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Deconvolution of chain-length distributions of linear polymers made by multiple-site-type catalysts

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Polyolefins made using most heterogeneous and some homogeneous Ziegler–Natta catalysts show a characteristic broad molecular-weight distribution, generally assumed to be caused by the presence of more than one active site type, each type producing polymer with an instantaneous chain-length distribution that is most probable and having polydispersity of 2. Herein is reported a comparison of two numerical methods for the deconvolution of instantaneous chain-length distributions of linear homo- and copolymers made using multiple-site-type catalysts giving an individual most probable chain-length distribution for each site type, and a methodology is proposed for the efficient deconvolution of measured chain-length distributions.

(Keywords: Ziegler–Natta catalysts; multiple-site-type model; chain-length distributions)

INTRODUCTION

Polyolefins produced using most heterogeneous and some homogeneous Ziegler–Natta catalysts have broad weight chain-length distributions (*WCLD*s), with polydispersities that range from 4 to 20. These values are significantly larger than the polydispersity of 2 expected for ionic chain growth polymerization, where the mechanisms of chain termination (such as chain transfer to a small molecule) produce instantaneous *WCLD*s that are time- or monomer-conversion-independent for batch or semi-batch processes[1].

For a long time the explanations for broad *WLCD*s have been found in two main schools of thought. One of these advocated that, under certain polymerization conditions, mass- and heat-transfer resistances broadened the *WLCD* of polymer made by heterogeneous Ziegler–Natta catalysts[2]. The other one disregarded transport effects and assumed that more than one catalytic species type was active during the polymerization, each one making polymer with different molecular-weight averages[3]. Recently, mathematical models incorporating both multiple site types and mass- and heat-transfer resistances have been proposed[4,5], owing to the realization that both phenomena may contribute to the breadth of the *WCLD* of polymer made using heterogeneous Ziegler–Natta catalysts.

However, under most polymerization conditions, the effect of multiple site types is far more important than mass- and heat-transfer resistances[4–6]. Under these conditions, each site type *instantaneously* produces polymer that has the most probable *WCLD*. Therefore, the *instantaneous WCLD* of the accumulated polymer can be considered an average of that produced by the individual site types, weighted by the weight fraction of polymer produced by each site type.

Assuming that the polymerization conditions are such that the *WCLD* of the accumulated polymer is equal to the instantaneous *WCLD*, it is possible to obtain information about the number and activity of catalytic species by decomposing the *WCLD* of the whole polymer into individual most probable *WCLD* of each active site type. This approach was suggested by Vickroy *et al.*[7], but very few details were given about their numerical method and polymerization conditions required for its validity. In this work we will compare two numerical methods for performing the necessary deconvolution, and propose an efficient methodology for its use with experimental *WCLD*s measured by size exclusion chromatography.

MODEL DEVELOPMENT

Representation of WCLD *as a weighted sum of most probable* WCLD*s*

The most probable *WCLD* of linear homo- and binary copolymers may be expressed by the equation:

$$w(r, j) = \tau^2(j) r \exp[-\tau(j) r] \tag{1}$$

where $w(r, j)$ is the most probable *WCLD* (weight fraction of polymer of chain length r produced on site type j instantaneously), $\tau(j)$ is the ratio of rate of production of dead polymer chain to rate of propagation‡, r is the polymer chain length and j is the active site type.

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‡ Dead polymer chain can be produced by β-hydride elimination and chain transfer to a small molecule. It is assumed that for batch and semi-batch polymerizations $\tau(j)$ is time- or monomer-conversion-independent and for continuous processes also spatially independent

The instantaneous *WCLD* of the whole polymer is obtained by averaging the distributions of each individual site type:

$$\hat{W}(r)=\sum_{j=1}^{n} m(j)w(r,j) \tag{2}$$

where $\hat{W}(r)$ is the instantaneous *WCLD* of the whole polymer produced by n site types, $m(j)$ is the weight or mass fraction of polymer made by site type j and n is the number of active site types.

Equation (2) is modified to include the constraint:

$$\sum_{j=1}^{n} m(j)=1 \tag{3}$$

and is finally expressed as:

$$\hat{W}(r)=w(r,n)+\sum_{j=1}^{n-1} m(j)[w(r,j)-w(r,n)] \tag{4}$$

We want to minimize the difference between $\hat{W}(r)$ computed by equation (4) and the measured distribution $W(r)$ in order to determine the adjustable parameters $\tau(1)$, $\tau(2), \ldots, \tau(n)$ and $m(1), m(2), \ldots, m(n)$.

