Tacticity Distribution and Simulation[†]

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ABSTRACT: In many homopolymers the tacticity may be compositionally or sequentially heterogeneous. A computer simulation approach has been developed to simulate tacticity sequence and tacticity distribution for polymers made under a variety of conditions. Included in the simulation are the effects of molecular weight, consecutive and concurrent propagation models, and multiple catalyst/initiator states. In addition, heterogeneity brought about by the fluctuations in the reaction process conditions can also be incorporated. The effect of sequential heterogeneity can be separately visualized through the use of sequence index. Simulations have been made of the tacticity of poly(methyl methacrylate), poly(isopropenylpyridine), and polypropylene. In general, compositional heterogeneity has a large effect on the composition distribution curve but a lesser effect on NMR tacticity.

Introduction

Tacticity is a fundamental microstructural feature in polymers that directly affects the physical properties and the chemical reactivity of the polymers. Although the importance of tacticity is widely known,[1-5] there has been little attention paid to tacticity *distribution*. Most measurements of tacticity, carried out by NMR, provide the average tacticity in terms of diad (m or r), triads (mm, mr, rr), and higher *n*-ads. Yet, under suitable circumstances the tacticity may be compositionally or sequentially heterogeneous. One way to probe the tacticity heterogeneity is to fractionate the polymer in question through conventional fractionation[6] or temperature rising elution fractionation[7-9] and then analyze the NMR spectra of the fractions.[9-13] Computer analysis has been used for this purpose[11-14] and the results have been very promising.

Previously, it has been shown[15] that computer simulation approaches can be an effective way to examine compositional heterogeneity in copolymers. We have extended the work to examine the tacticity distribution using computer simulation approaches.

Sources of Tacticity Heterogeneity

In this work "composition" refers to the overall content of either meso (m) or racemic (r) configuration for a given polymer. Compositional "distribution" refers to the number of polymer chains as a function of the (m) or (r) content. Tacticity "sequences" refer to diads, triads, tetrads, and higher *n*-ads.

Before we can simulate tacticity, we need to know the sources of the tacticity distribution. By analogy to copolymers,[15] four kinds of tacticity heterogeneity can be distinguished. First, tacticity distribution should have a molecular weight dependence. At low molecular weights the statistical nature of polymerization would cause a spread in the tacticity composition. This effect becomes small when the molecular weight becomes large. This kind of heterogeneity (called *statistical* or instantaneous) is well known in copolymers and can be treated using Stockmayer's equation.[16]

A second kind of tacticity heterogeneity occurs if the reaction probability governing tacticity changes as a function of molecular weight, conversion, or time. This will be called chain-end heterogeneity. For example, in some anionic polymerizations, chain-end effects on tacticity have been reported.[17-19] Similarly, in telomerization tacticity can depend on molecular weight.[20,21] Admittedly, these occurrences are not common and are only seen for oligomers (degree of polymerization less than 10).

A third source of heterogeneity occurs when the polymer in question is made up of several components. This may be due to deliberate polymer blending, multistaged polymer synthesis, or the presence of different kinds of initiators, catalytic sites, or propagating species that produce different polymer chains. This is often the case for polymers made with Ziegler–Natta catalysts.[22] The tacticity of the resulting polymer would have contributions from all its component.[11] A case of multiple propagating species also occurs in anionic polymerization where the propagating anions may be either solvated or free.[23-25] Alternatively, the propagating anions may switch between two states upon monomer addition.[26,27] Recently, some homogeneous Ziegler–Natta catalysts are claimed to have two states that interconvert during propagation.[28-30] These kinds of heterogeneity will be collectively called *multistate* heterogeneity.

Another possible source of heterogeneity arises as a result of fluctuations in reaction process conditions, e.g., temperature variations, inadequate stirring, dead volume in reactor, and gel effect. These fluctuations can be treated using the perturbed Markovian statistical model.[31,32] This kind of heterogeneity will be referred to as *process* heterogeneity in analogy to the similar effect of reaction process on copolymer composition.[15] For convenience, the various kinds of tacticity heterogeneity are summarized in Table I.

Reaction Probability Models

Reaction probability models are commonly used as theoretical frameworks to describe polymerization behavior and to rationalize NMR tacticity data.[1,2,5] In the past several years, a number of new reaction probability models have been devised.[31-42] In this work, most of these models have been explicitly included. These models are used (with computer simulation) to predict tacticity distribution and to relate the distribution to the nature of the heterogeneity.

In general, chain propagation can be either chain-end controlled or catalytic-site controlled. Chain-end control is commonly encountered in free radical, cationic, or anionic polymerization, and includes Bernoullian (B), first-order Markovian (M1), and second-order Markovian (M2) models,[1,2] corresponding respectively to the effect of terminal, penultimate, and penpenultimate monomer units at the chain end on the tacticity of the incoming monomer.

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Table I. Tacticity Heterogeneity and Computer Approaches Designed To Study Heterogeneity

kind of heterogeneity	probable occurrence	nature of heterogeneity	program
1. statistical	low mol wt polymers	statistical variations	TADIS1
2. chain end	anionic polymers	mol wt dependent probabilities	TADIS3
3. multistate	Ziegler–Natta, some anionic, and emulsion polymers	(concurrent) multiple components	TADIS4
	anionic and Ziegler–Natta polymers	(consecutive) multiple components	TADIS2
4. process	commercial polymers	fluctuations in process variables	TADIS5

The catalytic-site model is found in Ziegler–Natta polymers, and usually obeys the enantiomorphic-site (E) model.[33–35] Models that combine chain-end and catalytic-site control have also been formulated.[36–38] The nature and the use of these models have been recently reviewed.[5,39]

Many polymerizations involve more than one propagation state. For such polymerizations, a distinction needs to be made between consecutive and concurrent models.[40] In the consecutive two-state models, the two propagating states switch back and forth as polymerization proceeds. If the rate of switching is slower than the rate of propagation but faster than the rate of termination (or chain transfer), then we have blocks of polymer segments which conform to different propagation statistics. The consecutive B/B model has been previously described by Coleman and Fox.[23,24] A general treatment of consecutive models including B/B, B/E, and E/E, models has been recently given.[40] Computer programs (analytical approach) have been written[40] to assist in the analysis of NMR tetrad and pentad data.

