Determination of Tacticity in Polypropylene by FTIR with Multivariate Calibration

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ABSTRACT: A method for determination of tacticity in polypropylene (PP) using FTIR associated with multivariate analysis is presented. Blends of PP with known tacticity were prepared with isotactic, syndiotactic, and atactic polymer and analyzed by ^{13}C-NMR. The FTIR spectra were recorded and processed through principal components regression (PCR) and partial least-squares regression (PLS), using information from several different portions of the spectra. The method was compared with the classical methods of tacticity determination by FTIR based on the intensities of the bands at 998 cm^{-1} (isotactic), 868 cm^{-1} (syndiotactic), and 975 cm^{-1} (internal standard), which are known to be dependent on the crystallinity of the polymer and, thus, affected by temperature and sample preparation. The models obtained with multivariate calibration, both with PCR and PLS, gave prediction errors up to fivefold smaller than that of the classical methods, and were also shown not to be heavily dependent on the bands that are affected by the crystallinity of the polymer, but rather on the methyl and methylene bendings at 1375 and 1462 cm^{-1}. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 734–745, 2002

Key words: polypropylene; isotactic; syndiotactic; FTIR; multivariate calibration

INTRODUCTION

Polypropylene (PP) is one of the most widely used materials in formulations, especially in the automotive industry, because of its chemical resistance, high melting point, good dimensional stability, and high tenacity at room temperature. These properties are related to the crystallinity of the polymer, which depends on its tacticity. PP has three possible stereochemical configurations: isotactic (i-PP, with all methyls on the same side of the chain), syndiotactic (s-PP, with methyls on alternating sides of the chain), and atactic (a-PP, without any regular order).

Determination of tacticity in PP is usually carried out by three methods: extraction of the atactic polymer, ^{13}C-NMR,[1] and FTIR spectroscopy,[2–4] the most commonly used of which is extraction with hydrocarbons. This method is based on the fact that highly crystalline i-PP is insoluble in boiling *n*-heptane, whereas the atactic polymer is soluble. In spite of the low cost, extraction with hydrocarbons is time consuming and subject to errors. Small chains of isotactic polymer are also soluble and would be quantified as atactic frac-

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tions. Furthermore, fractions of a-PP inserted in an isotactic chain, which is not soluble, would be measured as isotactic polymer. In ^{13}C-NMR, the chemical shift of the methyl signal is related to the configuration of the neighboring methyl groups. Zambelli and Ammendola[5] showed that, with 300-MHz equipment, it is possible to observe 10 distinct peaks in the 20–22 ppm region of the proton-decoupled spectrum, which can be related to the methyl resonance being affected by the two nearest neighbors on each side (thus making it possible to observe pentad arrangements). This method is the most exact, although it is expensive and difficult to carry out, given that the analyses are made at high temperature (125–135°C) and typically take hours to be completed. The other method is FTIR, which uses the ratio of the intensities of some bands,[6,7] usually at 998 cm^{-1} (related to the α-helix conformation of the isotactic chain)[2] and 868 cm^{-1} (related to the double helices[8] of the syndiotactic chain),[3] to the band at 975 cm^{-1}, to build a calibration curve. Although easy and quick, the method is not always exact because of the weak intensity of the bands used, which can have great variation in the presence of contaminants. This work describes a method to determine the tacticity of PP by FTIR with *multivariate analysis,* using information from several portions of the spectra to obtain more reliable results.

MULTIVARIATE ANALYSIS

Multivariate analysis is a set of mathematical tools designed to treat large amounts of data, usually including tens or hundreds of measurements for each sample, to take advantage of the large quantities of information extracted through instrumental analysis. Among these techniques, factor analysis, which includes principal components analysis or regression (PCA and PCR, respectively) and partial least-squares regression (PLS), has been extensively applied in several studies to obtain regression models from IR, UV–Vis, NMR, and other spectra.[9–12] Explanation of multivariate analysis and the involved math and statistics can be found in the works of Kowalski et al.[13–15]

In multivariate analysis, to predict the values of dependent variables **Y**, which are linearly related to sets of measurements x_j (j = 1, 2, 3,. . ., m), it is necessary to build a calibration model similar to the one used in univariate calibration, called *multivariate linear regression* (MLR):

$$\mathbf{Y} = \mathbf{X}\boldsymbol{\beta} + \mathbf{E} \tag{1}$$

where **Y** is the matrix of dependent values (e.g., isotacticity), **X** is a matrix with the sets of measurements (e.g., intensity of absorption at each wavelength) in its rows, $\boldsymbol{\beta}$ is a matrix with the regression coefficients in its columns, and **E** is the error matrix. The matrix of regression coefficients $\boldsymbol{\beta}$ is found by minimizing the error matrix with a least-squares criterion, and can be calculated by simple matrix algebra[13]:

$$\boldsymbol{\beta} = (\mathbf{X}^T\mathbf{X})^{-1}\mathbf{X}^T\mathbf{Y} \tag{2}$$