Equation (4) is valid for describing an instantaneous *WCLD* formed by the superposition of several individual most probable *WCLD*s. However, in practice, one has information only about *WCLD*s for polymer accumulated over a finite polymerization time. Therefore, to apply the proposed model to experimental *WCLD*s, we must assume that the *WCLD* for the accumulated polymer is essentially the same as the instantaneous *WCLD*. This assumption is valid when:

(i) The polymerization reactor is operated at steady-state conditions and the *WCLD* is spatially independent.

(ii) The ratio of transfer to propagation rates of all active sites does not change during the polymerization.

(iii) The relative amounts of polymer made by each site type do not change during the polymerization.

(iv) Mass- and heat-transfer effects are negligible, since these effects could give an instantaneous *WCLD* that is spatially dependent.

Numerical solution

Two numerical methods were compared by fitting the model equation (4) to a theoretical and to an experimental *WCLD*: the Levenberg–Marquardt method[8] and the Golub–Pereyra method[9].

The Levenberg–Marquardt method has become a standard method of non-linear least-squares routines. We used Press' FORTRAN routine for this algorithm[10]. It defines a chi-square merit function and determines best-fit parameters by its minimization:

$$\chi^2=\sum_{i=1}^{m}\left(\frac{W(r)_i-\hat{W}(r)_i}{\sigma(r)_i}\right)^2 \tag{5}$$

where m is the number of experimental points and $\sigma(r)$ is the standard deviation of the experimental points.

If the Levenberg–Marquardt method is used to estimate $\tau(j)$ and $m(j)$ directly, it often converges to values that have no physical meaning, such as negative values for $\tau(j)$ and values greater than unity for $m(j)$, especially when many site types are used. To overcome this problem, we defined new fitting variables according to the transformations:

$$\tau(j)=\frac{1}{1+\exp[-T(j)]} \tag{6}$$

$$m(j)=\frac{1}{1+\exp[-M(j)]} \tag{7}$$

The adjustable parameters are now $T(j)$ and $M(j)$, thus restraining the values of $\tau(j)$ and $m(j)$ to the interval [0, 1].

In the model defined by equation (4), the parameters $m(j)$ are called conditionally linear parameters[8]. The optimal values of these parameters, for fixed values of the non-linear parameters $\tau(j)$, can be estimated by linear least squares. The model of equation (4) can be partitioned into expressions containing only linear or non-linear parameters:

$$W(\tau, \boldsymbol{m})=A(\tau)\boldsymbol{m} \tag{8}$$

where the matrix $A_{m\times n}$ depends only on the non-linear parameters. For any given set of τ values, the estimated value of $\boldsymbol{m}$ is given by:

$$\hat{\boldsymbol{m}}(\tau)=A^{+}(\tau)W \tag{9}$$

where A^{+} is the pseudo-inverse of A, defined by:

$$A^{+}=(A^{\mathrm{T}}A)^{-1}A^{\mathrm{T}} \tag{10}$$

Golub and Pereyra[9] proposed a method to minimize:

$$r_2(\tau)=|W-A(\tau)\hat{\boldsymbol{m}}(\tau)|^2 \tag{11}$$

which depends only on the non-linear parameters. The objective function is first optimized in relation to the non-linear parameters $\tau(j)$ and then the linear parameters $m(j)$ are calculated. By using this method, we need to estimate only the first estimates of the n non-linear parameters $\tau(j)$.

We used the Golub–Pereyra method as implemented in the FORTRAN subroutine VARPRO. This subroutine is easily obtained from NETLIB through INTERNET[11].

Obtaining first estimates and increasing the number of site types

It is possible to estimate $\tau(1)$, $\tau(2)$ and $m(1)$ from the knowledge of the number-, mass- and z-average chain lengths ($\bar{r}_n$, $\bar{r}_w$, $\bar{r}_z$), which are easily available from the experimental *WCLD*. Although only two most probable *WCLD*s may not be sufficient to represent adequately the global *WCLD*, at least they provide an educated guess to start the decomposition algorithm.

For a two-site-type model, the chain-length averages are defined by the equations:

$$\bar{r}_n=\frac{1}{m(1)\tau(1)+m(2)\tau(2)} \tag{12}$$

$$\bar{r}_w=2\left(\frac{m(1)}{\tau(1)}+\frac{m(2)}{\tau(2)}\right) \tag{13}$$

$$\bar{r}_z=3\left(\frac{m(1)}{\tau^2(1)}+\frac{m(2)}{\tau^2(2)}\right)\left(\frac{m(1)}{\tau(1)}+\frac{m(2)}{\tau(2)}\right)^{-1} \tag{14}$$

Equations (12) to (14) are obtained by integrating the *WCLD*[1] and averaging the results of each individual site type. Equations (12) to (14) are easily solved by any algorithm for finding the roots of systems of non-linear algebraic equations, such as Newton's method[10].