A different kind of consecutive B/B model, as applied to anionic polymerization, is the *E*/*Z* model devised by Hogen-Esch et al.[26,27] In this case, polymerization can proceed from the *E* and *Z* anion isomers, each following the Bernoullian model. The two isomers interconvert through monomer addition. They can differ in reactivity or in stereochemistry of monomer addition. This model has been shown to hold[26,27] for the anionic polymerization of 2-vinylpyridine and methyl methacrylate.

In the concurrent two-state model, the two states conform to different propagation statistics, and they either do not interconvert or interconvert at a rate slower than chain termination or chain transfer. As a result, one obtains a mixture of polymer chains obeying the respective statistics, and the NMR data can be treated through a mixture (component) analysis.[11,12] Such treatment, of course, can be extended to polymers containing more than two states. In fact, in polypropylene four or more components have been obtained through a careful analysis[13] of NMR tacticity and molecular weight data.

Recently, a perturbation formalism has been introduced to the Bernoullian,[31,41] first-order Markovian,[31] and enantiomorphic-site[42] models. The perturbation is related to the second moment about the mean (SMM) of the tacticity composition curve:

$$\epsilon^2 = 3k(\mathrm{SMM}) \tag{1}$$

where k is a constant depending on the prevailing statistics. For our purpose (tacticity distribution),[31,32] this model is particularly useful in describing process heterogeneity (where compositional spread is due to fluctuations in process variables such as temperature, monomer concentration, and gel effect). The perturbed model has also been shown[42] to be useful in describing the tacticity of polyolefins made with group IV metallocene catalysts.

Computer Simulation Approaches

In NMR analysis it is customary to take the NMR data and fit them to a give reaction probability model (*analytical* approach). Most of the NMR studies involving the reaction probability models have been carried out in this way.

NMR data → spectral assignments → composition and sequence → reaction probabilities (model)

Whereas the analytical approach is highly successful in most cases, a different approach[43] (hereinafter called the synthetic or *simulation* approach) is to reverse the process and to simulate tacticity and tacticity distribution.

reaction probabilities (model) → chain generation → composition and sequence → NMR data

For example, in more complex reaction probability models the analytical approach can be mathematically involved and the fitting procedure cumbersome, especially when a large number of parameters are involved. Computer simulation can be simpler and in many cases provide equivalent information. Furthermore, the computer simulation approach can enable predictions to be made concerning NMR sequences and distributions of new or unknown polymers even when the polymer samples have not been prepared.

The general scheme for the computer simulation approaches is given in Figure 1. First, a suitable reaction probability model is used to generate an ensemble of polymer chains with a specific molecular weight distribution. Chain generation is then carried out using a Monte Carlo process. The chains are sorted and counted for tacticity composition, sequence, and sequence index (*vide infra*). The tacticity distribution, sequence index, and second moment about the mean can then be displayed.

To facilitate simulation of tacticity and tacticity distribution, five related computer programs have been written (called TADIS). Each of these programs is capable of handling different statistical models (Table II). Program TADIS1 is designed for one-state models in the steady state.[1,2,5] Program TADIS2 can simulate consecutive two-state B/B,[23–25,40] B/E,[40] E/E,[40] and M1/M1[44] models. Included in the program are the provisions for the *E*/*Z* model[26,27] in the case of anionic polymerization.

Program TADIS4 can simulate concurrent two-state and multistate models (up to six states). NMR characterization of multicomponent polymers (via the analytical approach) is typically very difficult;[11–13] the simulation approach given here is complementary to the analytical approach and is easier to carry out.

Program TADIS3 provides for the conversion or molecular weight dependence of reaction probabilities. Some common functional forms are

$$P_{\mathrm{m}}\ (\text{or } P_1) = A + Bx + Cx^2 \tag{2a}$$

$$P_{\mathrm{m}}\ (\text{or } P_1) = A\exp(-Bx) + C \tag{2b}$$

$$P_{\mathrm{m}}\ (\text{or } P_1) = A + B[1 - \exp(-Cx)] \tag{2c}$$

$$P_{\mathrm{m}}\ (\text{or } P_1) = A(1 + Bx^2)^{-1} + C \tag{2d}$$

where x = conversion or degree of polymerization, P_{m} = Bernoullian probabilities for monomer enchainment in the meso configuration, and P_1 = enantiomorphic-site probability. Finally, program TADIS5 provides simulation

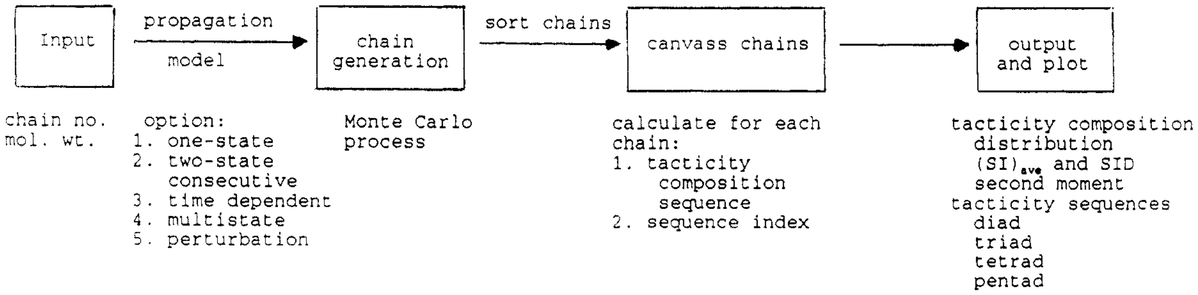


Figure 1. Schematic diagram of program TADIS.

Table II. Summary of TADIS Programs and Propagating Models

program	models
TADIS1	one-state B, M1, M2, E
TADIS2	one-state B, E two-state consecutive B/B, B/E, E/E, M1/M1
TADIS3	one-state B, E two-state consecutive B/B, B/E, E/E conversion and mol wt dependent probabilities
TADIS4	multistate (concurrent) models (up to six components) any weighted combination of TADIS1, TADIS2, and TADIS3
TADIS5	perturbed B, M1, M2, and E models

for perturbed probability models[31,41,42] and/or process heterogeneity. The perturbation (ϵ) can be superimposed[45] onto the reaction probability values as a rectangular function; e.g., in the first-order Markovian case

$$P_{ij} = P_{ij}^{\circ} \pm \epsilon \tag{3}$$

where P_{ij} and P_{ij}° are the reaction probabilities in the presence and in the absence of the perturbation, respectively. Alternatively, ϵ can be introduced as a Gaussian broadening (function g):

$$g(P_{ij}) = (2\pi\sigma^2)^{-1/2} \exp\left[-\frac{(P_{ij} - P_{ij}^{\circ})^2}{2\sigma^2}\right] \tag{4}$$

where the standard deviation $\sigma = \epsilon/3^{1/2}$. Although only the first-order Markovian expressions are shown, the expressions for the B and E models are exactly analogous.

