dyads, it consists of stereo sequences which are very close to those envisaged for an idealized atactic polymer, as given by equations (36) and (37) above. Nevertheless, the comparisons between the pentad stereo sequence distributions, obtained via n.m.r. for both the atactic epimerized polymer[25] and the most amorphous of the fractions produced with $\delta - TiCl_3 + AlEt_2Cl^3$, show the existence of strong differences[2]. For the [mmmm](= [DDDDD] + [LLLLL]) pentad concentration, for example, the application of

statistical expressions derived from equations (36), (37) and (22), (23) gives values of 0.063 and 0.053, respectively, which are close to the n.m.r. value (0.05) obtained for the epimerized polymer, but very different from the n.m.r. value (0.44) obtained for the polypropylene fraction soluble in cold solvent.

A proposed approach

For these reasons, a different approach must be developed to account for the production of the stereo-irregular fractions. Reference 3 has suggested that only more general models like that derived by Coleman and Fox[26] would be able to predict entirely the structure of the whole polymer. From the critical point of view of these authors, however, the model developed by Coleman and Fox can functionally be applied in order to verify whether a given kinetic approach is valid or not, by checking if the stereo sequence distributions are Bernoullian, Markovian or non-Markovian, but not in order to provide a mathematical structure suitable for practical and definite simulation purposes.

Kissin[2] has proposed, based on n.m.r., i.r. and melting point data analyses, that such a stereo sequence inhomogeneity is caused by the existence of a continuous distribution of active centres with respect to their stereo specificity, which gives rise to the formation of macromolecules with various degrees of stereo regularity.

This conceptual model is particularly important for our purposes because it allows us to extend the j distribution to cover all sites, independent of solubility fraction.

Kissin's suggestion seems to be correct because the melting temperatures of each fraction obtained by the multisolvent solubility technique are quite different. Conversely, if only two types of sites were to exist, one producing highly stereo regular polymer and the other producing purely atactic polymer, so that any fraction of intermediate stereo regularity would be accidental mixtures of these polymers (probably due to inefficient fractionation with respect to both molecular weight and stereo regularity), then the melting temperature of these fractions would lie close to that of the stereo regular polymer.

Flory's equation for correlation between the melting temperature of a semicrystalline polymer and its thermodynamic and structural characteristics

$$1/T_m - 1/T_m^0 = -(R/\Delta H_m)\ln(p^*) \tag{38}$$

can be used to demonstrate the wide range of melting temperatures associated with polymer fractions of different stereoregularity. T_m is the polymer equilibrium melting point, T_m^0 is the equilibrium melting point for the perfectly stereoregular polymer, ΔH_m is the heat of fusion per crystallized unit, and R is the gas constant. The parameter p^* is the probability for a given stereo unit selected at random to be followed by a unit with the same structure and configuration.

It predicts a significant melting temperature depression as the stereoregularity decreases. Furthermore, the plot of $1/T_m$ versus $-\ln(p^*)$ must be a straight line. Kissin[2] and Pavan et al.[3] have confirmed this prediction.

These plots do not prove that Kissin's[2] proposition is correct. They merely indicate that his idea is in accord with observations presently available. It also gives a basis for our interpretation, according to which if an ideal fractionation were to exist, dependent only on

stereoregularity, the $S(j)$ value, estimated via spectroscopic analysis of each fraction, would be the true stereoregulating factor associated with each j class of sites.

In practice, such an approach should be a rough approximation of the real world, because it is quite improbable that the fractionation technique available is capable of providing a perfect separation of the macromolecules based only on their stereo regularity. The fractionation may also depend on molecular weight.

For the polymer produced on a j-type site, the parameter $p^*(j)$ is associated with $S(j)$ by means of the following relationship, which involves the statistical expressions given by equations (30) and (32)

$$p^*(j) = (F_D(j))_D(p_{DD}(j))_D + (F_L(j))_D(p_{LL}(j))_D$$
$$= [S^2(j) + 1]/(S(j) + 1)^2 \qquad (39)$$

This equation was derived by using the expressions for the D-preferring centres. Notice that the same result would be obtained if the expressions for the L-preferring centres were used.

The parameter $S(j)$ can be evaluated from n.m.r. or i.r. data. With respect to the stereo sequence distribution measured by n.m.r. (mole fractions), the expressions below were directly obtained by using equations (30)–(32). The spectroscopic notation for meso (m) and racemic (r) is used in order to make them more concise. However, their meaning in terms of D and L configurations are explicitly shown for dyads and triads.

For dyads

$$m(j) = DD(j) + LL(j) = [S^2(j) + 1]/(S(j) + 1)^2$$
$$r(j) = LD(j) + DL(j) = 2S(j)/(S(j) + 1)^2 \qquad (40)$$

For triads

$$mm(j) = DDD(j) + LLL(j) = [S^3(j) + 1]/(S(j) + 1)^3$$
$$rr(j) = DLD(j) + LDL(j) = S(j)/(S(j) + 1)^2 \qquad (41)$$

(Notice that $rr(j) = mr(j) = DDL(j) + LLD(j) = rm(j) = LDD(j) + DLL(j)$)

For tetrads

$$mmm(j) = [S^4(j) + 1]/(S(j) + 1)^4$$
$$rrr(j) = 2S^2(j)/(S(j) + 1)^4 \qquad (42)$$

(Notice that $rrr(j) = mrm(j) = rmr(j)$)

$$mmr(j) = [S^3(j) + S(j)]/(S(j) + 1)^4$$

(Notice that $mmr(j) = rmm(j) = mrr(j) = rrm(j)$)

For pentads

$$mmmm(j) = [S^5(j) + 1]/(S(j) + 1)^5$$
$$mmrr(j) = [S^4(j) + S(j)]/(S(j) + 1)^5 \qquad (43)$$

(Notice that $mmrr(j) = rrmm(j) = mmmr(j) = rmmm(j) = mrrm(j)$)

$$rrrr(j) = [S^3(j) + S^2(j)]/(S(j) + 1)^5$$

(Notice that $rrrr(j) = rmmr(j) = rrrm(j) = mrrr(j) = rrmr(j) = rmrr(j) = rmrm(j) = mrmm(j) = mmrm(j)$)

The relationship between the parameter $S(j)$ and i.r. data involves more complex statistical calculations. The absorbance (A) of a regularity band in a polymer i.r. spectrum is given by[2]

$$A = K_{ab}\pi_{n+1}L_w \qquad (44)$$

where K_{ab} is the absorption coefficient of the regularity band, L_w is the sample thickness, and

$$\pi_{D(n+1)}(j) = \frac{S^{n+1}(j)(S(j) + n + 1) + S(j)(n + 1) + 1}{(S(j) + 1)^{n+2}} \qquad (45)$$

is the distribution of monomer units in isotactic sequences larger than some minimum size n, as the fraction of monomer units in isotactic sequences of length $n + 1$ to infinity, normalized over the total number of these units in a polymer chain. For polypropylene specifically, the following expression has been reported[2,27]

$$\pi_{11\ 12} = \left(\frac{A_{998}}{A_{1460}}\right)\left(\frac{1}{N_{ab}}\right) \qquad (46)$$

where N_{ab} is the absorption coefficient ratio.

It should be recognized that equations (39)–(43) and (45) are to be applied for each $S(j)$ value separately. It means that each fraction obtained through multisolvent solubility should be envisaged as a fraction produced by a particular class of sites with respect to $S(j)$, but not necessarily with respect to $k_i(j)$. In other words, each fraction will be thought of as if it came from those j classes of sites which, although having different pairs of values for the isotactic and syndiotactic placements rate constants, possess the same value for the ratio between them. As it has been pointed out above, two or more j classes might have equal stereo regulating power.

Figure 1 presents Mw versus $1/S(j)$ evaluated in fractions of polypropylene segregated by multisolvent fractionation. It was generated by using Kissin's[2] data for polypropylene produced with $\delta - TiCl_3 + AlEt_2Cl$ at 70°C. As can be noted, the molecular weight decreases exponentially as the polymer stereo regularity decreases.

If the MWD does not affect the fractionation process to a significant extent, there will be only one explanation for the decrease in molecular weight with stereo regularity: the sites which produce the stereo irregular polymer have a larger chain transfer rate constant to propagation rate constant ratio than those which produce isotactic polymer. It has been reported[28] that for the $MgCl_2 + TiCl_4 + AlEt_3$ catalytic system at 60°C, most of the active sites (90%) are aspecific. In addition, the average propagation rate constant for the isospecific sites is two times larger than the overall propagation rate
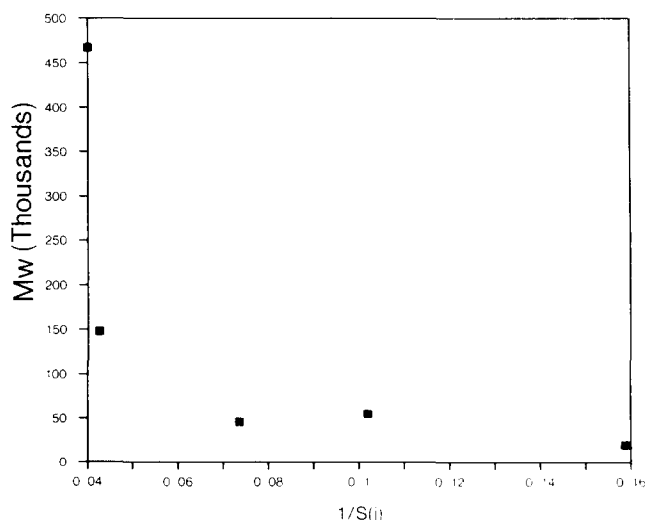

Figure 1 Polypropylene stereoregularity distribution: molecular weight as a function of stereoregularity

constant, indicating that the propagation rate constant for the aspecific sites is at most one half of the propagation rate constant for the isospecific sites. By adding ethyl benzoate to this catalyst the mean propagation rate constant increased by a factor of six, indicating that the ester has possibly poisoned the aspecific sites because the total number of sites became equal to the number of isospecific sites. Analogous conclusions have also been drawn[29] for the same catalytic system. Conversely, Chien[30] has reported, based on qualitative evidence, that for the catalyst $\alpha - TiCl_3 + AlEt_2Cl$ the propagation rate constant for the aspecific sites is not appreciably different from that for the isospecific ones.