Table 1 Model chain-length distribution parameters

Site type j	$\tau(j)$	$m(j)$
1	1.0×10^{-4}	0.10
2	1.5×10^{-4}	0.15
3	2.5×10^{-4}	0.25
4	5.0×10^{-4}	0.25
5	1.0×10^{-3}	0.15
6	2.5×10^{-3}	0.10

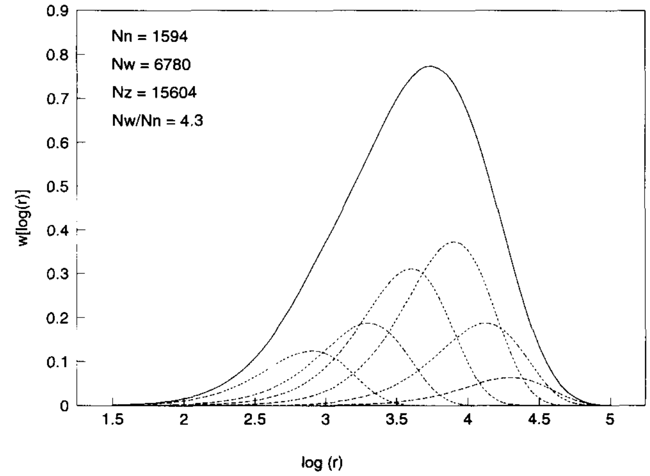

Figure 1 Model chain-length distribution generated by a six-site-type catalyst

The following 'rules of thumb' proved to be useful in helping to achieve convergence and to decide when to stop increasing the number of site types; for the Golub–Pereyra method, it is not necessary to obtain first estimates for $m(j)$:

(i) Obtain first guesses for $\tau(1)$, $\tau(2)$ and $m(1)$ by solving equations (12) to (14).

(ii) Start running the estimation program using those estimates.

(iii) Gradually increase the number of site types by estimating $\tau(n+1)$ and $m(n+1)$:

- $\tau(n+1)$ as $\tau(n+1)=\sum_{j=1}^{n} \tau(j)m(j)$.
- $m(n+1)$ as the average between the $m(j)$ corresponding to the $\tau(j)$ adjacent to $\tau(n+1)$ and normalizing the new values so that $\sum_{j=1}^{n+1} m(j)=1$.

(iv) χ^2 generally decreases significantly when site types that are needed to improve the fit are added.

(v) The number of site types should be considered adequate when the sum of the squares of the residuals does not improve significantly by adding another site type and when the residuals are not correlated.

SIMULATION RESULTS

We will first analyse the performance of the two numerical methods and the proposed methodology for estimating the site types using a *WCLD* produced by a model catalyst containing six site types. In this way we can verify if the methods work well for a case in which all of our assumptions about the catalyst are valid, since the global *WCLD* is the actual result of the superposition of six individual instantaneous most probable *WCLD*s.

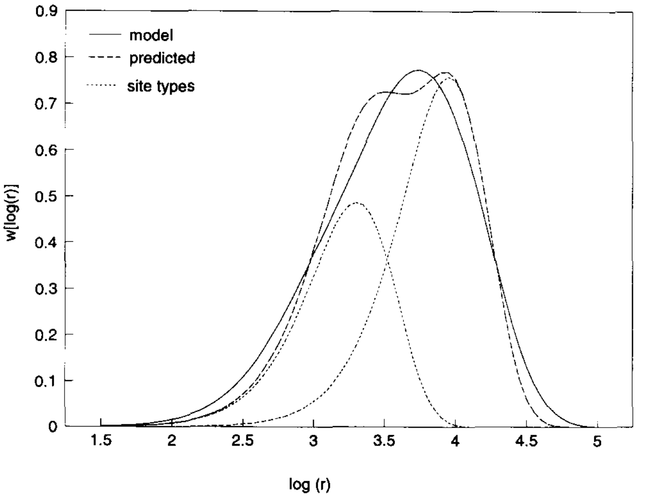

Figure 2 Deconvolution of a model chain-length distribution generated by a six-site-type catalyst into two most probable chain-length distributions