Through proper choice of molecular weights, statistical heterogeneity can be simulated through any one of the TADIS programs. The effects of chain-end heterogeneity can be studied through program TADIS3. Multistate heterogeneity can be simulated either with program TADIS2 (consecutive two-state models) or with program TADIS4 (concurrent multistate models), whereas process heterogeneity can be examined using program TADIS5.

Illustrative Examples

Free Radical Polymerization. With respect to NMR tacticity, one of the most widely studied polymers is poly(methyl methacrylate) (PMMA). The pentad intensities of a PMMA sample[46] made by free radical means are given in Table III. Straightforward analysis by the computerized analytical approach[43,47] (program FITCO) gives $P_m = 0.214$ for Bernoullian propagation statistics. With this Bernoullian probability, we can use program TADIS1 to produce an ensemble of PMMA polymer chains, from which we can obtain the tacticity composition and sequences. Two simulations have been made, with degrees of polymerization (n) of 5000 and 100 (Table III). The agreement between the observed and the simulated pentads is very good. The effect of n on tacticity sequences in the range of 100–5000 is small.

Table III. Observed and Simulated Pentad Tacticity for PMMA

pentad	obsd[a]	calc[c] $n = 5000$	calc[c] $n = 100$
mrrm	2.83	2.81	2.83
rrrm	21.26	20.63	20.64
rrrr	36.85	37.88	38.05
rmrm	7.40	5.62	5.44
mrmm		1.53	1.44
rrmr	26.93	20.61	20.71
rrmm		5.61	5.64
mmmm	1.42	0.96	0.98
rmmm		1.52	1.46
rmmr	3.31	2.82	2.81
P_m	0.214[b]	0.214	0.214
From the distribution curves:			
SMM		4.15×10^{-5}	1.65×10^{-3}
ϵ^2		1.24×10^{-4}	4.95×10^{-3}
ϵ		0.011	0.070

[a] Observed data from ref 46. [b] Calculated from program FITCO.[47] [c] Simulation carried out with program TADIS1 using 1000 chains, two different degrees of polymerization (n), and $P_m = 0.214$.

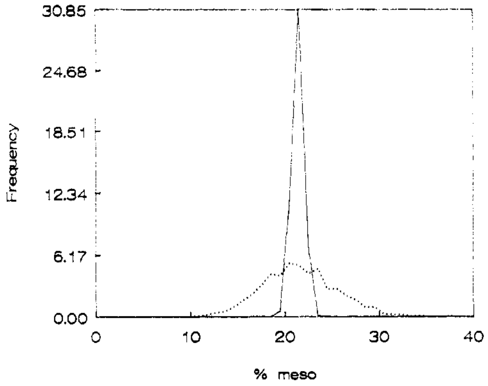


Figure 2. Simulated tacticity distribution of PMMA at two degrees of polymerizations (n). Solid line, $n = 5000$; dotted line $n = 100$. Simulation through program TADIS1.

It is of interest to plot the tacticity composition distribution curve for the two degrees of polymerization (Figure 2). As expected, the high molecular weight polymer gives a narrow distribution. In contrast, the $n = 100$ polymer shows a wide compositional spread. The second moments for these two curves are 4.15×10^{-5} and 1.65×10^{-3}, respectively. For Bernoullian models, $P_{mr} + P_{rm} = 1$ and $\epsilon^2 = 3(\text{SMM})$ from eq 4. For the two distribution curves, the values of ϵ^2 are 1.24×10^{-4} and 4.95×10^{-3}. These simulated values can be compared with the theoretical values. From Stockmayer's equation[16] and the

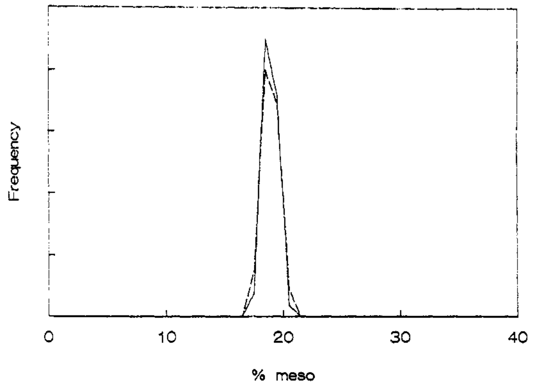


Figure 3. Simulated tacticity distribution of PMMA with no variation in temperature (solid line) and 10 K variation in temperature (dashed line). Simulation through program TADIS5.

perturbation formalism, it can be shown[31] that

$$\epsilon^2 = \frac{3P_m(1-P_m)}{n} \tag{5}$$

Using eq 5, one obtains the theoretical values of ϵ^2 as 1.0 × 10^{-4} and 5.0 × 10^{-3}, in excellent agreement with the simulated results.

Note that the compositional spread is a Gaussian function where the standard deviation σ depends linearly on ϵ ($\sigma = \epsilon/3^{1/2}$). In contrast, the NMR tacticity expressions depend on ϵ^2. Thus, whereas the effect of molecular weight on the tacticity distribution is sizeable (Figure 2), the effect is barely noticeable on the NMR tacticity data (Table III).

Since vinyl polymerization is usually an exothermic process, temperature increases during polymerization are sometimes difficult to avoid. Bovey[1] has plotted the relationship between P_m and temperature for the free radical polymerization of PMMA. The plot can be described approximately by the equation

$$\ln \frac{P_m}{1-P_m} = -\frac{401.1}{T} - 0.217 \tag{6}$$

where the temperature (T) is in K. Thus, if one polymerizes at 323 K and controls the temperature to within ±10 K, this corresponds to Bernoullian probabilities $P_m = 0.189 \pm 0.006$. This situation can be described by the perturbed Bernoullian model, where $P_m = 0.189$ and $\epsilon = 0.006$. We can use program TADIS5 to simulate this case and see the effect of temperature fluctuations. The tacticity distribution curves for both the unperturbed ($\epsilon = 0$) and the perturbed Bernoullian models are given in Figure 3. The tacticity sequences (up to pentads) are shown in Table IV. In this case, the effect of nonzero ϵ is negligible on tacticity sequence and barely noticeable on compositional distribution. In fact, the temperature effect on tacticity for this free radical polymerized system is small[48] even for ±50 K fluctuation (Table IV, last column).