Despite all these limitations and controversy, the conceptual model presented here is expected to agree with experiment as fractionation efficiencies improve. Hence, the propagation rate expression will be generalized to be valid for each j-type of site, by means of the following bivariate equation

$$R(j) = (1 + 1/S(u))(k_i(j)\eta(j))MN \qquad (47)$$

where the index u denotes the fraction, and j varies over values from j_0 to j_n such that

$$S(u) = k_i(j)/k_s(j) \qquad (48)$$

is true.

The propagation rate for each u fraction will then be given by

$$R(u) = (1 + 1/S(u))(\bar{k}_i(u)\eta(u))MN \qquad (49)$$

where

$$\bar{k}_i(u)\eta(u) = \sum_{i_0}^{j_n} k_i(j)\eta(j) \qquad (50)$$

The total propagation rate, considering all j, will be given by

$$R = \bar{k}MN \qquad (51)$$

where

$$\bar{k} = \sum_u (1 + 1/S(u))(\bar{k}_i(u)\eta(u)) \qquad (52)$$

Equations (47)–(52) constitute the basis for the development of a mathematical structure capable of accounting for the production of polymer fractions with different stereo regularity. Using equations (49) and (51) it is possible to calculate the instantaneous weight fraction of each u fraction

$$W_f(u) = R(u)/R \qquad (53)$$

which will be a constant value throughout the polymerization if it is carried out in a continuous stirred tank reactor (CSTR) under steady state conditions with stable catalyst. In this case, the relationship

$$\bar{k}_i(u)\eta(u) = (S(u)/[S(u)+1])\bar{k}_iW_f(u) = F_i(u)\bar{k}_iW_f(u) \quad (54)$$

will provide the estimation for the product between the mean isotactic rate constant within each u fraction and its corresponding fraction of sites, or rather, the estimation of the empirical distribution of the propagation rate constant.

Figure 2 was also created using Kissin's[2] data. It shows the cumulative weight of the fractions versus $1/S(u)$. According to Kissin's interpretation, the pattern of this curve should be expected for all highly isospecific heterogeneous Ziegler–Natta catalysts. There would be a maxi-
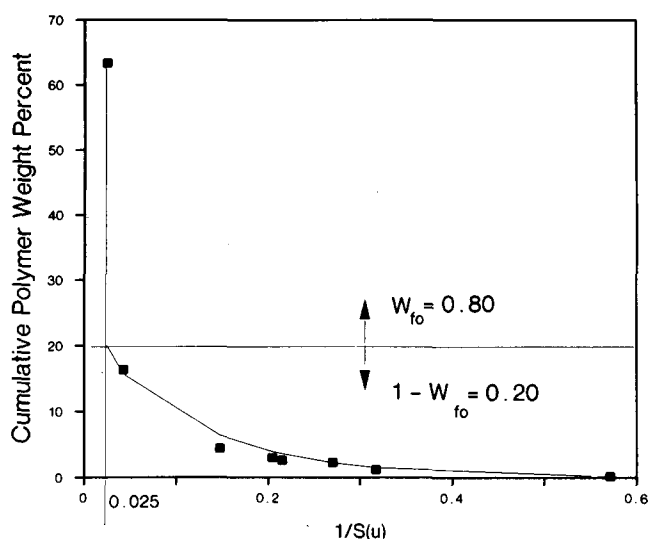

Figure 2 Polypropylene stereoregularity distribution: mass fraction of polymer as a function of stereoregularity

mum value for $S(u)$, or minimum for $1/S(u)$, which would be associated with that fraction of polymer which can not be further fractionated, W_{f0}. The other portion, $1 - W_{f0}$, would be composed of fractions which would possess different degrees of stereoregularity, so that a cumulative distribution would exist from $(1/S(u)_{max}; 1 - W_{f0})$ to $(1/S(u)_{min}; 0)$. For the simplest cases, which include $\delta - TiCl_3 + AlEt_2Cl$, Kissin has suggested that a normalized exponential function can arbitrarily be adopted to fit this distribution, defined for $1/S(u)_{min} = 1$, as below

$$\sum_u E(1/S(u)) = W_{f0} + (1 - W_{f0})\int_{1/S(u)_{max}}^{1/S(u)_{min}} E(1/S(u))$$

$$\times d(1/S(u)) = 1$$

$$E(1/S(u)) = \lambda\frac{\exp(-\lambda(1/S(u) - 1/S(u)_{max}))}{1 - \exp(-\lambda(1 - 1/S(u)_{max}))} \qquad (55)$$

where λ is the width of the distribution.

For polypropylene produced at 70°C with $TiCl_3 + AlEt_2Cl$, Kissin[2] has reported the following values

$$1/S(u)_{max} = 0.025$$

$$W_{f0} = 0.80$$

$$\lambda = 3-4$$

The effect of temperature

It should be recognized that, except for change in temperature, equations (47)–(55) can be used to simulate the production of polypropylene provided that both the kind and the method of catalyst preparation remain unchanged. Actually, the kind of catalyst system, including both the type and the concentration of co-catalyst and promoter agent, affect the polymer stereoregularity to a great extent[32].
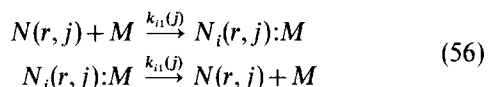
It is also well known that the temperature may have, depending on the catalyst type, a strong influence upon the polymer stereo regularity. It has been found[31] that during propylene polymerization with the commercial Stauffer catalyst $TiCl_30.33AlCl_3 + AlEt_2Cl$ the polymer tacticity (as the weight percent of the fraction insoluble in boiling heptane) increased slightly from 30 to 50°C and

then decreased sharply from 60 to 70°C. In addition, the presence of hydrogen as chain transfer agent did not affect the polymer tacticity.
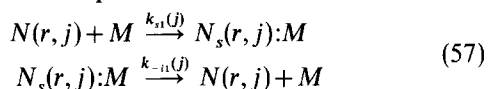
Working with $TiCl_3 + HPT + AlEt_2Cl$, Clombs *et al.*[32] has presented stereo regularity distributions for polypropylene, as the cumulative weight of fractions *versus* the parameter p^*, at three temperatures (40, 70, and 80°C). According to his plots, higher temperatures give broader distributions, but do not affect significantly the stereo regularity limit $S(u)_{max}$. In equation (55), the parameter $\lambda(1 - W_{f0})$ should increase as the temperature increases.

On the other hand, Rishina *et al.*[33] have reported that for less isospecific catalysts $\alpha - TiCl_3 + AlEt_3$ and $VCl_3 + AlEt_3$ the parameter $S(u)_{max}$ depends strongly on temperature. They have adopted an approach which assumes that the mechanism for propagation involves two consecutive steps. If one incorporates the j distribution for the site types, it can be developed as follows.
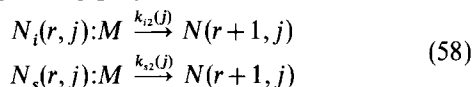
The reversible coordination of the olefin molecule with the transition metal on the active site, forms either an isotactic

$$N(r,j) + M \xrightarrow{k_{i1}(j)} N_i(r,j){:}M$$
$$N_i(r,j){:}M \xrightarrow{k_{i1}(j)} N(r,j) + M \tag{56}$$

or a syndiotactic complex

$$N(r,j) + M \xrightarrow{k_{s1}(j)} N_s(r,j){:}M$$
$$N_s(r,j){:}M \xrightarrow{k_{-s1}(j)} N(r,j) + M \tag{57}$$

The insertion of the olefin molecule between the metal atom and the growing polymer chain

$$N_i(r,j){:}M \xrightarrow{k_{i2}(j)} N(r+1,j)$$
$$N_s(r,j){:}M \xrightarrow{k_{s2}(j)} N(r+1,j) \tag{58}$$

As has already been pointed out[34], the two-step mechanism, which was initially proposed in Natta's early publications, remains as the most likely one despite all subsequent propositions. Assuming the stationary state hypothesis for the complex, and neglecting chain length effects, one can show that the j propagation rate, in terms of monomer consumption, is given by

$$R(j) = \frac{k_1(j)k_2(j)MN(j)}{k_1(j)M + k_{-1}(j) + k_2(j)} \tag{59}$$

where

$$N(j) = N(r,j) + N(r+1,j) \tag{60}$$

and

$$k_1(j) = k_{i1}(j) + k_{s1}(j)$$
$$k_{-1}(j) = k_{-i1}(j) + k_{-s1}(j) \tag{61}$$
$$k_2(j) = k_{i2}(j) + k_{s2}(j)$$