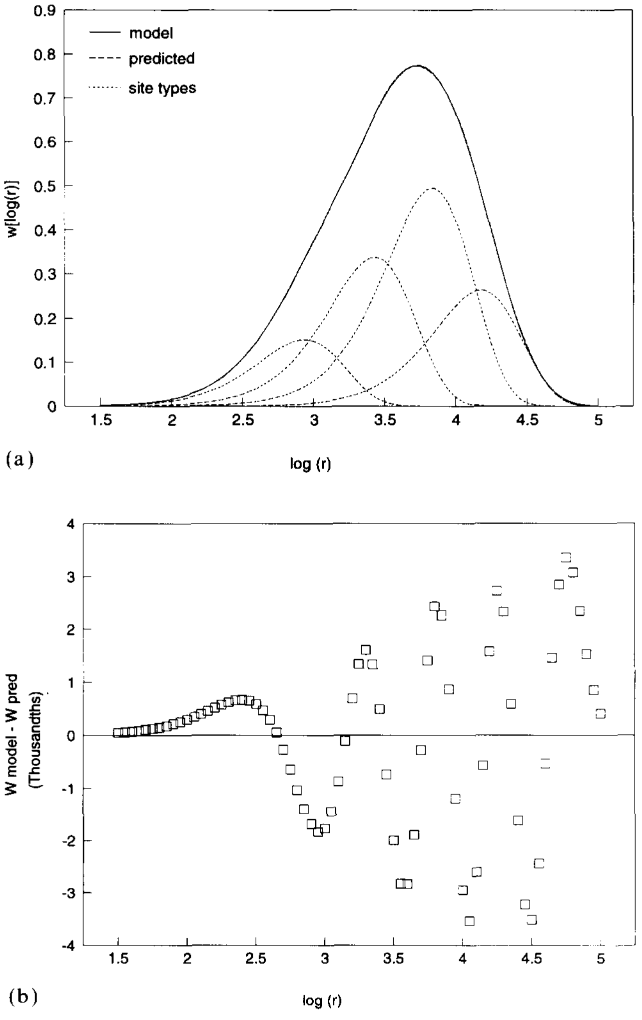

Figure 3 (a) Deconvolution of a model chain-length distribution generated by a six-site-type catalyst into four most probable chain-length distributions. (b) Residuals of the predicted four-site-type chain-length distribution and the model six-site-type chain-length distribution

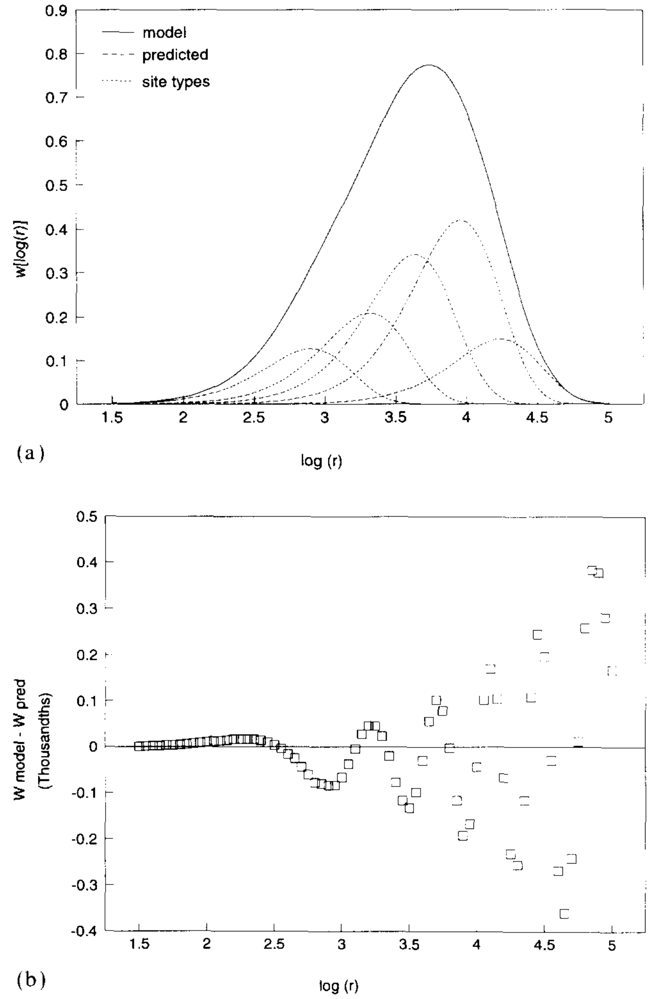

Figure 4 (a) Deconvolution of a model chain-length distribution generated by a six-site-type catalyst into five most probable chain-length distributions. (b) Residuals of the predicted five-site-type chain-length distribution and the model six-site-type chain-length distribution

Next we will use the above methods to decompose an experimental *WCLD* of a polypropylene sample measured by high-temperature g.p.c.

Table 1 presents the parameters $\tau(j)$ and $m(j)$ used to obtain the model *WCLD* of *Figure 1*. By solving equations (12) to (14) we obtain the following estimates for the parameters: $\tau(1)=0.001\,08$, $\tau(2)=0.000\,17$ and $m(1)=0.503$. Those estimates are used as first guesses in both numerical methods. The following discussion is valid for both methods, since they converge to the same parameters, provided that their initial guesses are the same.

