

An Alternative Neural Network Approach to Calculate the Molecular Weight Distribution from Dynamic Rheological Properties of i-PP Resins

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ABSTRACT: The calculation of the molecular weight distribution (MWD) of a polymer from its rheological properties is an attractive method since rheological measurements are comparatively faster and cheaper than the classical gel permeation chromatography technique (GPC). The calculation, however, still has some drawbacks, such as the sensitivity of the mathematical solution involved (ill-posed problem) and the limited frequency range covered by commercial rheometers, which can be especially critical for crystalline polymers, for which the time–temperature superposition is of limited worth. In this article, a new approach for evaluating the MWD from the storage modulus and the relaxation modulus curves is proposed. The method, based on the use of a neural network model, was employed to evaluate MWD from rheological data obtained with different isotactic polypropylene resins. The results show that this approach can be successfully used to compute MWD curves and should expand the range of application of the rheological technique. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1416–1423, 2000

Key words: molecular weight distribution; dynamic rheological properties; neural networks

INTRODUCTION

In recent years, substantial effort has been made to calculate the molecular weight distribution (MWD) curve of a polymer from its rheological properties, mainly from the relaxation spectrum^{1–4} and the steady state shear viscosity.^{5,6}

The advantages of the use of this technique, compared to traditional gel permeation chromatography (GPC) are related to the lower costs and shorted analysis times. In addition, the sample

does not need to be dissolved, and this technique is more sensitive to the high-molecular-weight fractions.

In order to calculate the MWD from the relaxation spectrum, the dual reptation theory^{7,8} can be used. This theory allows one to correlate the relaxation modulus $G(t)$ of the polymer with the molecular weight of each polymeric fraction by the following equation:

$$\frac{G(t)}{G_N^0} = \left[\sum_{i=1}^c w_i F^{1/2}(M_i, t) \right]^2 \quad (1)$$

where G_N^0 is the experimentally determinable plateau modulus, w_i is the weight fraction of poly-

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mer chains with molecular weight M_i , and $F(M, t)$ is the relaxation function.

The relaxation function $F(M, t)$ represents the contribution to the relaxation modulus that each monodisperse fraction of the polymer has at each time t . Different forms have been assumed for this relaxation function, for example, the BSW model³ that gives

$$F(M, t) = \frac{\alpha}{\tau^\alpha} \int_0^c x^{(\alpha-1)} \exp(-t/x) dx \quad (2)$$

where

$$J_e^0 G_N^0 = \frac{(1 + \alpha)^2}{\alpha(2 + \alpha)} \quad (3)$$

$$\tau(M) = \frac{(1 + \alpha)\eta_0(M)}{\alpha G_N^0} \quad (4)$$

In these equations, τ represents the relaxation time, J_e^0 is the equilibrium compliance, α is a constant ($= 0.56$), $\eta_0(M)$ is the zero-shear viscosity of a monodisperse polymer of molecular weight M , and x is a dummy variable.

From dynamic rheological experiments, the shear storage modulus $G'(\omega)$ and the shear loss modulus $G''(\omega)$ can be obtained. From these moduli, the relaxation spectrum and the relaxation modulus can be computed.^{9,10}

Extracting the MWD from eqs. (1) to (4) is a typical, so-called, ill-posed problem, meaning that even small experimental errors in the determination of $G(t)$ can generate large deviations in the final solution. One way to minimize this problem is to use the regularization method of Tikhonov as given in Hansen.¹¹

Another difficulty is related to the experimental rheological technique for measuring $G''(\omega)$ and $G'(\omega)$. It is well known that commercial rheometers have a limited frequency span, usually between 10^{-3} and 10^2 rad/s. This narrow frequency span does not constitute a problem when dealing with amorphous polymers because the frequency range can be extended if the time-temperature superposition principle is used.^{12,13} However, for crystalline polymers, like isotactic polypropylene (i-PP) this limitation in the frequency makes it difficult to reach the terminal relaxation region that occurs at very low frequencies, especially when the polymer has a broad MWD.¹⁴ The detection of the plateau modulus that occurs at in-

termediate frequencies also becomes difficult. In other words, the thermal analysis window of the polymer becomes very narrow, due to the surging of the polymer crystallization; consequently, the applicability of the time-temperature superposition principle also becomes limited.