Notice that equation (59) is compatible with equations (5) and (11) on the condition that one of the following is true:

Very weak monomer coordination, i.e.

$$k_{-1}(j) \gg k_1(j)M \tag{62}$$

Or, very fast insertion stage, i.e.

$$k_2(j) \gg k_1(j)M$$
$$k_2(j) \gg k_{-1}(j) \tag{63}$$

In addition, for such a mechanism, in which $j_0 < j < j_n$, it

can be stated that

$$S(u) = \frac{[N_i(j){:}M]k_{i2}(j)}{[N_s(j){:}M]k_{s2}(j)} \tag{64}$$

Applying the stationary state hypothesis for both complexes

$$\frac{d}{dt}[N_i(j){:}M] = 0$$
$$\frac{d}{dt}[N_s(j){:}M] = 0 \tag{65}$$

one gets

$$[N_i(j){:}M] = \frac{k_{i1}(j)N(j)M}{(k_{-i1}(j) + k_{i2}(j))}$$
$$[N_s(j){:}M] = \frac{k_{s1}(j)N(j)M}{(k_{-s1}(j) + k_{s2}(j))} \tag{66}$$

where $N(j)$ is the initial concentration of the j active centres minus the corresponding complex concentrations, i.e.

$$N(j) = N_0(j) - [N_i(j){:}M] - [N_s(j){:}M] \tag{67}$$

Therefore, it can be established, by combining equations (64) and (66), that

$$S(u) = \frac{k_{i1}(j)(1 + k_{-i1}(j)/k_{i2}(j))}{k_{s1}(j)(1 + k_{-s1}(j)/k_{s2}(j))} \tag{68}$$

Or, in terms of Arrhenius temperature dependence for all rate constants

$$S(u) = Z_1(j)(Z_2(j)/Z_3(j)) \tag{69}$$

where

$$Z_1(j) = \left(\frac{A_{i1}(j)}{A_{s1}(j)}\right)\exp\left(-\left(\frac{E_{i1}(j) - E_{s1}(j)}{RT}\right)\right)$$
$$Z_2(j) = 1 + \left(\frac{A_{-s1}(j)}{A_{s2}(j)}\right)\exp\left(-\left(\frac{E_{-s1}(j) - E_{s2}(j)}{RT}\right)\right) \tag{70}$$
$$Z_3(j) = 1 + \left(\frac{A_{-i1}(j)}{A_{i2}(j)}\right)\exp\left(-\left(\frac{E_{-i1}(j) - E_{i2}(j)}{RT}\right)\right)$$

Equations (69) and (70) express the dependence of the parameter $S(u)$ on temperature, for each one of the u fractions considered. Consequently, the number of unknowns is enormous. However, a rough approximation can be used by recognizing that the parameter λ in equation (55) is related to the mean of the $E(1/S(u))$ distribution by means of

$$\text{mean}(1/S(u)) = 1/\lambda = \int_{1/S(u)_{max}}^{1/S(u)_{min}} (1/S(u))E(1/S(u))d(1/S(u)) \tag{71}$$

Thus, it can be stated that

$$\text{mean}(S) = \lambda = \text{mean}(Z_1)\left(\frac{\text{mean}(Z_2)}{\text{mean}(Z_3)}\right) \tag{72}$$

where each mean(Z) corresponds to $Z(j)$ in equation (70), but is considered to be independent of j.

Moreover, equation (72) can also be applied for the insoluble fraction

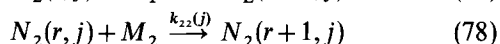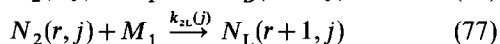$$S_{max} = Z_{1_{max}}\left(\frac{Z_{2_{max}}}{Z_{3_{max}}}\right) \tag{73}$$
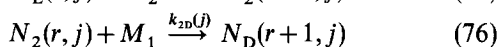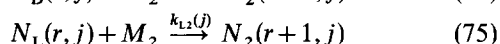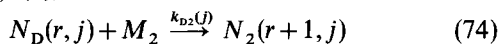
Even so, some unknowns will remain. Viezen *et al.*[33] have used equations (69) and (70), without considering any *j* distribution, in order to simulate the dependence of $1/S(u)_{max}$ with temperature, for the catalyst $\alpha - TiCl_3 + AlEt_3$. This has provided some guidelines for choosing the unknowns. Firstly, A_{i1}/A_{s1} should be close to 1, because the entropy factors for these two types of monomer coordination on an active site are similar. Notice that such an assumption should be valid for any fraction *u* to be considered. The value adopted was 1.5. Secondly, $E_{i1} - E_{s1}$ should be negative and equal to a few kcal/mol (-3.5 was adopted). The ratios A_{-i1}/A_{i2} and A_{-s1}/A_{s2} should be substantially greater than 1, since $A_{-1} \gg 10^3$ and $A_2 \ll 10^3$ for both cases. In addition, $A_{-s1}/A_{s2} \gg A_{-i1}/A_{i2}$ should prevail. The values 15 000 and 10 were adopted for syndiotactic and isotactic placements. Somewhat arbitrarily $E_{-i1} - E_{i2} = -0.9$ kcal/mol and $E_{-s1} - E_{s2} = 6.0$ kcal/mol were used.

Copolymer stereochemical pattern

It has been proven that Zieger–Natta catalysts are capable of producing true propylene–ethylene copolymers[36-50], not just mixtures of homopolymers. Even for the so-called block copolymers, with respect to which there was, for a long time, doubt about whether such copolymers were true copolymers or merely a mixture of homopolymers[51], it has been demonstrated[2,52,53] that the formation of true multi-blocks of ethylene and propylene actually takes place. However, the production of perfect block copolymers is quite improbable[2,51] because the catalyst centres would have to satisfy many unlikely demands, such as simultaneous activation, absence of deactivation and transfer reactions, equal activity, equal accessibility for all monomers, high crossover propagation rate constant, high, and equal, isospecificity and regiospecificity.

It has also been shown[42,46,48,50] that the presence of ethylene does not affect the regioselectivity of the Ti-based (whether supported or not) heterogeneous Ziegler–Natta catalysts. Independently of the ethylene content, the amount of propylene inversion remains negligible[48,50]. Significant amounts of propylene inversion have been reported only for copolymers prepared with V-based or soluble catalysts, which produce syndiotactic homopolymer[45,46,48,50]. In that case the copolymerization mechanism should account not only for the stereo additions, but also for the regio-additions, i.e., it should be considered a terpolymerization between ethylene and two pseudomonomers: head–tail and tail–head oriented propylene[46,55,57].

When only the stereo additions are of interest, the simplest kinetic mechanism for the α-olefin–ethylene copolymer propagation involves five more reactions, in addition to those for the polypropylene production equations (1)–(4), as shown below

$$N_D(r,j) + M_2 \xrightarrow{k_{D2}(j)} N_2(r+1,j) \qquad (74)$$

$$N_L(r,j) + M_2 \xrightarrow{k_{L2}(j)} N_2(r+1,j) \qquad (75)$$

$$N_2(r,j) + M_1 \xrightarrow{k_{2D}(j)} N_D(r+1,j) \qquad (76)$$

$$N_2(r,j) + M_1 \xrightarrow{k_{2L}(j)} N_L(r+1,j) \qquad (77)$$

$$N_2(r,j) + M_2 \xrightarrow{k_{22}(j)} N_2(r+1,j) \qquad (78)$$

Notice that ethylene is a symmetrical molecule and therefore can have no D or L orientation.

This scheme does not consider either penultimate or complex participation or any other higher order effects, so that it is implicitly assumed that a terminal model is suitable for this heterogeneous Ziegler–Natta polymerization system. Notice that M_2 represents an ethylene molecule and that M_1 represents the α-olefin.