Figure 2 illustrates the fitted curve when only two site types are used. It is readily seen that two sites cannot describe properly the whole distribution. By using the 'rules of thumb' described before, we obtain a three-site-types prediction that still does not describe the distribution adequately. *Figure 3a* compares a four-site-types predicted curve with the model curve. The agreement is very good* and one might have been tempted to stop the regression at this point. However, the residuals are significantly correlated, as presented in *Figure 3b*, indicating that the model is inadequate. The same is observed for a five-site-type curve, as shown in *Figures 4a* and *4b*. Correlated residuals are usually an indication of model inadequacy[8]. Finally, for the six-site-types model, one gets a very good agreement between prediction and model curve (as expected for this case) and residuals that are almost randomly distributed, as seen in *Figures 5a* and *5b*. The small discrepancies observed in the residual in *Figure 5b* were caused by round-off errors when generating and fitting the model distribution.

It is also illustrative to observe how the sum of the squares of the residuals changes by the addition of site types. *Table 2* shows how this value decreases significantly

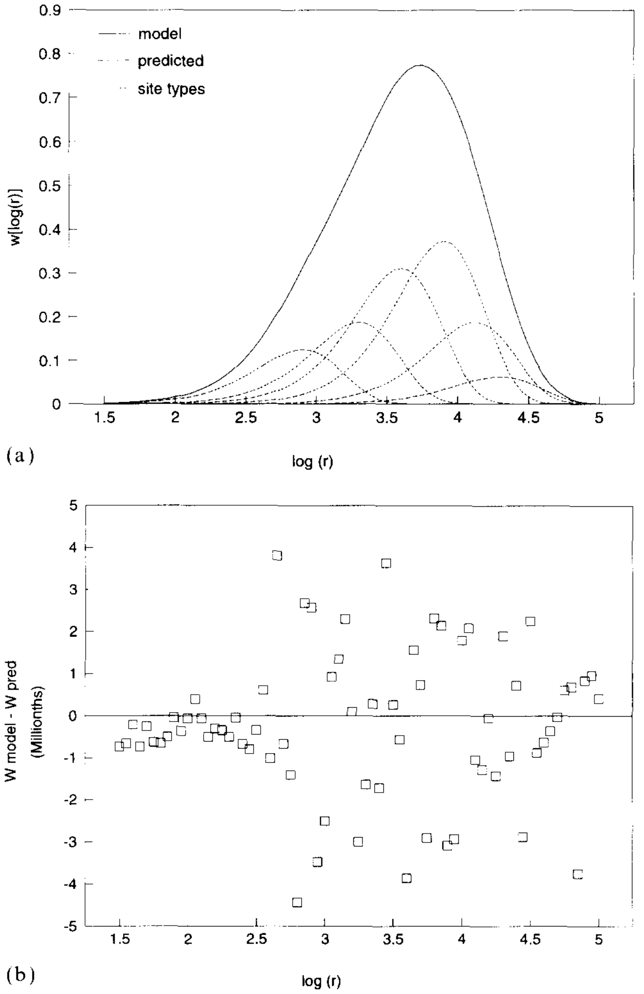

Figure 5 (a) Deconvolution of a model chain-length distribution generated by a six-site-type catalyst into six most probable chain-length distributions. (b) Residuals of the predicted six-site-type chain-length distribution and the model six-site-type chain-length distribution

Table 2 Sum of the squares of residuals as a function of number of site types for prediction of the model chain-length distribution

Number of site types	$\sum(\text{residuals})^2$
2	1.40×10^{-1}
3	6.76×10^{-3}
4	1.80×10^{-4}
5	1.22×10^{-6}
6	2.14×10^{-10}
7	2.09×10^{-10}

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*In *Figures 3a–5a* and *7a–9a*, the model curves and predicted curves are (practically) coincident at the scale of the diagrams

Table 3 Total computational times and total number of iterations required for convergence as a function of number of site types for the model chain-length distribution

	Marquardt		Golub	
Number of site types	Time (s)	Iter.	Time (s)	Iter.
2	2	6	5	23
3	16	27	6	16
4	15	14	9	20
5	19	12	10	17
6	870	465	22	30
Total	922	524	52	106