Due to these experimental problems, the calculations of MWD from dynamic rheological properties have predominantly focused on amorphous polymers since studies with crystalline polymers show high discrepancies between the results from the rheological measurements and the GPC curves.³

In this work, an alternative approach for determining the MWD from rheological properties is proposed. The molecular weight distribution is obtained by a neural network model, which uses the shear storage and shear loss moduli curves as input variables, together with the temperature at which the rheological curves were measured. The validity of the procedure was illustrated for different i-PP resins.

NEURAL NETWORKS

Artificial neural networks (ANN) have been acclaimed as a universal approximator and their applications in several fields are growing rapidly. Neural networks possess the ability to “learn” nonlinear relationships without actually modeling the physical and chemical laws that govern the system. In this sense, ANN must be regarded as empirical relationships. The success in obtaining a reliable and robust ANN depends strongly on the choice of process variables involved, as well as on the quality of the available set of data and the domain used for training purposes.¹⁵

The most commonly employed ANN is the so-called feed-forward network with one hidden layer, as shown in Figure 1. Each processing neuron (represented by a circle in Fig. 1) calculates the weighted sum of the interconnected signals from the previous layer plus a bias term [eqs. (5) and (7)] and then generates an output through its activation function [eqs. (6) and (8)]. Thus, for a neural network with N input variables, NH neurons in the hidden layer, and P output variables, the equations for the hidden layer are as follows:

$$S_j = \sum_{i=1}^N W_{ij} X_i + W_{N+1,j} \quad j = 1, 2, \dots, NH \quad (5)$$

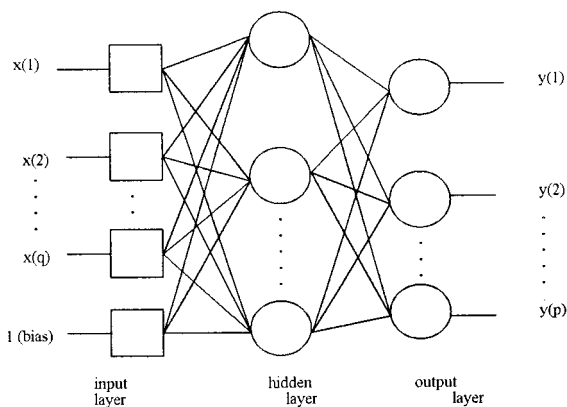


Figure 1 Scheme of a feed-forward neural network.

$$O_j = f(S_j) = \frac{1}{1 + \exp(-S_j)} \quad j = 1, 2, \dots, NH \quad (6)$$

and for the output layer:

$$S_k = \sum_{j=1}^{NH} W_{j,k} O_j + W_{NH+1,k} \quad k = 1, 2, \dots, P \quad (7)$$

$$O_k = f(S_k) = \frac{1}{1 + \exp(-S_k)} \quad k = 1, 2, \dots, P \quad (8)$$

The “training” or “learning” of the ANN consists of changing the network parameters, the weights W , in order to minimize the quadratic deviation E between the experimental values Y_k and the predicted output O_k , defined as

$$E = \sum_{m=1}^r \sum_{k=1}^P (Y_k^{(m)} - O_k^{(m)})^2 \quad (9)$$

where r is the number of experimental data used in the training. The input and the output variables are normalized in the range $[0, 1]$. The back-propagation algorithm was used to adjust the weights.¹⁵

EXPERIMENTAL

Four different i-PP resins, referred as A, B, C and D, were kindly donated by OPP Petroquímica do Brasil.