The propagation rate expression given by equation (5) continues to be valid. $N(j)$, $\eta(j)$, and N continue having the same definitions as above, but M represents now the total monomer (α-olefin and ethylene) concentration on the catalyst surface

$$M = M_1 + M_2 \qquad (79)$$

and $k_{(j)}$, the global *j* propagation rate constant, is a pseudo-rate constant[1] given by

$$k(j) = k_{11}(j)\phi_1(j)f_1 + k_{12}(j)\phi_1(j)f_2$$
$$+ k_{21}(j)\phi_2(j)f_1 + k_{22}(j)\phi_2(j)f_2 \qquad (80)$$

In this equation

$$\phi_1(j) = 1 - \phi_2(j) = N_1(j)/(N_1(j) + N_2(j)) \qquad (81)$$

is the fraction of α-olefin-attached *j*-type sites, and

$$f_1 = 1 - f_2 = M_1/(M_1 + M_2) \qquad (82)$$

is the monomer composition, as previously defined[1]. However, it should be recognized that for this copolymer case, in which (8) must be rewritten as

$$N(j) = N_1(j) + N_2(j)$$
$$N_1(j) = N_D(j) + N_L(j) \qquad (83)$$

Thus, the following relationship will prevail

$$\phi_1(j) = \phi_D^*(j) + \phi_L^*(j) = 1 - \phi_2(j) \qquad (84)$$

where

$$\phi_D^*(j) = \frac{N_D(j)}{N(j)} = \phi_D(j)\phi_1(j) = \left(\frac{N_D(j)}{N_1(j)}\right)\left(\frac{N_1(j)}{N(j)}\right)$$

$$\phi_L^*(j) = \frac{N_L(j)}{N(j)} = \phi_L(j)\phi_1(j) = \left(\frac{N_L(j)}{N_1(j)}\right)\left(\frac{N_1(j)}{N(j)}\right) \qquad (85)$$

Hence, equation (80) can be rewritten as

$$k(j) = ((k_{DD}(j) + k_{DL}(j))\phi_D^*(j) + (k_{LD}(j) + k_{LL}(j))\phi_L^*(j))f_1$$
$$+ (k_{D2}(j)\phi_D^*(j) + k_{L2}(j)\phi_L^*(j))f_2 + k_{21}(j)\phi_2(j)f_1$$
$$+ k_{22}(j)\phi_2(j)f_2 \qquad (86)$$

As above, the overall propagation rate for all *j*-type sites will be given by a first order equation with respect to the monomer concentration.

$$R = \sum_j R(j) = \bar{k}MN$$
$$\bar{k} = \sum_j k(j)\eta(j) \qquad (87)$$

Assuming that the following equalities are valid for all *j* (long chain approximation)

$$k_{12}(j)\phi_1(j)f_2 = k_{21}(j)\phi_2(j)f_1$$
$$k_{D2}(j) = k_{L2}(j)(= k_{12}(j))$$
$$\phi_1(j) = 1 - \phi_2(j) = \frac{k_{21}(j)f_1}{k_{12}(j)f_2 + k_{21}(j)f_1} \qquad (88)$$

one can express the instantaneous copolymer composition, as moles of α-olefin units in the polymer produced on

the j-type sites, as below

$$F_1(j)=1-F_2(j)=\frac{r_1(j)(f_1/f_2)+1}{(r_1(j)(f_1/f_2+1)+(r_2(j)(f_2/f_1)+1)} \quad (89)$$

where

$$r_1(j)=k_{11}(j)/k_{12}(j)$$
$$=((k_{DD}(j)+k_{DL}(j))\phi_D(j)+(k_{LD}(j)$$
$$+k_{LL}(j))\phi_L(j)/k_{12}(j))$$
$$r_2(j)=k_{22}(j)/k_{21}(j) \quad (90)$$

are the reactivity ratios. Notice that the reactivity ratio for the α-olefin propagation is related to the stereo reactivity ratios defined in equation (15) by means of

$$r_1(j)=\left(\frac{k_{DD}(j)\phi_D(j)}{k_{12}(j)}\right)\left(1+\frac{1}{S_D(j)}\right)$$
$$+\left(\frac{k_{LL}(j)\phi_L(j)}{k_{12}(j)}\right)\left(1+\frac{1}{S_L(j)}\right) \quad (91)$$

It ought to be recognized once more that the j classes of sites are defined in terms of propagation rate constants, so that, although it is quite unlikely to occur, two or more different classes of sites can possess the same copolymer composition as well as the same stereo composition.

The expressions for the chemical dyads will be

$$d_{11}(j)=\frac{r_1(j)(f_1/f_2)}{(r_1(j)(f_1/f_2)+1)+(r_2(j)(f_2/f_1)+1)}$$

$$d_{12}(j)+d_{21}(j)=\frac{2}{(r_1(j)(f_1/f_2)+1)+(r_2(j)(f_2/f_1)+1)} \quad (92)$$

$$d_{22}(j)=\frac{r_2(j)(f_2/f_1)}{(r_1(j)(f_1/f_2)+1)+(r_2(j)(f_2/f_1)+1)}$$

Therefore, the ratio between the chemical dyads and the copolymer composition will provide the conditional probabilities for chemical placements on both α-olefin and ethylene-attached j-type of sites separately

$$p_{11}(j)=\frac{k_{11}(j)\phi_1(j)f_1}{k_{11}(j)\phi_1(j)f_1+k_{12}(j)\phi_1(j)f_2}$$
$$=\frac{d_{11}(j)}{F_1(j)}=\frac{r_1(j)(f_1/f_2)}{(r_1(j)(f_1/f_2)+1)} \quad (93)$$

$$p_{12}(j)=1-p_{11}(j)=\frac{1}{(r_1(j)(f_1/f_2)+1)}$$

$$p_{22}(j)=\frac{k_{22}(j)\phi_2(j)f_2}{k_{22}(j)\phi_2(j)f_2+k_{21}(j)\phi_2(j)f_1}$$
$$=\frac{d_{22}(j)}{F_2(j)}=\frac{r_2(j)(f_2/f_1)}{(r_2(j)(f_2/f_1)+1)} \quad (94)$$

$$p_{21}(j)=1-p_{22}(j)=\frac{1}{(r_2(j)(f_2/f_1)+1)}$$

In terms of stereo regularity, however, each α-olefin-attached j-type site is comprised of D- and L-attached configurations. Thus, the conditional probabilities for consecutive stereoplacements will be obtained by multiplying equations (22) and (23) by (93), i.e.

For the D-attached j-type sites

$$p_{DDc}(j)=p_{DD}(j)p_{11}(j)=\frac{r_1(j)S_D(j)(f_1/f_2)}{(r_1(j)(S_D(j)+1)(f_1/f_2)+1)} \quad (95)$$

$$p_{DLc}(j)=p_{DL}(j)p_{11}(j)=\frac{r_1(j)(f_1/f_2)}{(r_1(j)(S_D(j)+1)(f_1/f_2)+1)}$$

For the L-attached type of sites

$$p_{LLc}(j)=p_{LL}(j)p_{11}(j)=\frac{r_1(j)S_L(j)(f_1/f_2)}{(r_1(j)(S_L(j)+1)(f_1/f_2)+1)} \quad (96)$$

$$p_{LDc}(j)=p_{LD}(j)p_{11}(j)=\frac{r_1(j)(f_1/f_2)}{(r_1(j)(S_L(j)+1)(f_1/f_2)+1)}$$

One of the most important characteristics of the Ti-based heterogeneous Ziegler–Natta catalysts is that their ability to promote isotactic placements is not affected by the presence of the ethylene comonomer[2,38,40–42,44,46]. In addition, Kissin[2] has demonstrated that the propylene distribution in sufficiently long isotactic sequences in C_3H_6–C_3D_6 and C_3H_6–C_2H_4 copolymers, produced with α- and δ-TiCl$_3$ catalysts, is not influenced by the chemical structure, conformation, or crystallinity of the polymer products, so that the probability of the formation of long isotactic propylene sequences does not depend on their neighbours, but only on the chirality of the catalyst centres. For this reason, the mathematical treatment developed for α-olefin homopolymer can be easily extended for the α-olefin–ethylene copolymer case. Therefore, if the single parameter enantiomorphic-site model is assumed for the propylene addition, equations (26) and (27) will remain valid and the following relationships for the inter-monomer propagation rate constants must be applied

$$(k_{D2}(j))_D=(k_{L2}(j))_L=(k_{L2}(j))_D=(k_{D2}(j))_L$$
$$(k_{2D}(j))_D=(k_{2L}(j))_L \gg (k_{2L}(j))_D=(k_{2D}(j))_L \quad (97)$$

Consequently, equations (95) and (96) can be rewritten in terms of D and L-preferring type sites

$$(p_{DDc}(j))_D=(p_{LLc}(j))_L=\frac{r_1(j)S(j)(f_1/f_2)}{(r_1(j)(S(j)+1)(f_1/f_2)+1)}$$

$$(p_{DLc}(j))_D=(p_{LDc}(j))_L=\frac{r_1(j)(f_1/f_2)}{(r_1(j)(S(j)+1)(f_1/f_2)+1)}$$

$$(p_{LLc}(j))_D=(p_{DDc}(j))_L=\frac{r_1(j)(f_1/f_2)}{(r_1(j)(S(j)+1)(f_1/f_2)+1)} \quad (98)$$

$$(p_{LDc}(j))_D=(p_{DLc}(j))_L=\frac{r_1(j)S(j)(f_1/f_2)}{(r_1(j)(S(j)+1)(f_1/f_2)+1)}$$

The copolymer (chemical) composition, the stereocomposition, and the probabilities given by equations (94), (95), and (98) can be used to evaluate the concentrations (mole fractions) of both the chemical and the stereo sequences. By defining the following variables

$$z_1(j)=r_1(j)(f_1/f_2) \quad (99)$$
$$z_2(j)=r_2(j)(f_2/f_1)=\frac{r_1(j)r_2(j)}{z_1(j)}$$

$$Q(j)=z_1^2(j)+2z_1(j)+r_1(j)r_2(j) \quad (100)$$

it will be possible to obtain more concise expressions for such sequences, mainly for those larger than dyads. The

copolymer composition will then be given by

$$F_1(j) = \frac{z_1(j)(z_1(j)+1)}{Q(j)}$$

$$F_2(j) = \frac{z_1(j)+r_1(j)r_2(j)}{Q(j)} \qquad (101)$$

where the following relationship prevails

$$z_1(j) = \frac{1}{2}\left(\left(\frac{F_1(j)}{F_2(j)}-1\right)+\left(\left(\frac{F_1(j)}{F_2(j)}-1\right)^2 + 4r_1(j)r_2(j)\frac{F_1(j)}{F_2(j)}\right)^{0.5}\right) \qquad (102)$$