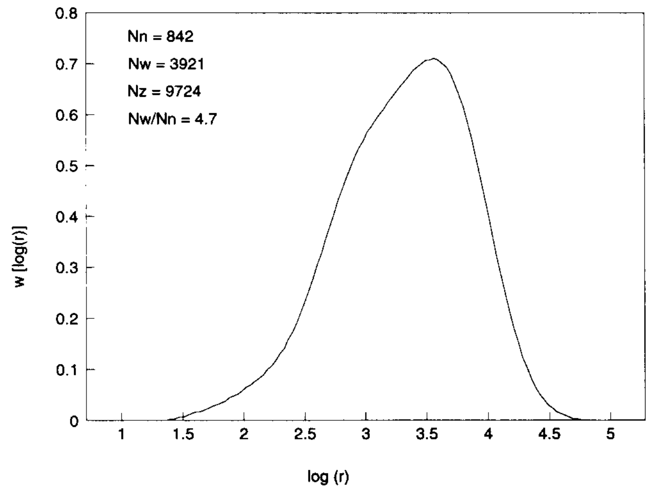

Figure 6 Experimental polypropylene chain-length distribution

when site types that are needed to improve the fitting are added to the model. Observe how the sum of the squares of the residuals is significantly smaller for the six-site-types model than for the five-site-types model but hardly decreases for the seven-site-types model.

Table 3 compares the total number of iterations and total computation time required by both methods, using a Dell system 325P with a 80387 math coprocessor. Although they both converge for the same values, the Golub–Pereyra method requires fewer iterations and is much faster than the Levenberg–Marquardt method, especially when the number of site types considered approaches that used in generating the model *WCLD*. For six site types, the Levenberg–Marquardt method converges very slowly while the convergence rate of the Golub–Pereyra method is not significantly reduced.

The two methods were also used to fit an experimental *WCLD* distribution of an isotactic polypropylene sample made by a heterogeneous Ziegler–Natta catalyst under steady-state polymerization conditions and no significant deactivation. The *WCLD* was determined using a Waters 150 high-temperature gel permeation chromatograph (g.p.c.). The experimental g.p.c. curve and chain-length averages are shown in *Figure 6*.

The same systematic approach was used for decomposing the polypropylene *WCLD*. First guesses were obtained by solving equations (12) to (14) using average chain lengths and the number of site types was increased one at a time. Again, both methods converge to the same values, but the Golub–Pereyra method is significantly faster.

Figure 7a shows the experimental and the predicted *WCLD* for a four-site-type model. From visual inspection, the fit seems adequate, but the residuals are still severely correlated, as depicted in *Figure 7b*. The fit can be improved by using a five-site-types model, as shown in *Figure 8a*. The residuals do not seem to be very correlated, except for the low-molecular-weight tail, as presented in *Figure 8b*. Adding one more site type does not significantly improve the fit or the residual correlations, as can be seen in *Figures 9a* and *9b*.

Table 4 depicts the sum of the squares of the residuals for models containing two to seven site types. As mentioned before, the five- and six-site-types model are almost equivalent, and no improvement is noticed by using a seven-site-type model. Therefore, it is reasonable to assume that the analysed polypropylene sample was produced by a catalyst containing five or, less likely, six different site types. The correlated residuals observed for the low-molecular-weight tail are probably related to higher chromatogram noise levels and increased variance of the observations or to peak broadening. For this polypropylene sample, temperature-rising elution