Molecular weight distributions of the resins were determined by GPC using a Waters Model 150C GPC apparatus at 145°C with trichlorobenzene as solvent. Table I presents the average molecular weights and polydispersity of the resins.

Rectangular samples of the resins were prepared by injection molding in a Pic-Boy injection molding machine; the barrel temperature was 200°C, and the mold temperature was 25°C. From these rectangular samples, disks of 25 mm diameter and 1 mm thickness were cut and used in the rheological measurements.

The $G'(\omega)$ and $G''(\omega)$ measurements were performed with a Rheometrics Model SR200 controlled tension rheometer at five different temperatures (180, 190, 200, 215, and 230°C). The parallel plates were 25 mm diameter with a 1 mm gap between the plates. The frequency span was varied between 0.01 and 500 rad/as

DATA TREATMENT

The $G'(\omega)$ and $G''(\omega)$ curves are used as input information for the neural network along with the temperature at which the rheological measurements were carried out. Each curve was digitized as 25 points, at previously chosen frequencies covering the range of interest. Most of the measured experimental points coincided with these frequencies. When the measurement was not available at these particular frequencies, the corresponding values of G' and G'' were obtained by interpolation. Therefore, for each run, the input vector consist of 51 values (25 values of G' , 25 values of G'' , and one temperature).

Each experimentally measured MWD curve was also digitized as 26 points by interpolating the GPC curves at specified molecular weight values covering the range of interest. Therefore, for each run, the output vector consists of 26 values

Table I Number- and Weight-Average Molecular Weights and Polydispersity of the Resins

Resin	M_n	M_w	M_w/M_n
A	48,900	301,900	6.17
B	75,100	448,800	5.98
C	99,600	606,800	6.09
D	98,700	567,400	5.75

of the fraction of polymer at each specified molecular weight.

For each of the four isotactic PP resins (A, B, C, and D), the rheological curves were measured at five different temperatures (180, 190, 200, 215, and 230°C), resulting in a total of 20 data sets.

As usual in ANN training, the whole collection of experimental data was split into two sets, as follows: one 13-run set was used for training the ANN, and the other remaining 7-run set was used for testing the predictive capability of the ANN. The following data sets were selected to test the performance of the neural network: A-180, A-200, B-180, B-215, C-190, C-230, and D-200 (the letter indicates the polymer sample, and the number indicates the temperature at which the rheological measurements were made). The selection of training and test sets was made at random.

An important step is the determination of the most adequate number of neurons in the hidden layer, NH . Neural networks with different NH s were tested, according to the criterion of minimum square deviation between the experimental results and the calculated output from the ANN, for the test set. The minimum number of neurons in the hidden layer that met this criterion and simultaneously prevent overfitting problems was $NH = 2$, as shown in Figure 2. A total of 10,000 iterations or cycles of the backpropagation algorithm were used in all cases (this number was also determined from previous tests to prevent overtraining).

RESULTS AND DISCUSSION

A sample of the storage and loss moduli is shown in Figure 3. In our earlier work,¹² we showed that the use of the BSW model to calculate the MWD of these resins failed to fit their GPC curves well. The low-molecular-weight fractions were not detected by that model; therefore, the calculated MWD curve was narrower and higher than the experimental GPC curves. A sample of this result is presented in Figure 4.

On the other hand, the results obtained with the neural network were excellent, in close agreement with the experimentally measured GPC curves. Figure 5 shows the comparison between experimental and calculated values of $w(\log MW)$, the weight fraction of polymer at each specified molecular weight, for the learning set and for the test set. The experimental and calculated MWD curves for the test set are shown in Figure