As for the conditional probabilities, it follows, for the chemical placements, that

$$p_{11}(j) = \frac{z_1(j)}{z_1(j)+1}$$

$$p_{12}(j) = \frac{1}{z_1(j)+1}$$

$$p_{21}(j) = \frac{z_1(j)}{z_1(j)+r_1(j)r_2(j)} \qquad (103)$$

$$p_{22}(j) = \frac{r_1(j)r_2(j)}{z_1(j)+r_1(j)r_2(j)}$$

and for the stereo probabilities, considering D-preferring type sites

$$p_{DDc}(j) = \frac{z_1(j)S(j)}{(z_1(j)+1)(S(j)+1)}$$

$$p_{LLc}(j) = \frac{z_1(j)}{(z_1(j)+1)(S(j)+1)}$$

$$p_{DLc}(j) = \frac{z_1(j)}{(z_1(j)+1)(S(j)+1)} \qquad (104)$$

$$p_{LDc}(j) = \frac{z_1(j)S(j)}{(z_1(j)+1)(S(j)+1)}$$

Therefore, the chemical dyads can be calculated by means of

$$PP(j) = z_1^2(j)/Q(j)$$

$$PE(j)+EP(j) = 2z_1(j)/Q(j) \qquad (105)$$

$$EE(j) = r_1(j)r_2(j)/Q(j)$$

and the stereo-dyads, meso-dyad (m = DD + LL) and racemic-dyad (r = DL + LD), can be evaluated using

$$m(j) = \frac{(S^2(j)+1)z_1^2(j)}{Q(j)(S(j)+1)^2}$$

$$r(j) = \frac{2S(j)z_1^2(j)}{Q(j)(S(j)+1)^2} \qquad (106)$$

where P and E mean α-olefin and ethylene, respectively.

Proceeding with similar combinatory calculations, one can establish the expressions for triads, tetrads, and some important pentads, as follows

Chemical Triads

$$PPP(j) = \frac{z_1^3(j)}{Q(j)(z_1(j)+1)}$$

$$PPE(j)+EPP(j) = \frac{2z_1^2(j)}{Q(j)(z_1(j)+1)}$$

$$PEP(j) = \frac{z_1^2}{Q(j)(z_1(j)+r_1(j)r_2(j))}$$

$$EEP(j)+PEE(j) = \frac{2r_1(j)r_2(j)z_1(j)}{Q(j)(z_1(j)+r_1(j)r_2(j))} \qquad (107)$$

$$EPE(j) = \frac{z_1(j)}{Q(j)(z_1(j)+1)}$$

$$EEE(j) = \frac{(r_1(j)r_2(j))^2}{Q(j)(z_1(j)+r_1(j)r_2(j))}$$

Stereo Triads

$$mm(j) = \frac{(S^3(j)+1)z_1^3(j)}{Q(j)(z_1(j)+1)(S(j)+1)^3}$$

$$rr(j) = \frac{S(j)z_1^3(j)}{Q(j)(z_1(j)+1)(S(j)+1)^3} \qquad (108)$$

(Notice that $rr(j) = rm(j) = mr(j)$)

Chemical Tetrads

$$PPPP(j) = \frac{z_1^4(j)}{Q(j)(z_1(j)+1)^2}$$

$$PPPE(j)+EPPP(j) = \frac{2z_1^3(j)}{Q(j)(z_1(j)+1)^2}$$

$$PPEP(j)+PEPP(j) = \frac{2z_1^3(j)}{Q(j)(z_1(j)+1)(z_1(j)+r_1r_2)}$$

$$PPEE(j)+EEPP(j) = \frac{2r_1(j)r_2(j)z_1^2(j)}{Q(j)(z_1(j)+r_1(j)r_2(j))(z_1(j)+1)}$$

$$PEPE(j)+EPEP(j) = \frac{2z_1^2(j)}{Q(j)(z_1(j)+r_1(j)r_2(j))(z_1(j)+1)} \qquad (109)$$

$$PEEE(j)+EEEP(j) = \frac{2z_1(j)(r_1(j)r_2(j))^2}{Q(j)(z_1(j)+r_1(j)r_2(j))^2}$$

$$EEPE(j)+EPEE(j) = \frac{2z_1(j)r_1(j)r_2(j)}{Q(j)(z_1(j)+r_1(j)r_2(j))(z_1(j)+1)}$$

$$PEEP(j) = \frac{z_1^2(j)r_1(j)r_2(j)}{Q(j)(z_1(j)+r_1(j)r_2(j))^2}$$

$$EPPE(j) = \frac{z_1^2(j)}{Q(j)(z_1(j)+1)^2}$$

$$EEEE(j) = \frac{(r_1(j)r_2(j))^3}{Q(j)(z_1(j)+r_1(j)r_2(j))^2}$$

Stereo Tetrads

$$mmm(j) = \frac{(S^4(j)+1)z_1^4(j)}{Q(j)(z_1(j)+1)^2(S(j)+1)^4}$$

$$rrr(j) = \frac{2S^2(j)z_1^4(j)}{Q(j)(z_1(j)+1)^2(S(j)+1)^4} \qquad (110)$$

(Notice that $rrr(j) = mrm(j) = rmr(j)$)

$$mmr(j) = \frac{(S^3(j)+S(j))z_1^4(j)}{Q(j)(z_1(j)+1)^2(S(j)+1)^4}$$

(Notice that $= rmm(j) = mrr(j) = rrm(j)$)

Stereo Pentads

$$mmmm(j) = \frac{(S^5(j)+1)z_1^5(j)}{Q(j)(z_1(j)+1)^3(S(j)+1)^5}$$

$$mmrr(j) = \frac{(S^4(j)+S(j))z_1^5(j)}{Q(j)(z_1(j)+1)^3(S(j)+1)^5} \quad (111)$$

(Notice that $mmrr(j) = rrmm(j) = mmmr(j) = rmmm(j) = mrrm(j)$)

$$rrrr(j) = \frac{(S^3(j)+S^2(j))z_1^5(j)}{Q(j)(z_1(j)+1)^3(S(j)+1)^5}$$

(Notice that $rrrr(j) = rrrm(j) = mrrr(j) = rrmr(j) = rmrr(j) = rmrm(j) = mrmr(j) = mrmm(j) = mmrm(j) = rmmr(j)$)

Kissin[2] has used equations (105) and (107), without considering a j distribution, and assuming the stereo regulating factor equal to ∞, to fit the chemical dyads and triads distributions calculated by Ray *et al.*[57] for the highly isospecific fraction of propylene–ethylene copolymer produced with Ti-based catalyst at 0°C. At this temperature the propylene addition was found to be an entirely meso one. Despite the existence of some scattered triad concentration points, due to chemical inhomogeneity, good agreement was found for the dyads and for some triads (*PPP*, *EEE* and *PPE+EPP*) when the reactivity ratio product was set equal to 1.9.

He has concluded that it is further evidence for the fact that the ability of the catalyst centres to produce long meso sequences of propylene units is not altered by the presence of ethylene sequences of any length in the copolymer chain.

Nevertheless, it must be recognized that both the chemical and the stereo inhomogeneity presented by copolymers produced with heterogeneous Ziegler–Natta catalysts can only be satisfactorily explained if a multiple site model is adopted[1].

Many authors have reported spectroscopic data which show that the monomer sequence distribution in these copolymers does not agree with the Markov first order process and consequently with any probabilistic outlook based either on this or upon Bernoullian derivations[57-60]. As shown by Cozewith[61], the data from [57-59] can be fit if a multiple activity site approach is adopted. For these reasons a j distribution has to be used.

The distribution of α-olefin units in isotactic sequences larger than some minimum size n, normalized over all α-olefin units, will be given by

$$\pi_{Dc(n+1)}(j) = z_1^n(j)G(j) \quad (112)$$

where

$$G(j) = \frac{S^{n+1}(j)((n+1)(z_1(j)+S(j)+1)+z_1(j)S(j))}{(S(j)+1)^{n+2}(z_1(j)+1)^{n+1}}$$

$$+ \frac{(z_1(j)+1)(nS(j)+S(j)+1)+n}{(S(j)+1)^{n+2}(z_1(j)+1)^{n+1}} \quad (113)$$

Thus, equation (112) can be used to estimate $S(j)$ from i.r. measurements, on the condition that the reactivity ratios are known.

Equation (91) can now be written as

$$r_1(j) = \left(\frac{k_i(j)}{k_{12}(j)}\right)\left(1 + \frac{1}{S(j)}\right) \quad (114)$$

where

$$k_i(j) = (k_{DD}(j))_D = (k_{LL}(j))_L \quad (115)$$

Considering that the $S(j)$ distribution is not affected by the presence of ethylene, and proceeding as before, it can be established that

$$r_1(j) = \left(\frac{k_i(j)}{k_{12}(j)}\right)\left(1 + \frac{1}{S(u)}\right) \quad (116)$$

for imperfectly fractionated polymer.

Notice that equations (55), (68), and (71)–(73) continue to be valid for the copolymer case. Notice that, in addition to the MWD influence, there should be two opposite factors related to the influence of the copolymer composition upon the fractionation based on stereo regularity. Firstly, an increase in the ethylene content, to a certain limit, should affect the fractionation by increasing the solubility of the chains, because the insertion of ethylene units along the backbone of the chain can reduce the helix conformation and consequently the mean crystallinity of the polymer. Secondly, the ethylene content, if higher than a certain limit, should affect the fractionation by decreasing the solubility of the chains because polyethylene is insoluble in boiling *n*-heptane.