Table IV. Effect of Fluctuations in Temperature of Polymerization on Pentad Tacticity[a] for PMMA

pentad	$\epsilon = 0$	$\epsilon = 0.006$	$\epsilon = 0.030$
mrrm	2.35	2.35	2.36
rrrm	20.05	20.05	20.00
rrrr	43.00	43.00	43.03
rmrm	4.69	4.66	4.63
mrmm	1.09	1.09	1.09
rrmr	20.06	20.06	19.94
rrmm	4.69	4.69	4.77
mmmm	0.67	0.68	0.69
rmmm	1.07	1.10	1.12
rmmr	2.34	2.33	2.36
temp	±0 K	±10 K	±50 K
SMM	3.72×10^{-5}	5.17×10^{-5}	3.42×10^{-4}

[a] Simulated with program TADIS5 using $P_m = 0.189$, 1000 chains, $n = 5000$, and rectangular perturbations.

Table V. Observed[a] and Simulated[b] Tacticity Sequences for a PMMA Sample That Conforms to the Consecutive Two-Site B/B Model

		I_{calc}		
sequence	I_{obsd}	$n = 5000$	$n = 100$	$n = 25$
diad				
m	0.82	0.82	0.86	0.90
r	0.18	0.18	0.14	0.10
triad				
mm	0.75	0.75	0.80	0.85
mr	0.14	0.14	0.12	0.10
rr	0.11	0.11	0.08	0.04
tetrad				
mmm	0.70	0.70	0.75	0.81
mmr	0.09	0.10	0.09	0.08
rmr	0.03	0.02	0.02	0.01
mrm	0.04	0.04	0.04	0.04
rrm	0.06	0.06	0.05	0.03
rrr	0.07	0.07	0.05	0.03
pentad				
mmmm	0.75	0.67	0.73	0.79
mmmr		0.08	0.08	0.07
rmmr		0.01	0.00	0.03
mmrr	0.07	0.03	0.02	0.01
rmrr		0.03	0.02	0.01
mmrm	0.07	0.06	0.06	0.06
rmrm		0.01	0.01	0.01
rrrr	0.07	0.05	0.04	0.02
rrrm	0.04	0.04	0.03	0.02
mrrm		0.01	0.01	0.00

[a] Tacticity data from ref 25. [b] Calculated by program TADIS3 with 2000 chains and constant degree of polymerization = 5000. Consecutive two-state B/B model (Coleman–Fox statistics) assumed.

Anionic Polymerization. PMMA can also be made through anionic polymerization, and NMR studies have been made of these polymers periodically. Earlier data suggested that Bernoullian, first-order Markovian, and Coleman–Fox models may be valid.[49–51] Under some reaction conditions, the NMR data have been observed[24,25,50] to obey the Coleman–Fox statistics. This is equivalent to the two-state consecutive B/B model.[40] Frisch et al.[25] have given the NMR tetrad and pentad intensities for such a polymer (Table V). Recently, using the analytical methodology developed for the two-state consecutive models, we have obtained[40] the following two-state B/B parameters:

state 1: $P_m = 0.959, \quad \alpha = 49$

state 2: $P_m = 0.210, \quad \beta = 11$

where α and β are the block lengths (in monomer residue units) of blocks A and B, respectively. It is now possible to simulate the tacticity and the tacticity distribution for such a polymer. We use program TADIS2 and simulate the tetrad and pentad sequences at three degrees of polymerization (Table V). The composition distribution curves for $n = 5000$ and $n = 100$ are given in Figure 4.

The tacticity data for polymers with $n = 5000$ (Table V) agree very well with the observed data. However, as n decreases to the same order of magnitude as α or β, both the average composition and the sequences change. This is because a polymer chain consists of only a few blocks of A or B, and the exact point of polymer termination

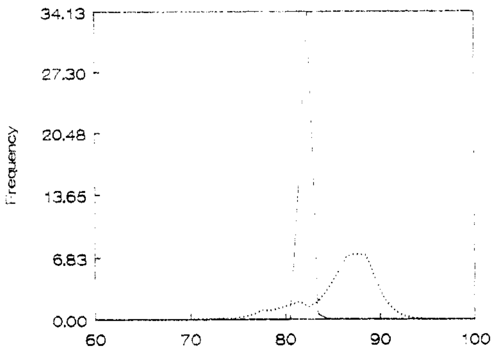
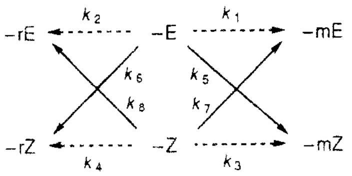


Figure 4. Simulated tacticity distribution of PMMA, exhibiting Coleman–Fox statistics (consecutive two-state B/B model). Solid line, $n = 5000$; dotted line, $n = 100$. Simulated through program TADIS2.

becomes important in determining the composition of the polymer chain in question.

The effect of n on the composition distribution curve is equally significant. The curve is sharp for $n = 5000$ but becomes bimodal at $n = 100$. At $n = 25$ (not shown), the bimodal nature becomes even more pronounced. In the limit where $n < \alpha$ and β, we would have separate chains for each state. In other words, we would have two separate distributions centered on (m) = 0.959 and (m) = 0.210.