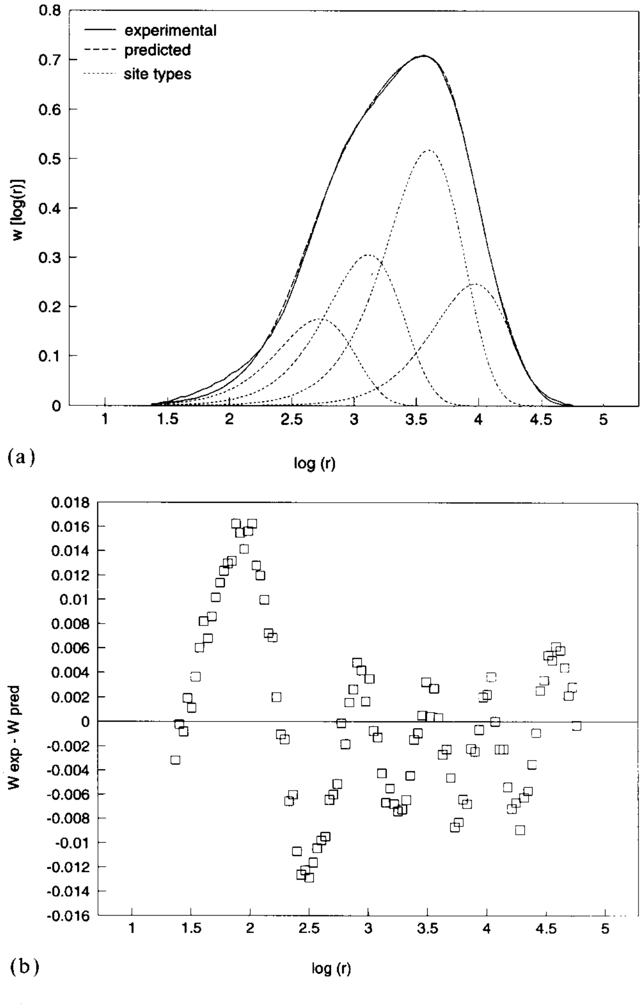

Figure 7 (a) Deconvolution of an experimental polypropylene chain-length distribution into four most probable chain-length distributions. (b) Residuals of the predicted four-site-type chain-length distribution and the experimental polypropylene chain-length distribution

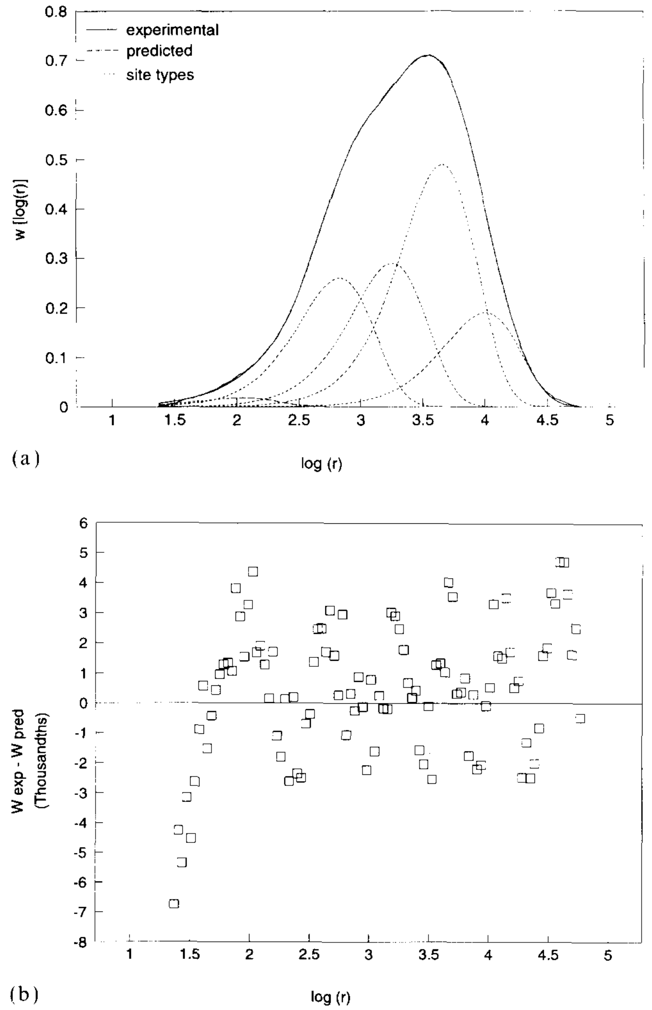

Figure 8 (a) Deconvolution of an experimental polypropylene chain-length distribution into five most probable chain-length distributions. (b) Residuals of the predicted five-site-type chain-length distribution and the experimental polypropylene chain-length distribution