According to our proposition[1], if each fraction separated upon stereo regularity basis is subjected to TREF fractionation, then the main parameters of the whole model can be estimated by performing n.m.r. and g.p.c. measurements on each TREF fraction. In that case it is assumed that each class of site is associated with an unique copolymer composition. It seems to be a reasonable approximation because the TREF fractionation is much more precise than the fractionation based on stereo regularity.

Kissin[2] has presented correlations for the parameters of equations (117)–(119), without taking into account any j distribution, for several catalysts. For the α-TiCl$_3$ + AlEt$_3$ catalytic system, the following values have been reported

$$\bar{r}_1 = 0.110$$

$$\bar{r}_2 = 15.72$$

$$S(u)_{max} = 25.0$$

$$\frac{\bar{k}_{12}}{\bar{k}_{DD}} = 9.47$$

Chemical sequences larger than some size n

When only the chemical composition is of interest, one defines a chemical sequence as a sequence of monomer units flanked by two different monomer units. For a α-olefin–ethylene copolymer they can be represented by either (...*PEEEEEEEP*...) or (...*EPPPPPPPE*...).

The distribution of ethylene sequences, as the fraction of ethylene sequences containing n units normalized over the total amount of all sequences produced, is, for a j-type site, given by

$$\zeta_{2(n)}(j) = \frac{p_{12}(j)p_{22}^{n-1}(j)p_{21}(j)}{\sum_{n=1}^{\infty} p_{12}(j)p_{22}^{n-1}(j)p_{21}(j)} = \frac{z_2^{n-1}(j)}{(z_2(j)+1)^n} \quad (118)$$

Thus, the distribution of ethylene sequences larger than some minimum size n, as the fraction of ethylene sequences of length $n+1$ to infinity, normalized over the

total amount of all sequences, is, for a j-type site, given by

$$\zeta_{2(n+1)}(j) = 1 - \sum_{1}^{n} \zeta_{2(n)}(j) = \frac{z_2^n(j)}{(z_2(j)+1)^n} \quad (119)$$

The distribution of ethylene units in sequences of size n, as the fraction of ethylene units in sequences of length n normalized over the total amount of these ethylene units in a polymer chain, is, for a j-type site, given by

$$\chi_{2(n)}(j) = \frac{n\zeta_{2(n)}(j)}{\sum\limits_{n=1}^{\infty} n\zeta_{2(n)}(j)} = \frac{nz_2^{n-1}(j)}{(z_2(j)+1)^{n+1}} \quad (120)$$

Thus, the distribution of ethylene units in sequences larger than some minimum size n, as the fraction of ethylene units in sequences of length $n+1$ to infinity, normalized over the total amount of ethylene units in a polymer chain, is, for a j-type site, given by

$$\pi_{2(n+1)}(j) = 1 - \sum_{1}^{n} \chi_{2(n)}(j) = \frac{z_2^n(j)(z_2(j)+n+1)}{(z_2(j)+1)^{n+1}} \quad (121)$$

SIMULATION BASIS AND RESULTS

It has been pointed out[1] that the kinetic parameters of a multiple active site model can only be estimated if an extensive characterization of the polymer is performed. Such a characterization must basically involve a fractionation of the polymer based on its stereo regularity, followed by TREF fractionation, and n.m.r. and g.p.c. analysis of each TREF fraction.

The kinetic parameter estimation work is necessary because we cannot carry out realistic simulation studies, if we do not know the values of the main model parameters. To predict production rates we need to know only the average values for propagation rate constants and initiation, deactivation, and reactivation rate constants. Nevertheless, to forecast accurately the considerably nonhomogeneous polymer microstructure, we have to be acquainted with three basic empirical j distributions. The knowledge of $(k_{ik}(j)\eta(j))$ enables us to predict copolymer composition and chemical sequence distributions. The molecular weight investigation requires, as well, that $(\lambda(j)\eta(j))$ is determined[1]. Furthermore, if the stereo regularity pattern of the polymer is of interest, we must evaluate $(S(j)\eta(j))$.

Because we know nothing about the actual j distributions, we can adopt an empirical distribution for the propagation rate constants so as to have the parameters of these distributions as adjustable model parameters. These distributions must be in agreement with experimental evidence, i.e., they ought to be positively skewed. Proceeding in this manner, we can only generate speculative results for the polymer microstructure simulation. Unfortunately, any choice of distributions for $\lambda(j)$ and $S(j)$ will be completely arbitrary, because there are no reasonable guidelines for the choice of these distributions.

BASIS

Active site distribution

The chosen distribution for the propagation rate constants must be consistent with the experimental evidence available. Kissin[2] has reported that for propylene polymerization with δ-TiCl$_3$ + AlEt$_2$Cl at 30°C, the range for the propagation rate constant is quite wide: 2.0–500.0 l/mol s. The average value (about 10.0 l/mol s)

is, however, much smaller than the upper limit. Bohm[70,71] has also reported analogous figures for ethylene polymerization at 85°C, using a highly active catalyst system, obtained by reacting $Mg(OEt)_2$ with $TiCl_4$. Interpreting g.p.c. data from polymer produced in different stages of polymerization (15 and 7200 s), he has concluded that 2% of the active sites have a very high propagation rate constant (greater than 2900 l/mol s), whereas most of them (68%) have propagation rate constant values near the average value of 80 l/mol s.

Therefore, one can say that

$$\bar{k} = \int_{k_{min}}^{k_{max}} k f_d(k) dk \quad (122)$$

where k is a continuous random variable, having a positively skewed density function such that

$$\int_{k_{min}}^{k_{max}} f_d(k) dk = 1 \quad (123)$$

Indeed, it has been shown[1] that the instantaneous polydispersity of the polymer produced on each j-type site must be equal to 2. In addition, if the catalyst is stable and the polymerization takes place under steady state conditions, the overall polydispersity can be expressed by

$$\frac{r_w}{r_n} = \frac{2}{\bar{k}^2}\left(\sum_j \frac{k^2(j)\eta(j)}{\lambda(j)}\right)\left(\sum_j \lambda(j)\eta(j)\right) \quad (124)$$

where

$$\lambda(j) = k(j)\tau(j)$$
$$= k_{fm}(j) + (k_{fs}(j) + k_{fr}(j)[A] + k_{fh}(j)[H_2])/[M] \quad (125)$$

is the ratio between the total transfer rate and the monomer concentration.

If this ratio is assumed to be independent of j, then equation (6) can be written in terms of the mean and the variance of the $k(j)$ distribution

$$\frac{r_w}{r_n} = 2\left(1 + \frac{\sum\limits_j \left(k(j) - \sum\limits_j k(j)\eta(j)\right)^2 \eta(j)}{\left(\sum\limits_j k(j)\eta(j)\right)^2}\right)$$

Basically, two positively skewed distributions have been adopted, in the literature, to represent the propagation rate constant distribution, namely the exponential[75] and the log-normal[66].

Applying an exponential distribution for the propagation rate constant in this equation, we get a polydispersity of only four. Since the exponential distribution provides smaller variation coefficient than the log-normal distribution, the latter should be adopted. It should be noted that a log-normal distribution for the propagation rate constant implies that (if the frequency factor is assumed to be constant for all j) the activation energy is normally distributed, because of the Arrhenius expression which relates them.

Therefore, each $N(j)$ associated with its correspondent $k(j)$, can be evaluated by solving the following relationships

$$N(j) = \int_{k(j-1)}^{k(j+1)} N f_d(k) d(k)$$
$$k(j) = (k(j-1) + k(j+1))/2$$
$$\int_0^{k_{max}} f_d(k) dk = \sum_j \eta(j) = 1 \quad (126)$$

$$f_a(k) = \left(\frac{k^{-1}}{(2\pi)^{1/2}\sigma^*}\right)\exp\left(-\frac{(k^* - \mu^*)^2}{2\sigma^{*2}}\right)$$

where $k^* = \ln(k)$ is normally distributed with parameters (mean and variance) μ^* and σ^{*2}, respectively. These parameters are related to the mean and variance of the log-normally distributed k variable by means of

$$\mu = \exp(\mu^* + \sigma^{*2}/2)$$

$$\sigma^2 = \exp(2\mu^* + \sigma^{*2})(\exp(\sigma^{*2}) - 1) \tag{127}$$

Equation (125) can therefore be rewritten as

$$r_w/r_n = 2\exp(\sigma^{*2})$$

Notice that if one lets μ^* and σ^{*2} be the mean and the variance of the normal activation energy distribution, then equation (127) can be used to calculate the mean and the variance of the corresponding quasi-log-normal distribution for the propagation rate constant by means of

$$\mu_{k(j)} = A \exp\left(\left(-\frac{\mu_{E(j)}}{RT}\right) + \frac{(-\sigma_{E(j)}/RT)^2}{2}\right)$$

$$\sigma_{k(j)}^2 = A^2 \exp\left(2\left(\frac{-\mu_{E(j)}}{RT}\right)\right) \tag{129}$$

$$+ \left(\frac{-\sigma_{E(j)}}{RT}\right)^2 \left(\exp\left(\left(\frac{-\sigma_{E(j)}}{RT}\right)^2\right) - 1\right)$$

where the subscripts $k(j)$ and $E(j)$ denote, respectively, the rate constant and the activation energy of the j-type sites. A, R, and T represent the frequency factor, assumed to be independent of j, the gas constant, and the reactor temperature.