Recently, very detailed kinetic and structural studies[26,27,52,53] have been carried out on anionic polymerization. Much is now known of the propagating anions and the effects of counterions. Khan and Hogen-Esch,[26] on the basis of experimental observations, devised the *E*/*Z* mechanism:



$k_1 = k_{ee,m}$
$k_2 = k_{ee,r}$
$k_3 = k_{zz,m}$
$k_4 = k_{zz,r}$
$k_5 = k_{ez,m}$
$k_6 = k_{ez,r}$
$k_7 = k_{ze,m}$
$k_8 = k_{ze,r}$

where $-E$ and $-Z$ represent the propagating anions, and (upon monomer addition) these isomers may be preceded by a meso or a racemic diad. Thus, the monomer can add to either the E or the Z anion, leaving the configuration unchanged (reactions 1–4) or interconverting the configuration (reactions 5–8). The rate constants and the reaction probabilities will be denoted in this work as $\{k_{\alpha\beta,i}\}$ and $\{P_{\alpha\beta,i}\}$, respectively, where α and β are e or z corresponding to the beginning state (α) and the final state (β) and i is the tacticity after monomer addition. In the simplest form, the configuration of the incoming monomer follows the Bernoullian statistics. A refined *E*/*Z* model where the monomer addition to each of the E and Z states follows the first-order Markovian statistics has also been mentioned.[27]

In view of the importance of the *E*/*Z* model in anionic polymerization, a provision has been made in program TADIS2 to simulate this model. Eight input reaction probabilities are needed: $P_{ee,m}$, $P_{ee,r}$, $P_{zz,m}$, $P_{zz,r}$, $P_{ez,m}$, $P_{ez,r}$, $P_{ze,m}$, and $P_{ze,r}$. Two normalization conditions reduce the number of independent parameters to six:

$$P_{ee,m} + P_{ee,r} + P_{ez,m} + P_{ez,r} = 1 \qquad (7a)$$

$$P_{zz,m} + P_{zz,r} + P_{ze,m} + P_{ze,r} = 1 \qquad (7b)$$

Table VI. Simulated Results of Four Test Polymers According to the Anionic *E*/*Z* Model

	polymer 2	polymer 4	polymer 5	polymer 6
	Input Rate Parameters[a]			
$k_{ee,m}$	75	2	8	3
$k_{ee,r}$	4	0	9	1
$k_{zz,m}$	1	0	1	7
$k_{zz,r}$	6	6	3	2
$k_{ez,m}$	25	1	8	7
$k_{ez,r}$	30	0	9	2
$k_{ze,m}$	1	0	1	3
$k_{ze,r}$	5	4	9	1
	Predicted Tacticity			
(m)	54.6	46.7	76.9	33.5
(r)	45.4	53.2	23.1	66.5
(mm)	36.4	26.9	59.2	10.3
(mr)	36.3	39.6	35.5	46.5
(rr)	27.2	33.4	5.3	43.2
(mmm)	24.3	15.8	45.5	3.2
(mmr)	24.3	22.1	27.3	14.3
(rmr)	6.0	8.7	4.1	16.1
(mrm)	7.3	6.7	13.7	8.3
(mrr)	21.7	26.2	8.2	30.0
(rrr)	16.3	20.3	1.2	28.2
(mmmm)	16.2	9.4	35.0	1.0
(mmmr)	16.2	13.0	21.0	4.4
(rmmr)	4.0	4.6	3.2	4.9
(mmrr)	14.5	14.8	6.3	9.2
(rmrr)	7.2	11.5	1.9	20.8
(mmrm)	9.7	7.4	21.0	5.1
(mrmr)	4.9	6.0	6.3	11.5
(mrrm)	4.3	5.2	3.2	5.2
(rrrm)	13.1	15.8	1.9	19.6
(rrrr)	9.8	12.4	0.3	18.4
	Tacticity Distribution			
SMM[b]	4.055×10^{-4}	3.730×10^{-4}	1.905×10^{-4}	1.847×10^{-4}

[a] The rate probabilities are proportional to the rate constants, $P_{\alpha\beta,i} \propto k_{\alpha\beta,i}$. The proportionality constants are the normalization constants required by eqs 7a and 7b. The input rate parameters are taken from ref 26. [b] Second moment about the mean of the tacticity distribution curve.

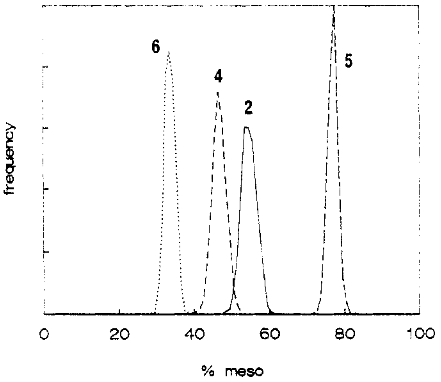


Figure 5. Simulated tacticity distribution of four test polymers obeying the anionic *E*/*Z* model. Simulation through program TADIS2; kinetic constants given in Table VI; 1000 chains used with a constant degree of polymerization of 1000.

The program has been checked on the data reported by Khan and Hogen-Esch.[26] For four of the test polymers, the input rate parameters and the predicted n-ad sequences are given in Table VI. Khan and Hogen-Esch[26] have previously reported the expected (m) and (mm) values for these polymers. The agreements between their (m) and (mm) values and the values given here are excellent, except for the (mm) triad of polymer 4.

The tacticity distributions for these four polymers are given in Figure 5. Even though a relatively high degree of polymerization (1000) has been used, there are slight differences in the widths of the distributions, polymer 2 being the broadest and polymer 4 the narrowest. The widths of the distributions are also shown by the second moments (Table VI).

Recently, a thorough and elegant study of anionically polymerized PMMA was carried out by Baumgarten et al.[27] Polymerization was shown to proceed through the *E* and *Z* anions. The counterions (Li^+, Na^+, K^+, and Cs^+) were found to have strong effects on the ratio of the *E*/*Z* anions and on the tacticity. The tacticities of both the polymer main chain and the anionic chain ends were reported. For Li^+, Na^+, and Cs^+, the main chain meso/racemic ratios were similar to the meso/racemic ratios of the chain ends; however, for K^+ a difference was noted.

Baumgarten et al.[27] showed that with Li^+ and Na^+ counterions the predominant (>95%) propagating anions are the *Z* stereoisomers, whereas with Cs^+ counterion, the predominant anion (95%) is in the *E* form. For K^+ counterion, the propagating anions consist of 60% *Z* and 40% *E*. The first-order Markovian probabilities and the tacticities at the chain ends are[27]

$$Z\text{ anion:}\quad P_{mr} = 0.950,\ P_{rm} = 0.375,\ (m) = 0.283$$

$$E\text{ anion:}\quad P_{mr} = 0.951,\ P_{rm} = 0.250,\ (m) = 0.208$$

For the polymer main chain, the following first-order Markovian probabilities and overall meso content are observed:[27]