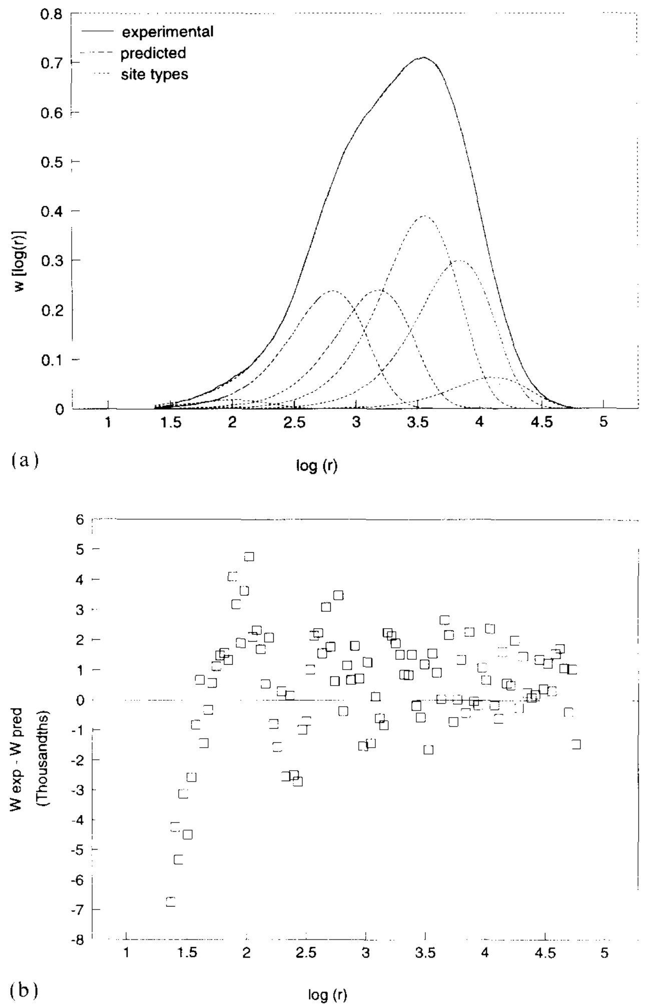

Figure 9 (a) Deconvolution of an experimental polypropylene chain-length distribution into six most probable chain-length distributions. (b) Residuals of the predicted six-site-type chain-length distribution and the experimental polypropylene chain-length distribution

fractionation/^{13}C nuclear magnetic resonance (t.r.e.f./^{13}C n.m.r.) measurements have shown chains at significant concentration levels having quite different stereoregularity. The g.p.c. relationship of molecular weight *versus* retention time may differ for chains with different microstructure, and of course this may make g.p.c. analysis of whole polypropylene samples suspect.

The close similarity of results obtained for the model *WCLD* and the experimental *WCLD*, plus the good fitting of the five- or six-site-types model, indicates that our initial assumptions about the nature of active sites of the catalyst are reasonable. The converged parameters for the polypropylene sample are shown in *Table 5*.

Total computational times and total number of iterations required by each method are compared in *Table 6* for the polypropylene sample. As for the case of the model catalyst, the Golub–Pereyra method is also faster and requires fewer iterations for decomposing the experimental *WCLD*.

Although it is not possible to obtain a formal proof of uniqueness of this solution, the fact that two significantly different optimization methods converge to the same solution provides some indirect evidence that the converged values are indeed the optimal solution for the problem.

Table 4 Sum of the squares of residuals as a function of number of site types for prediction of the g.p.c. chain-length distribution of polypropylene

Number of site types	$\sum$(residuals)^2
2	1.98×10^{-1}
3	1.62×10^{-2}
4	5.08×10^{-3}
5	5.12×10^{-4}
6	3.75×10^{-4}
7	3.76×10^{-4}

Table 5 Converged parameters of the five- and six-site-types model for the g.p.c. chain-length distribution of polypropylene

	Five-site-types model		Six-site-types model	
Site types	τ	m	τ	m
1	1.99×10^{-4}	0.152	1.51×10^{-4}	0.051
2	4.39×10^{-4}	0.393	2.87×10^{-4}	0.240
3	1.11×10^{-3}	0.232	5.49×10^{-4}	0.311
4	2.95×10^{-3}	0.208	1.3×10^{-3}	0.193
5	1.82×10^{-2}	0.015	3.06×10^{-3}	0.191
6			1.86×10^{-3}	0.014

Table 6 Total computational times and total number of iterations required for convergence as a function of number of site types for the g.p.c. chain-length distribution of polypropylene

	Marquardt		Golub	
Number of site types	Time (s)	Iter.	Time (s)	Iter.
2	2	7	4	21
3	6	11	5	15
4	9	10	19	38
5	24	19	15	23
6	197	120	20	22
Total	238	167	63	119

CONCLUSIONS

The instantaneous chain-length distribution of polymers made by multiple-site-type catalysts and synthesized under appropriate polymerization conditions can be described reasonably well as a weighted sum of most probable chain-length distributions. If polymerization conditions are such that the cumulative *WCLD*s are close to the instantaneous *WCLD*s, then this model can be extended to describe polymer samples obtained under realistic experimental conditions.

The deconvolution of the global *WCLD* can be performed by several non-linear optimization techniques. The algorithm proposed by Golub and Pereyra takes advantage of the conditional linear parameters of the model and is generally faster than the Levenberg–Marquardt method, although both algorithms converge to the same values when the same initial conditions are used. One additional advantage of the Golub–Pereyra method is that it is not necessary to provide a first estimate of the linear parameters of the model.

The proposed methodology of obtaining first estimates for a two-site-type model and of systematically increasing the number of site types of the model is capable of obtaining an optimum solution for the deconvolution problem, as attested by the correct deconvolution of a model six-site-type *WCLD*. It can also be successfully employed for deconvoluting experimental *WCLD*s.

Finally, the good agreement between the multiple-site-type model and the experimental *WCLD* of a polypropylene sample supports the hypothesis that heterogeneous Ziegler–Natta catalysts possess multiple active site types, each one instantaneously producing polymer chains with a most probable chain-length distribution.

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