Furthermore, equation (128) can also be established in terms of the activation energy (normal) distribution as follows

$$r_w/r_n = 2\left(1 + \frac{\sigma_{k(j)}^2}{\mu_{k(j)}^2}\right) = 2\exp\left(\left(\frac{-\sigma_{E(j)}}{RT}\right)^2\right) \tag{130}$$

These equations show that instead of defining a log-normal distribution for the propagation rate constant, one can take an easier path by adopting a normal distribution for the activation energy, obtaining a quasi-log-normal distribution for the propagation rate constant. In this case, the standard deviation of the activation energy distribution should be regarded as an adjustable parameter for the model simulation.

Catalyst reactivity profiles

Figure 3 shows the adopted site fraction distribution for 23 j-type sites of differing reactivities. This represents the site type distribution on the catalyst surface. It is calculated by integrating numerically any of the selected normal distributions for the propagation activation energies.

The discretized normal distributions for the activation energies are found by attributing the corresponding site fraction to each middle point of the 23 activation energy intervals. *Figure 4* shows normalized activation energy distributions. For both the propylene and the ethylene self-propagation cases, their mean values are assumed to be 13.0 kcal/mol for the δ-TiCl$_3$ + AlEt$_2$Cl catalyst system. For the cross-propagation cases, the overall values were determined under the assumption that the reactivity
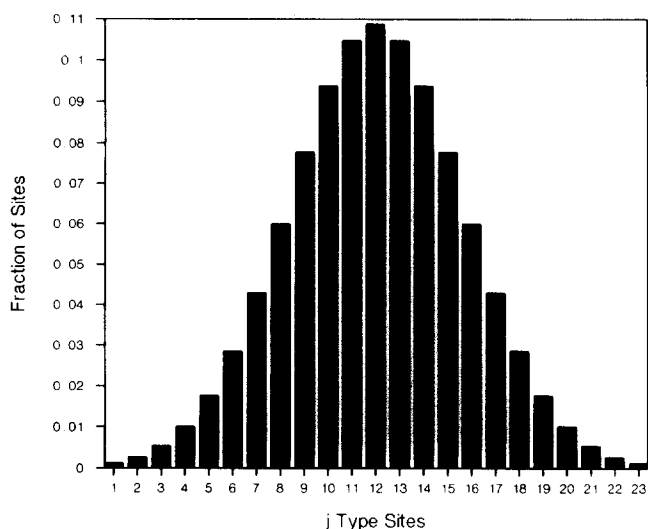

Figure 3 Normalized reactive site distribution; grouping sites in 23 class intervals
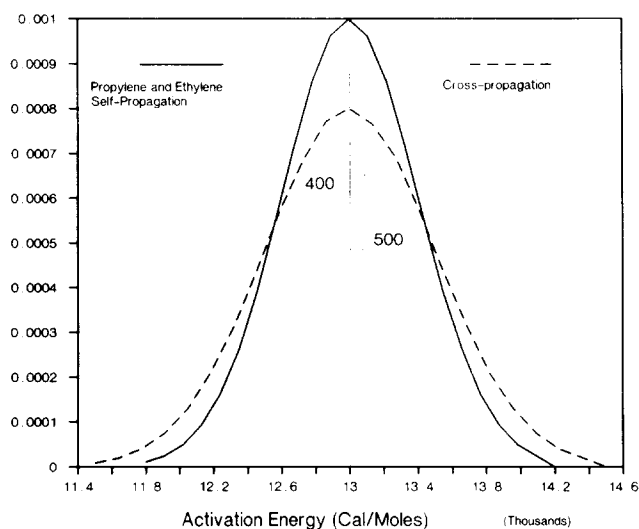

Figure 4 Normalized propagation activation energy profiles

ratios are independent of temperature. Hence

$$E_{12} = E_{11} = 13\,000 \text{ cal/mol}$$

$$E_{21} = E_{22} = 13\,000 \text{ cal/mol}$$

where the subscripts 1 and 2 denote propylene and ethylene, respectively. The standard deviation for each distribution has been chosen somewhat arbitrarily to give the observed wide polydispersities.

The pseudo-propagation rate constant distribution is easily found, using the Arrhenius equation, the appropriate frequency factors and activation energies. *Figure 5* illustrates the normalized pseudo rate constant distribution for 60°C. Notice that on the condition that the reactivity ratios do not depend on temperature, the mean frequency factors for the cross-propagation cases can be calculated from the self-propagation. The mean reactivity ratio values, from Kakugo's data[58], are $r_1 = 0.50$ and $r_2 = 7.0$.

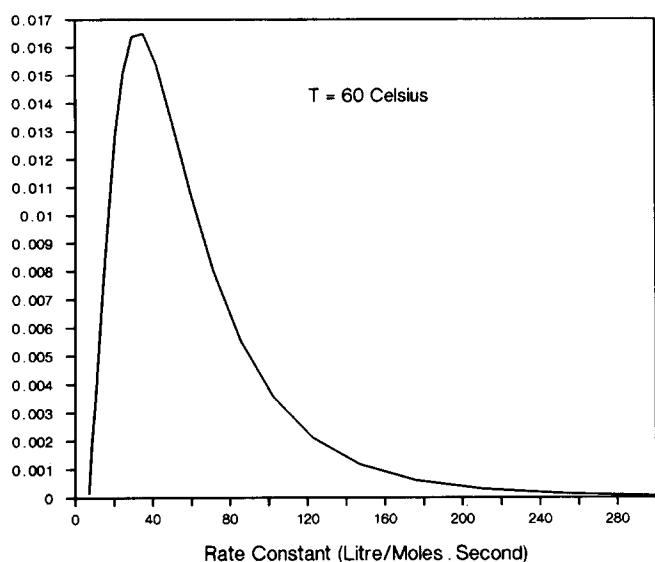Therefore, assuming that the catalyst has 0.010 active sites per moles of[titanium, one may set for the pure

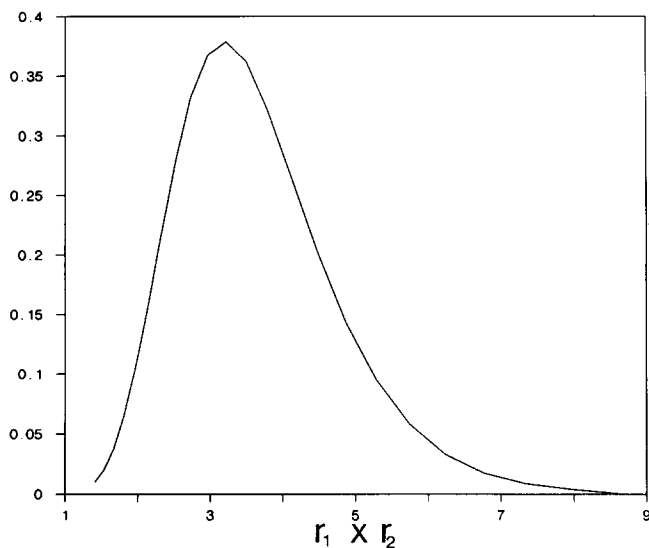**Figure 5** Normalized pseudo propagation rate constant profile

Figure 6 Normalized reactivity ratio product profile

result of the active site distribution, there is an envelope into which the dyad distribution of each polymer fraction is expected to lie. The averaged values are also presented by means of solid line. These are compared with Kakugo's[58] and Ray's[57] data.

Even though Kakugo's and Ray's data have been obtained at different temperatures (60 and 0°C, respec-
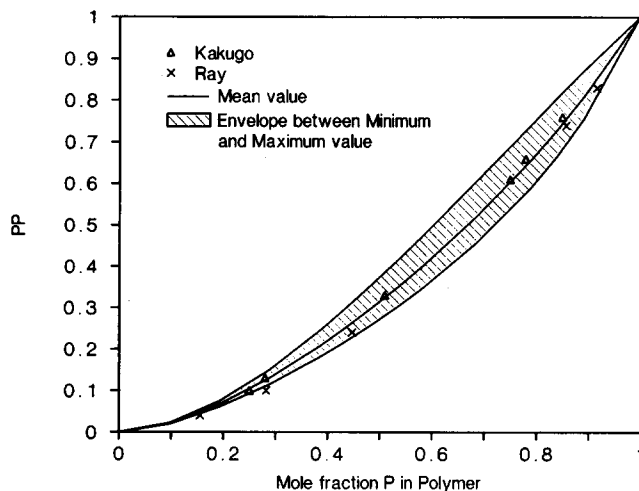
Figure 7 Propylene–propylene chemical dyad distribution
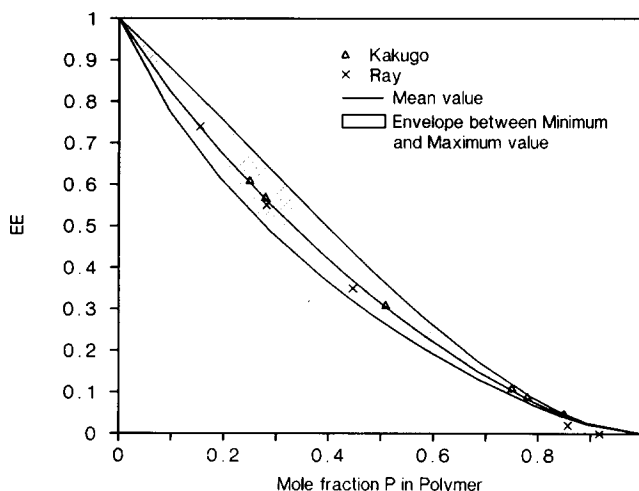
Figure 8 Ethylene–ethylene chemical dyad distribution

frequency factors the following mean values

$$A_{11} = 8.58 \times 10^9 \text{ l/mol s}$$

$$A_{12} = 1.72 \times 10^{10} \text{ l/mol s}$$

$$A_{22} = 1.42 \times 10^{12} \text{ l/mol s}$$

$$A_{21} = 2.03 \times 10^{11} \text{ l/mol s}$$

Figure 6 presents the normalized propylene reactivity ratio product distribution. Notice that the reactivity ratio product varies over a wide range of values, allowing the formation of copolymer with alternating character as well as copolymer with preponderantly block character.