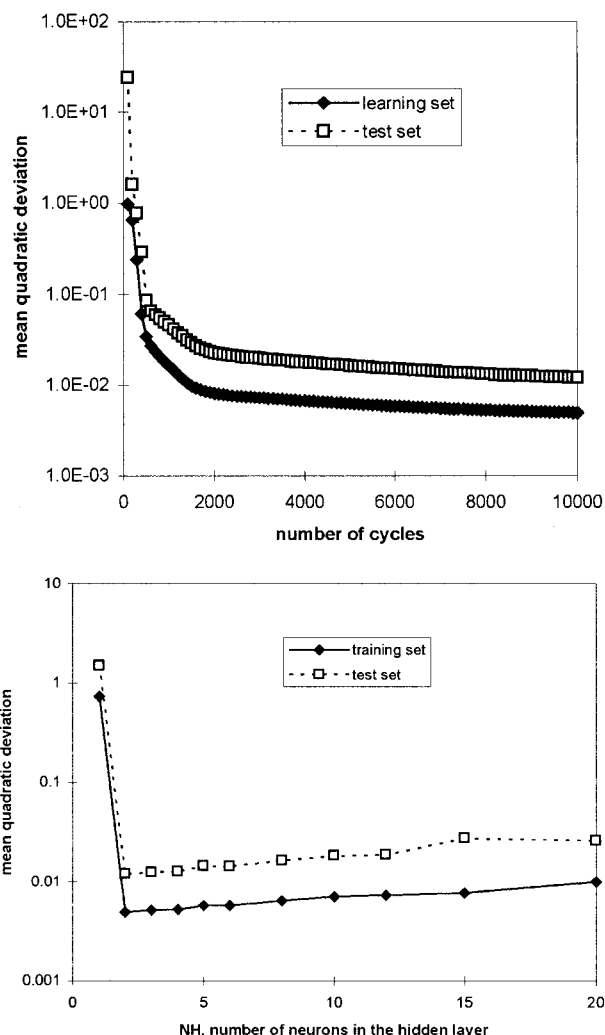


Figure 2 Effect of the number of cycles and the number of neurons in the hidden layer on the mean quadratic deviation.

6. One can see that, after being adequately trained, the ANN model is able to extract the MWD information from the rheological curves correctly, even when rheological curves were determined over a limited frequency span, as in the present work (the ANN treatment was used for each individual temperature, without using any temperature–time superposition). In addition, the ANN training is able to accommodate and filter spurious behavior caused by equipment limitations (for example, the descending part of $G'(\omega)$ curves observed at high frequencies in the present case).

In comparison to the conventional treatment, the only drawback of the ANN is that it is a fully

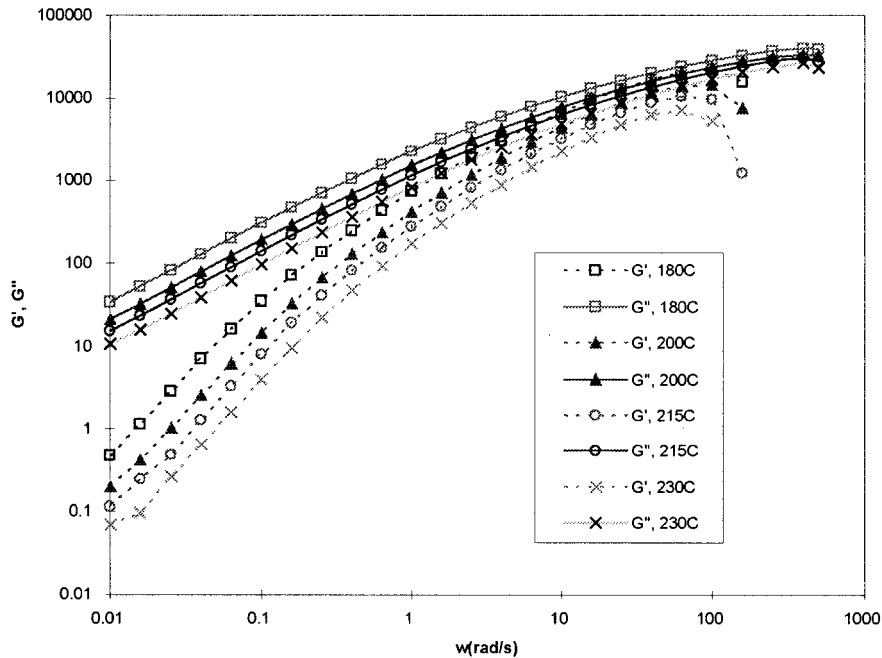


Figure 3 Storage and loss moduli curves measured for an i-PP resin (resin A).