$$P_{mr} = 0.822,\ P_{rm} = 0.426,\ (m) = 0.34$$

We have attempted the simulation of the reported tacticity data with the *E*/*Z* model. A difficulty was encountered; if we use the tacticity of the *E* and *Z* anions (meso contents 0.208 and 0.283, respectively), then the meso content of the final polymer would lie between 0.208 and 0.283, not 0.34 as observed. For illustrative purposes, we have used a hypothetical scenario based on two (not necessarily tenable) assumptions: (1) meso addition is favored in a switching reaction, and (2) when the polymerization is terminated, $ClSi(CH_3)_3$ preferentially adds to the products of reactions 1–4. Thus, the two propagating anions are assumed to have the following reaction probabilities (before normalization):

$$P_{ee,m} = 0.375,\ P_{ee,r} = 0.951$$

$$P_{zz,m} = 0.375,\ P_{zz,r} = 0.951$$

These values correspond to the observed chain-end tacticities. Iterations are carried out on the probabilities for the four interconversion reactions (reactions 5–8). The best results are shown below (before normalization):

$$P_{ez,m} = 0.500,\ P_{ez,r} = 0.375$$

$$P_{ze,m} = 0.500,\ P_{ze,r} = 0.250$$

In this hypothetical scenario, in order to compatibilize the tacticities of chain ends with the main chain, we need to invoke rather sizeable interconversion reactions. Monomer addition has the highest probability to proceed through reactions 2 and 4 (racemic addition, retention of configuration), followed by reactions 5 and 7 (meso addition, reversal of configuration). The observed and the calculated NMR pentad data are given in Table VII. The fit is only fair; the calculated mm-centered pentads are higher than the observed values. The fit would improve if the first-order Markovian *E*/*Z* model is used.

Table VII. Observed and Calculated Pentad Intensities of a Hypothetical PMMA Sample Obeying the Anionic *E*/*Z* Model

pentad	obsd[a]	calc[b]
mmmm	0.6	2.3
mmmr	1.7	7.2
rmmr	3.6	5.6
mmrr + rmrr	34.7	29.2
mmrm + mrmr	21.7	18.0
mrrm	6.6	5.6
rrrm	17.5	18.0
rrrr	13.6	14.1

[a] Taken from ref 27; reported for a PMMA made with K^+ counterion in THF solvent. [b] Calculated results of program TADIS2; the normalized rate probabilities are $P_{ee,m} = 0.170$, $P_{ee,r} = 0.432$, $P_{zz,m} = 0.128$, $P_{zz,r} = 0.487$, $P_{ez,m} = 0.227$, $P_{ez,r} = 0.170$, $P_{ze,m} = 0.256$, and $P_{ze,r} = 0.128$. Fraction of chains started with the *E* anion = 0.60; 2500 chains used; degree of polymerization = 30. The calculated results include the effect of statistical heterogeneity due to the low molecular weight.[31,32]

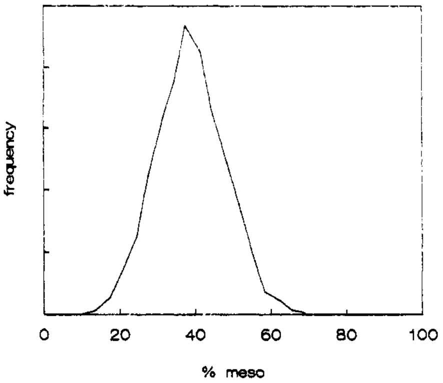


Figure 6. Predicted tacticity distribution of a hypothetical PMMA sample obeying the anionic *E*/*Z* model. Simulation through program TADIS2; reaction probabilities given in the text; 2500 chains used with constant degree of polymerization of 30.

The tacticity distribution for this hypothetical scenario is shown in Figure 6. A very broad distribution is observed. Within the same sample, there are polymer chains where the meso content is less than 20% and also over 60%. This distribution is primarily due to the low degree of polymerization (30) and would stay broad even with different reaction probability values. *This tacticity heterogeneity needs to be taken into account in the consideration of the mechanism of the reaction.*

It is well known that anionic polymerization can be used to produce low molecular weight polymers. For some of these polymers the prevailing reaction probability may vary with molecular weight (chain-end heterogeneity). This can be simulated with program TADIS3. Two anionic polymer systems exhibiting chain-end heterogeneities are poly(4-isopropenylpyridine) and poly(2-isopropenylpyridine). Hogen-Esch et al.[18] have found the polymerization to be Bernoullian with P_r (probability of racemic placement) depending on the degree of polymerization. Their result is summarized in Table VIII. Through curve fitting, their result can be expressed in the following form:

$$P_r = Ae^{-Bn} + C \tag{8}$$

We can use program TADIS3 to obtain the tacticity distribution curves for $n = 3$, $n = 8$, and $n = 1000$ (Figure 7). At the low-n values, the curves are broad due to statistical and chain-end heterogeneities. At $n = 1000$ the distribution is narrow because the heterogeneities are small. The maxima of the curves drift downward (toward smaller P_r values) as n increases.

Table VIII. Dependence of P_r on the Degree of Polymerization

	P_r[a]		
n	4IP[b]	2IP[c]	assumed %
3	0.90	0.90	3.125
4	0.87	0.90	15.625
5	0.80	0.88	31.250
6		0.86	31.250
7		0.86	15.625
8		0.86	3.125
ca. 1000	0.78	0.85	

[a] Reported in ref 18 for Li-catalyzed polymerization at −78 °C. 4IP = 4-isopropenylpyridine, 2IP = 2-isopropenylpyridine. [b] Data conform to the equation $P_r = 1.26e^{-0.57n} + 0.78$. [c] Data conform to the equation $P_r = 0.23e^{-0.35n} + 0.85$.

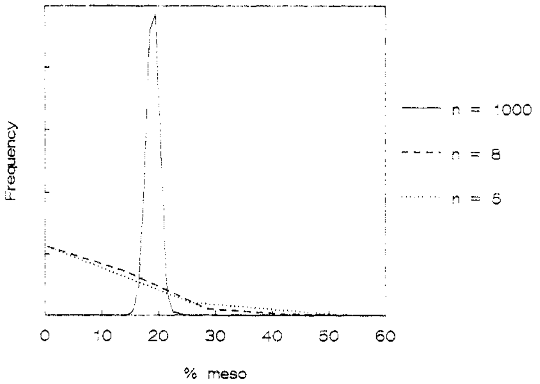


Figure 7. Simulated tacticity distribution of poly(2-propenylpyridine) with different degrees of polymerization (n). Simulation through program TADIS3.