RESULTS

The multiple active site model explains the polymer inhomogeneity by envisaging that the polymer is composed of differing fractions, each of them being produced by a particular type of catalyst site.

Figure 7, 8, and *9* show the simulated dyad distributions versus the moles of propylene in the copolymer. As a

Figure 9 Ethylene–propylene chemical dyad distribution

tively), the dyad distributions are quite close. It supports the assumption that the reactivity ratios are not strongly influenced by temperature.

CONCLUSIONS

The polymer microstructure has been mathematically described in terms of both the chemical and the stereo compositions and sequence length distributions. The set of equations developed are able to account for the n-ads (dyads through pentads) distributions of chains polymerized on each j-type site.
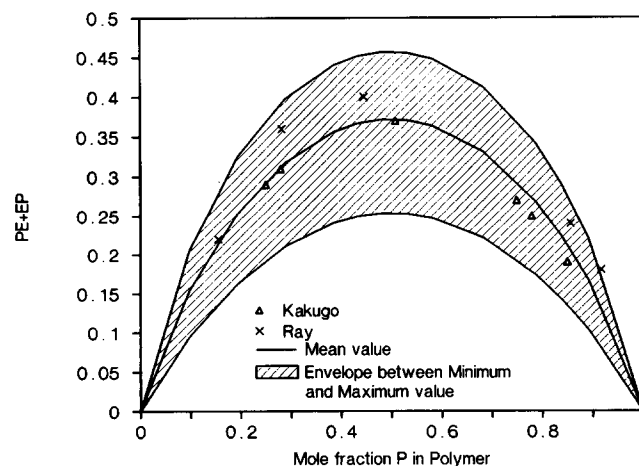
The estimation of the parameters associated with each j-type site has also been discussed. It is suggested that the enantiomorphic stereo reactivity ratio of each u fraction, obtained via fractionation based on stereo regularity, should be envisaged as a parameter which characterizes the stereo regulating power of the uth group of j sites on which the uth polymer fraction was produced. Furthermore, if TREF fractionation is subsequently performed in each u fraction, then it should be possible to estimate, for each j-type site separately, the propagation rate constant multiplied by the respective fraction of sites.

The ability of the model to calculate regions in which the chemical sequence length distributions of the differing polymer fractions are likely to be found was demonstrated using simulations. The averaged values have been compared with experimental data.

The model equations can fit experimental data. By modelling this process one obtains a systematic structure for looking at the polymerization, enabling us to better understand the complex phenomena involved.

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NOMENCLATURE

j specifies each type of site based upon its set of rate constants

u denotes a group of j type sites on which the uth fraction of polymer, segregated according to its stereoregularity, was produced

M_1 α-olefin molecule; α-olefin concentration on the catalyst surface

M_2 ethylene molecule; ethylene concentration on the catalyst surface

D α-olefin configuration in stereo n-ads

L α-olefin configuration in stereo n-ads

P α-olefin unit in chemical n-ads

E ethylene unit in chemical n-ads

m α-olefin meso $(DD + LL)$ dyad sequence in n-ads

r α-olefin racemic $(DL + KD)$ dyad sequence in n-ads

$F_D(j)$ stereocomposition of the homopolymer produced on the j type site, as moles of α-olefin having D configuration per mole of polymer

$S_D(j)$ stereoreactivity ratio of the D-attached j-type site

$S_L(j)$ stereoreactivity ratio of the L-attached j-type site

$S(j)$ stereoreactivity ratio for the j type site, defined in terms of the single enantiomorphic-site model

$d_{DL}(j)$ stereo-dyad of the homopolymer produced on the j type site, as moles of DL sequences per mole of polymer. Similar definition applies for the others stereo-dyads (DD, LD, LL)

$p_{LD}(j)$ probability that an L-attached j-type site has reacted given that a D-addition has taken place, during homopolymer production. A similar definition applies for the other stereoplacements (DD, DL, LL)

$F_1(j)$ chemical composition of the copolymer produced on the j-type site, as moles of α-olefin per mole of copolymer

$r_1(j)$ reactivity ratio of the α-olefin-attached j-type site

$r_2(j)$ reactivity ratio of the ethylene-attached j-type site

f_1 monomer composition, as moles of α-olefin per moles of α-olefin plus ethylene

$d_{12}(j)$ chemical dyad of the copolymer produced on the j-type site, as moles of α-olefin–ethylene sequences per mole of copolymer. A similar definition applies for the others chemical dyads[11,21,22]

$p_{12}(j)$ probability that a α-olefin-attached j-type site has reacted given that an ethylene insertion has taken place. A similar definition applies for the other chemical placements[11,21,22]

$p_{LDc}(j)$ probability that a L-attached j-type site has reacted given that a D-addition has taken place, during copolymer production. Similar definition

applies for the other stereoplacements (DDc, DLc, LLc)

T_m equilibrium melt point of the polymer

T_m^0 equilibrium melt point of the perfectly stereoregular polymer

ΔH_m heat of fusion per crystallized unit

R gas constant

p^* probability for a given stereo-unit selected at random to be followed by a unit with the same structure and configuration

$W_f(u)$ instantaneous weight fraction of the polymer produced on the uth group of sites

W_{f0} fraction of polymer which can be further fractionated based on stereoregularity

A absorbance

K_{ab} absorption coefficient

L_w sample thickness

A, E, Z Frequency factor, activation energy, and a group of Arrhenius expressions

$\Phi_D(j)$ fraction of the D-attached j-type site, as moles of D-attached sites per moles of α-olefin-attached sites. A similar definition applies for the L-attached j-type site

$\phi_L^*(j)$ fraction of the L-attached j-type sites, as moles of L-attached sites per mole of α-olefin-attached + ethylene-attached type sites. A similar definition applies for the D-attached type site

λ width of the three parameter distribution for $1/S(u)$

$\pi_{D(n+1)}(j)$ distribution of α-olefin units in isotactic sequences larger than the size n, for homopolymer produced on the j-type site.

$\pi_{Dc(n+1)}(j)$ distribution of α-olefin units in isotactic sequences larger than the size n, for copolymer produced on the j-type site

$\zeta_{2(n)}(j)$ distribution of ethylene sequences of size n, for copolymer produced on the j-type site

$\xi_{2(n+1)}(j)$ distribution of ethylene sequences longer than n, for copolymer produced on the j-type site

$\chi_{2(n)}(j)$ distribution of ethylene units in sequences of size n, for copolymer produced on the j-type site

$\pi_{2(n+1)}(j)$ distribution of ethylene units in sequences larger than the size n, for copolymer produced on the j-type site

Subscripts

D   denotes one of the two possible spatial configurations of the α-olefin in the chain

L   denotes one of the two possible spatial configurations of the α-olefin in the chain

1   denotes α-olefin

2   denotes ethylene

DD   denotes a D-addition on a D-attached site. Similar definition applies for the other additions (DL, LD, LL)

D2   denotes an ethylene insertion on the D-attached type site. Similar definition applies for the L-attached type site

2D   denotes a D-addition on an ethylene-attached type site. Similar definition applies for a L-addition

12   denotes an ethylene addition on a α-olefin-attached type site. Similar definition applies for the other chemical additions[11,21,22]

i   denotes an isotactic placement (DD or LL)

s   denotes a syndiotactic placement (DL or LD)

i1   denotes the reversible isotactic complex formation in a two step mechanism for the olefin polymerization on the catalyst centre. Similar definition applies for the syndiotactic complex formation

−i1   denotes the reversible isotactic complex disappearance in a two step mechanism for the olefin polymerization on the catalyst centre. Similar definition applies for the syndiotactic complex disappearance

2i   denotes the irreversible isotactic insertion between the active centre and the growing polymer chain in a two step mechanism for the olefin polymerization. A similar definition applies for the syndiotactic insertion

Kinetic constants and rates

The rate constants associated with j-type site are represented as $k(j)$. When they are expressed in terms of the Arrhenius equation, the frequency factor and the activation energy are respectively given by $A(j)$ and $E(j)$. Their specific meaning is provided by the subscript which composes them. $\bar{k}$ refers to a mean value.

The rates are given either by $R(j)$, to denote the rate of a j-type site, or by R to denote the overall rate.