“black box” model, in the sense that no physical meaning can be associated with the network parameters (the adjusted weights). In fact, as a purely empirical model, the ANN is strongly dependent on the “calibration,” that is, the availability and the quality of the experimental data used in the training, as well as the domain covered by these data. On the other hand, the ANN

procedure overcomes several difficulties encountered in the conventional treatment, especially for crystalline polymers, offering the possibility of a reliable method for obtaining rapid measurements of MWD.

More work is required to extend the results of the treatment proposed here to wider domains, different polymers, and bimodal MWDs.

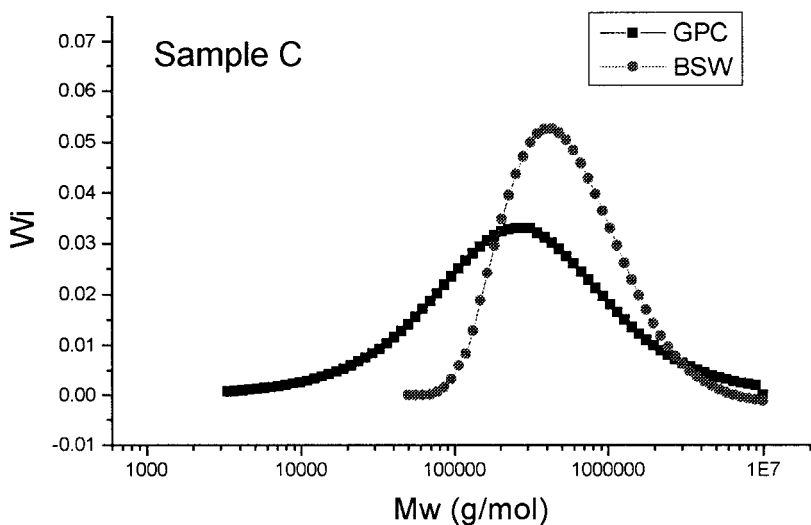


Figure 4 Comparison between the experimental MWD curve (GPC) and the curve obtained from conventional data treatment (relaxation spectrum, BWS model, and Tikhonov regularization).