Ziegler–Natta Polymerization. A good example of Ziegler–Natta polymers is polypropylene. Because of the heterogeneous nature of the conventional heterogeneous Ziegler–Natta catalysts,[22] this polymer comprises many components, each of which may obey a different propagation statistics. NMR analyses of polypropylene, therefore, need to be done with care. Recently, Kawamura et al.[54] made a sample of polypropylene with δ-$TiCl_3/Et_2AlCl$ at 65 °C in the presence of molecular hydrogen, fractionated the polymer, and reported the NMR data of the fractions. Through a computer-assisted analytical approach, the polymer was shown[13] to consist of at least four components, three components conforming to the enantiomorphic-site model (P_1 = 0.997, 0.991, and 0.800) and one component conforming to the Bernoullian model (P_m = 0.230) (Table IX, lower section). The weight fractions for these components are 0.645, 0.285, 0.035, and 0.035, respectively. For this multicomponent polymer, we can use program TADIS4 to simulate the NMR tacticity and composition distribution. The results are shown in Table IX and in Figure 8.

The simulated tacticity results (Table IX) agree well with the observed data. The composition distribution curve shows a very wide compositional spread. This predicted compositional distribution can be used to rationalize the temperature rising elution fractionation (TREF) results. Previously, Kakugo et al.[9,55] reported the TREF data for polypropylene samples made with a similar catalyst system. Kakugo's samples have lower isotacticity indices than Kawamura's sample, but the trends in the data are similar. Kakugo's TREF data[9] (for his sample 13) are plotted in Figure 9.

It is clear that Figures 8 and 9 have similar shapes. On the basis of Kakugo's work, we can assign components 1 and 2 (the most isotactic components, $P_1 > 0.98$) to the large peak in the TREF curve above 100 °C. Component 3 (the less isotactic component, P_1 between 0.98 and 0.80) elutes between 40 and 100 °C; component 4 (Bernoullian atactic component) elutes at less than 40 °C.

It is of interest that the TREF curve (Figure 9) in the 40–100 °C range shows a continuous band. In contrast, the calculated tacticity distribution for the four-component model gives only one discrete band at (meso) ≈ 0.65. Perhaps a case can be made that more than one catalytic site contributes to "component" 3. Previously, it has been noted[13] that the less isotactic sites may actually consist of multiple sites, but detailed information on these sites is not easily extracted from the NMR and molecular weight data alone. It appears that the use of TREF together with computer simulation can provide additional information.

Table IX. Simulation of a Polypropylene Sample Containing Four Components[a]

sequence	total calc intensity	component 1	2	3	4	total obsd intensity[b]
(m)	95.2	99.4	98.0	67.7	23.3	
(r)	4.8	0.6	2.0	32.3	76.7	
(mm)	93.6	99.1	97.1	51.4	5.4	
(mr)	3.4	0.6	2.0	32.8	35.8	
(rr)	3.1	0.3	0.9	15.8	58.7	
(mmm)	92.6	98.8	96.2	40.5	1.3	
(mmr)	2.0	0.6	1.8	22.1	8.3	
(rmr)	0.7	0.0	0.1	5.4	13.8	
(mrm)	0.4	0.0	0.1	5.5	4.3	
(mrr)	2.6	0.6	1.8	21.5	27.3	
(rrr)	1.8	0.0	0.0	5.1	45.1	
(mmmm)	91.8	98.5	95.3	32.2	0.3	92.5
(mmmr)	1.6	0.6	1.8	16.7	2.0	1.5
(rmmr)	0.2	0.0	0.0	2.7	3.2	0.6
(mmrr)	1.7	0.6	1.7	16.5	6.3	1.5
(mmrm)	0.3	0.0	0.1	5.6	2.0	1.0
(rmrr)	0.9	0.0	0.0	5.1	21.0	
(mrmr)	0.5	0.0	0.1	5.4	6.5	0.2
(rrrr)	1.3	0.0	0.0	2.5	34.6	1.0
(mrrr)	0.9	0.0	0.0	5.2	20.9	0.7
(mrrm)	0.8	0.3	0.9	8.2	3.2	0.9
M_n	34 600	362 000	50 000	10 000	2000	45 000
M_w	316 000	499 000	50 000	10 000	2000	300 000

Input data for the components:

weight	0.646	0.285	0.035	0.035
P_1	0.997	0.991	0.800	
P_m				0.230

[a] Resolution of the data into four components described in ref 13. [b] Observed NMR data calculated from the pentad intensities reported for polypropylene fractions in ref 54.

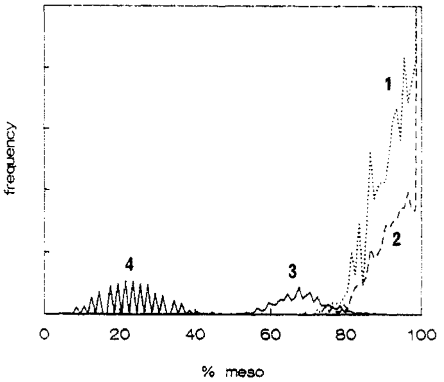


Figure 8. Simulated tacticity distribution of a four-component polypropylene sample. Simulation through program TADIS4; 1000 chains used for all components with Gaussian broadening of ϵ = 0.04. The four components are labeled. The vertical scale has been expanded for better visualization of components 3 and 4.

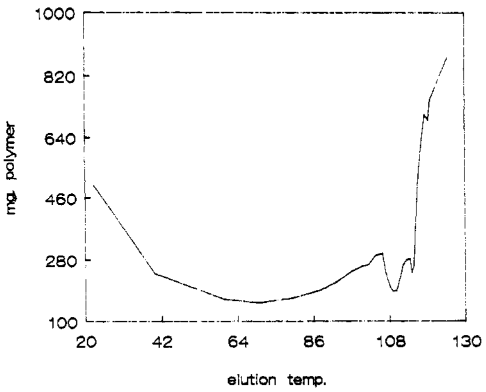


Figure 9. Plot of TREF results (weight of polymer vs elution temperature) for a sample of polypropylene reported in ref 9 (sample 13).

Compositional versus Sequential Heterogeneity

A distinction may be made[56] between compositional (chemical) heterogeneity and sequential heterogeneity. Compositional heterogeneity occurs when different polymer chains have different compositions. This results in a compositional distribution curve, as exemplified by Figures 2–8. Sequential heterogeneity occurs when within a polymer chain some segments of the chain show different tacticity sequences than others. This effect may be present to some degree in polymers but is most noticeable when the polymer has a blocklike structure, with one block obeying one propagation model and the other obeying a different propagation model. For example, polymers whose structure conforms with the consecutive two-state models would be expected to have sequential heterogeneity.

Note that compositional and sequential heterogeneity differ *kinetically* only in degree and not in kind. In the case of the consecutive two-state model, they reflect the relative rates of interconversion between the two states versus the rates of propagation, termination, and chain transfer. Nevertheless, as far as chemical and physical properties are concerned, large differences may be discernible. In the case of compositional heterogeneity, the polymer chains corresponding to different compositions can be separated through fractionation. If the compositional range is sufficiently large, the different fractions may separate into different phases in the bulk state, thereby leading to different physical properties. For a sequentially heterogeneous polymer, the tendency to fractionate is much reduced. In fact, such a polymer may be useful as an interfacial agent.

Experimentally, if one obtains a tacticity distribution curve (e.g., through fractionation or TREF), one may know about the compositional heterogeneity but not necessarily know about the sequential heterogeneity or the propagation statistics. The availability of NMR data, together with computer simulation, would be useful. A sequence index (SI) can be defined from the (mr) triad sequence and the tacticity composition:

$$\mathrm{SI} = \frac{(\mathrm{mr}) - 2(\mathrm{m})(\mathrm{r})}{2(\mathrm{m})(\mathrm{r})} \quad (9)$$

As defined, the SI is 0 for a random-tacticity (Bernoullian) polymer, +100 for a polymer where the m and r units alternate, and −100 for a polymer where m and r form long blocks. Thus, SI is a measure of the sequential heterogeneity for a given polymer chain. For convenience, the SI values for all the chains with the same tacticity composition are averaged to give $(\mathrm{SI})_{\mathrm{ave}}$. This feature has been incorportaed into all the TADIS programs. A composition distribution curve can be plotted with an overlaying $(\mathrm{SI})_{\mathrm{ave}}$ curve (e.g., Figure 10).

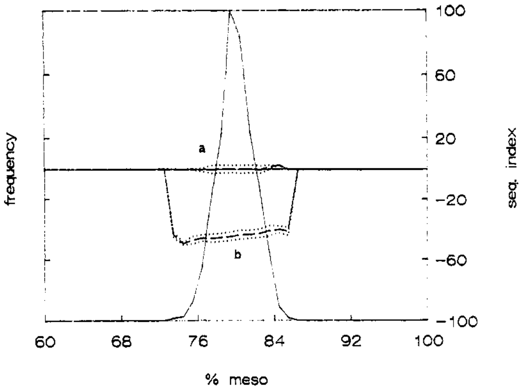


Figure 10. Compositional distribution and sequence index curves. (a) Bernoullian polymer, $P_{\mathrm{m}} = 0.8$: compositional distribution, solid line; $(\mathrm{PI})_{\mathrm{ave}}$, dashed line; SID, dotted line. (b) M1 polymer, $P_{\mathrm{mr}} = 0.111$, $P_{\mathrm{rm}} = 0.444$: $(\mathrm{SI})_{\mathrm{ave}}$, dashed line; SID, dotted line. Simulation through program TADIS1.

In addition, it is useful at every tacticity composition to calculate not only the average SI for all the polymer chains but also the mean deviation. This will be called hereinafter the sequence index dispersity (SID). Thus, SID = $(1/N)\sum|(\mathrm{SI})_i - (\mathrm{SI})_{\mathrm{ave}}|$, where N is the number of polymer chains at a given tacticity composition. On the composition/SI plot, the SID is indicated as curves above and below the SI curve. Thus, for each composition, $(\mathrm{SI})_{\mathrm{ave}}$ ± SID can be directly visualized on the tacticity composition distribution curve.

For example, we can simulate the tacticity distribution of two polymers, one random in sequence placement and the other blocky. For the random case, the Bernoullian model is used with $P_{\mathrm{m}} = 0.8$. In the blocky case, the first-order Markovian model is used with $P_{\mathrm{mr}} = 0.111$ and $P_{\mathrm{rm}} = 0.444$. These reaction probabilities correspond to $r_{\mathrm{m}}r_{\mathrm{r}} = 10$. In both cases 1000 polymer chains and 1000 monomer residue units per chain are used for simulation. The tacticity composition and the sequence index information are given in Figure 10. As expected, $(\mathrm{SI})_{\mathrm{ave}}$ is approximately zero for the random polymer and negative for the blocky polymer.

We next simulate a consecutive two-state model. We keep the same overall m content (0.80) and use two Bernoullian states:

state 1: $P_{\mathrm{m}} = 0.95, \quad \alpha = 50$

state 2: $P_{\mathrm{m}} = 0.50, \quad \beta = 25$

The tacticity distribution and the sequence index are shown in Figure 11. The sequence index is again negative, indicating the blocky nature of the polymer. Thus, the combination of composition distribution plot and $(\mathrm{SI})_{\mathrm{ave}}$ curve can provide rather detailed information on sequential heterogeneity and on the nature of polymerization.

Conclusion

This work aims to show the effects of tacticity heterogeneity on NMR data and on the tacticity distribution curve. In commercial or experimental polymers the polymerization processes are frequently complex. The simulation methods given in this work may provide the means to predict the outcome of different events and (where data are available) to compare the predicted with the observed data. In this way, a better understanding of the polymerization mechansim may be achieved.

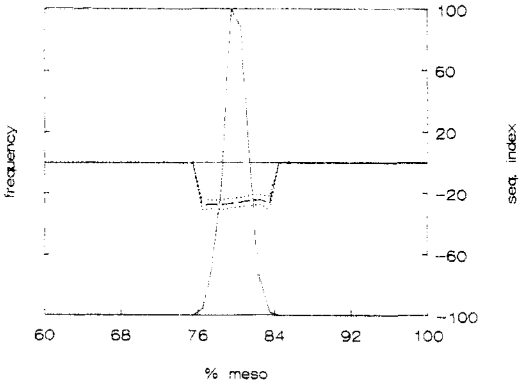


Figure 11. Simulation of a polymer obeying the consecutive two-state (B/B) model. Compositional distribution, solid line; $(\mathrm{SI})_{\mathrm{ave}}$, dashed line; SID, dotted line. Simulation through program TADIS2.

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