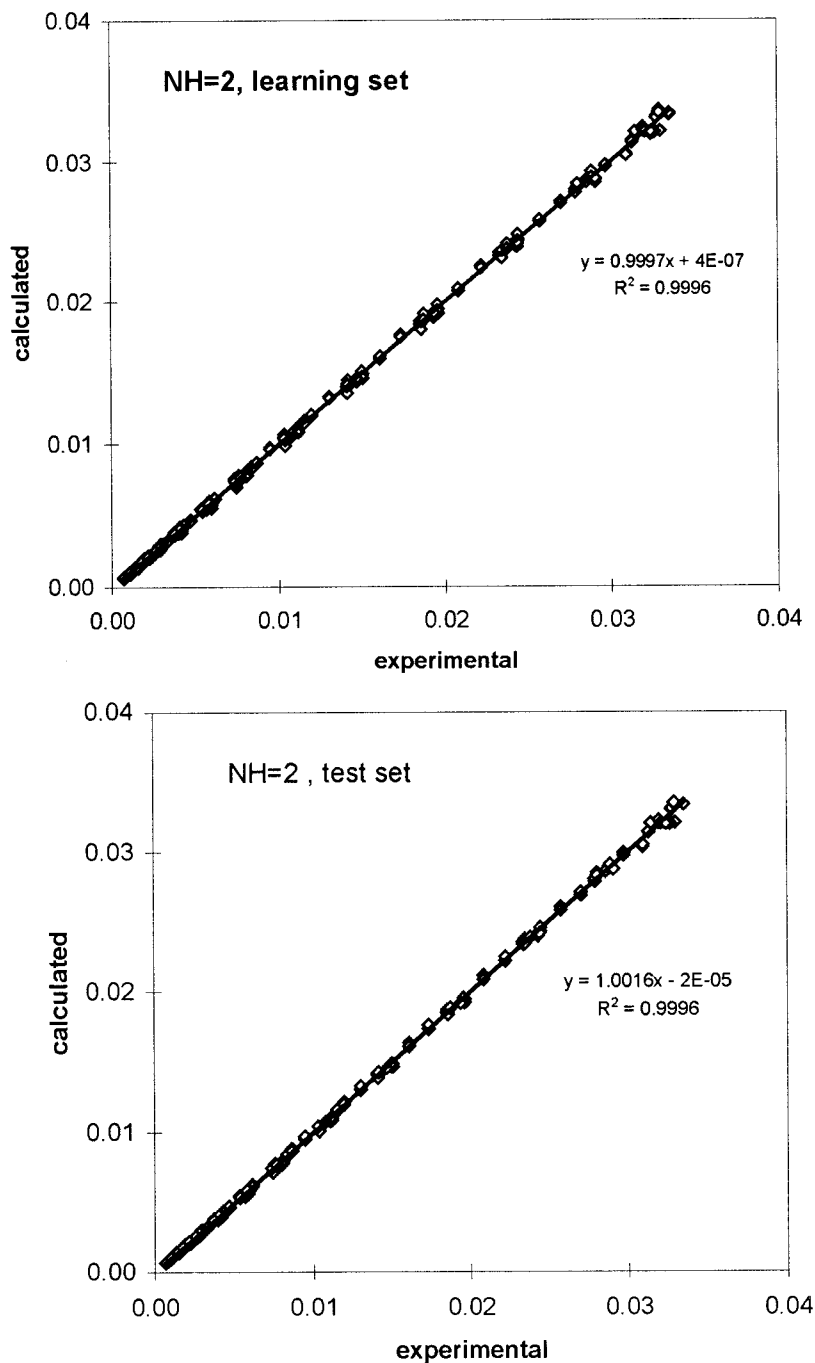


Figure 5 Comparison between experimental and calculated values of $w(\log MW)$, the weight fraction of polymer at each specified molecular weight, for the learning set and for the test set.

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NOTATION

E quadratic deviation between the experimental and predicted values
 $F(M, t)$ relaxation function

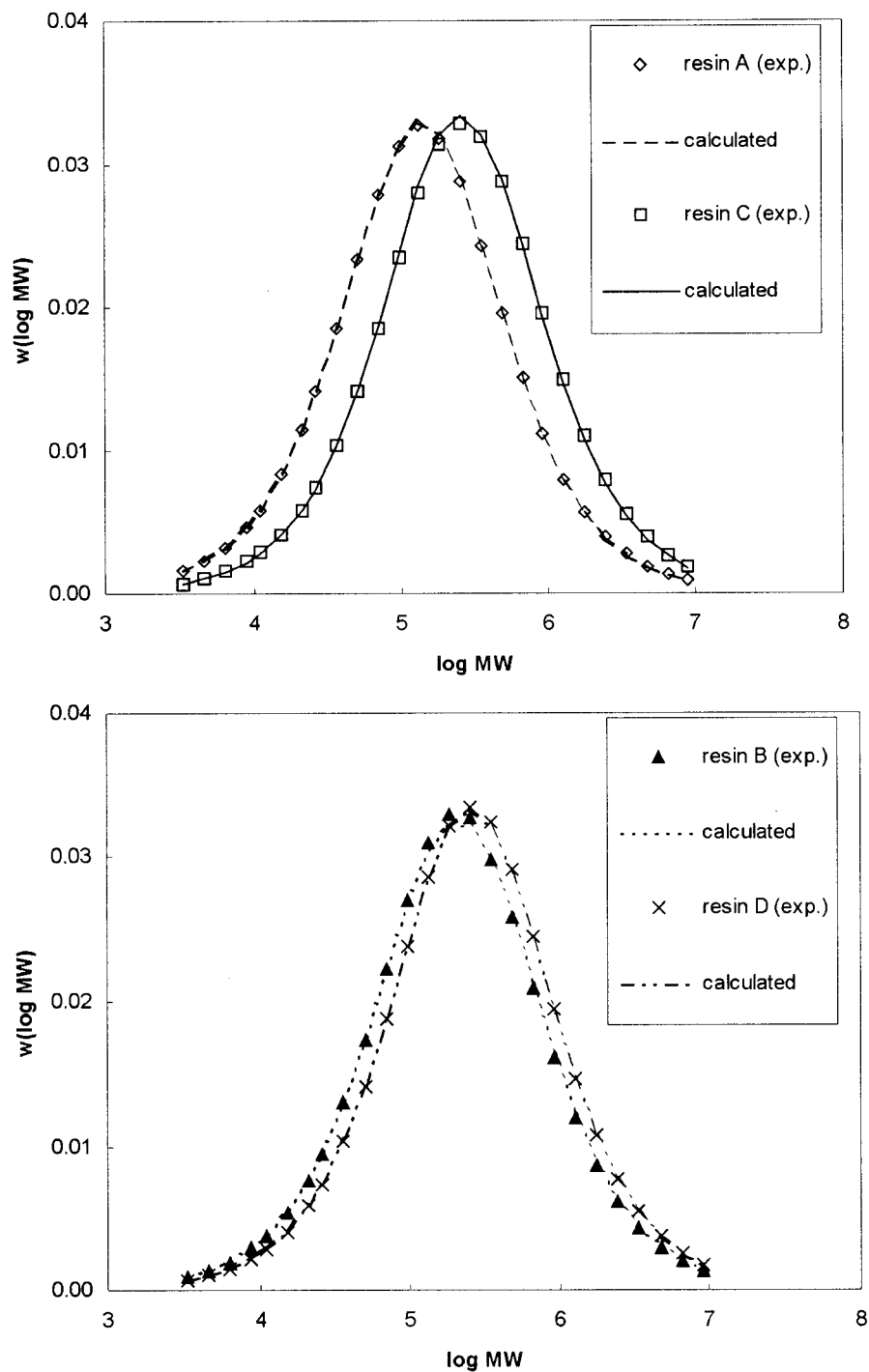


Figure 6 Comparison between experimental and calculated MWD curves for the test set.

$G'(\omega)$	shear storage modulus	NH	number of neurons in the hidden layer
$G''(\omega)$	shear loss modulus	O_k	output variable of the neuron k of the output layer
$G(t)$	relaxation modulus		
G_N^0	plateau modulus	O_j	output variable of the neuron j of the hidden layer
J_e^0	equilibrium compliance	P	number of output variables
N	number of input variables		

r	number of experimental data (input–output pairs) used in the training
S_k	weighted sum of the inputs to the neuron k in the output layer
S_j	weighted sum of the inputs to the neuron j in the hidden layer
Y_k	experimental values for the output variable k
X_i	input variable I of the neural network
x	dummy variable
w_i	weight fraction of polymer chains with molecular weight M_i
$W_{i,j}$	neural network weights
$W_{j,k}$	

Greek Letters

τ	relaxation time
α	a constant (= 0.56)
$\eta_0(M)$	zero-shear viscosity of a monodisperse polymer of molecular weight M

Superscripts

(m)	point in learning set
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