However, MLR has some practical problems: because of mathematic properties, the inversion of the $\mathbf{X}^T\mathbf{X}$ matrix does not yield good results if **X** has more columns than lines. Thus, using a spectra with 1000 different wavelengths it would be necessary to prepare at least 1000 samples to build the model.[13] Furthermore, if the columns are highly correlated, as is the case in most spectroscopic data, matrix inversion will also not be possible.[16] Therefore, a method must be used to reduce the amount of data to a few measurements with low correlation. The usual choice to avoid having to choose and discard data is factor analysis (PCR or PLS).[17]

Factor analysis is basically a decomposition of **X** into a new set of coordinates described by linear combinations of the original independent variables, obtaining a "projection" of the data in a set of a few orthogonal axes—the principal components (PC)—containing all the significant information from the original data. This information can be used to build the calibration model.[13,14] PCR uses principal components analysis to decompose **X** into two other matrices:

$$\mathbf{X} = \mathbf{T}\mathbf{L}^T + \mathbf{E} \tag{3}$$

called the *scores* (T) and *loadings* (L) of **X**. The columns of **L** are the principal components (PC) of the model and the columns of **T** are the coordinates of the original data in this new set of axes. These matrices are built so that their columns are orthogonal vectors and the first columns always contain more information than the last ones, which usually contain only measurement noise, and may be discarded.

PLS modeling is similar to PCR, but decomposes both **X** and **Y** data, using the columns in **Y** to estimate the factors in **X** and vice versa:

$$\mathbf{X} = \mathbf{TL}^T + \mathbf{E} \quad (4)$$

$$\mathbf{Y} = \mathbf{UQ}^T + \mathbf{F} \quad (5)$$

The new matrices are not as good as the PCR scores and loadings to describe the original data because they are influenced by the correlation between the **X** and **Y** matrices. However, because of this influence, the first principal components contain more correlated information and so they are better for the construction of calibration models. Thus, PLS often requires fewer principal components than PCR for multivariate calibration.[14,18]

Validation

A multivariate model must also be tested to verify its precision, by using an independent set of samples with known properties (e.g., tacticity), which are submitted to prediction by the model, allowing the determination of the prediction error. However, a separate set of samples is not always available. Thus it is common to use a method of validation with the same samples used in calibration, known as *cross-validation.*[19] This works by removing some samples from the calibration set, building a regression model with the remaining ones, then using the excluded samples for validation. The process is repeated several times, each time taking out different samples, until all of them were used for validation. The standard error of cross-validation (root mean square of the prediction errors obtained by this method) is a good estimate of the standard error of prediction.

EXPERIMENTAL

Materials

Isotactic polypropylene (i-PP) was obtained from commercially available samples supplied by PPH (Triunfo, RS, Brazil). Atactic polypropylene (a-PP) was obtained through extraction with boiling *n*-heptane from a batch of polymer prepared in our laboratory by polymerization with a $TiCl_4$/$AlEt_3$ catalyst.[20] Syndiotactic polypropylene (s-PP), which was produced by polymerization with a chiral metallocene catalyst, was donated by Dr. Márcio Nele de Souza (Universidade Federal do Rio de Janeiro, COPPE, Programa de Engenharia Química, Rio de Janeiro, Brazil). Polyethylene (PE) used in the blends was produced in our laboratory with a zirconocene/methylaluminoxane catalyst.[21]

^{13}C-NMR

The polymers used to make the blends were analyzed by ^{13}C-NMR to determine their exact tacticities. Polymer (500 mg) and chromium acetylacetonate (30 mg) were dissolved in 3.0 mL of 1,2,4-trichlorobenzene (TCB) maintained at 135°C for 24 h, under an argon atmosphere, in a 10-mm

Table I Compositions of the Blends Used in Calibration (1–27) and External Validation (A1–D3)

Sample	i-PP Fraction	s-PP Fraction	Total PP Fraction	Isotacticity (i-PP/total PP)	Syndiotacticity (s-PP/total PP)
1–3	0.293	0.041	0.521	0.562	0.079
4–6	0.045	0.275	0.518	0.087	0.530
7–9	0.181	0.153	0.507	0.357	0.302
10–12	0.392	0.021	0.508	0.772	0.041
13–15	0.019	0.420	0.546	0.035	0.770
16–18	0.203	0.198	0.494	0.411	0.401
19–21	0.246	0.235	0.499	0.493	0.472
22–24	0.000	0.482	0.518	0.000	0.930
25–27	0.494	0.000	0.494	1.000	0.000
A1–A3	0.108	0.240	0.496	0.217	0.483
B1–B3	0.265	0.105	0.501	0.529	0.209
C1–C3	0.120	0.312	0.504	0.238	0.618
D1–D3	0.317	0.104	0.472	0.670	0.221

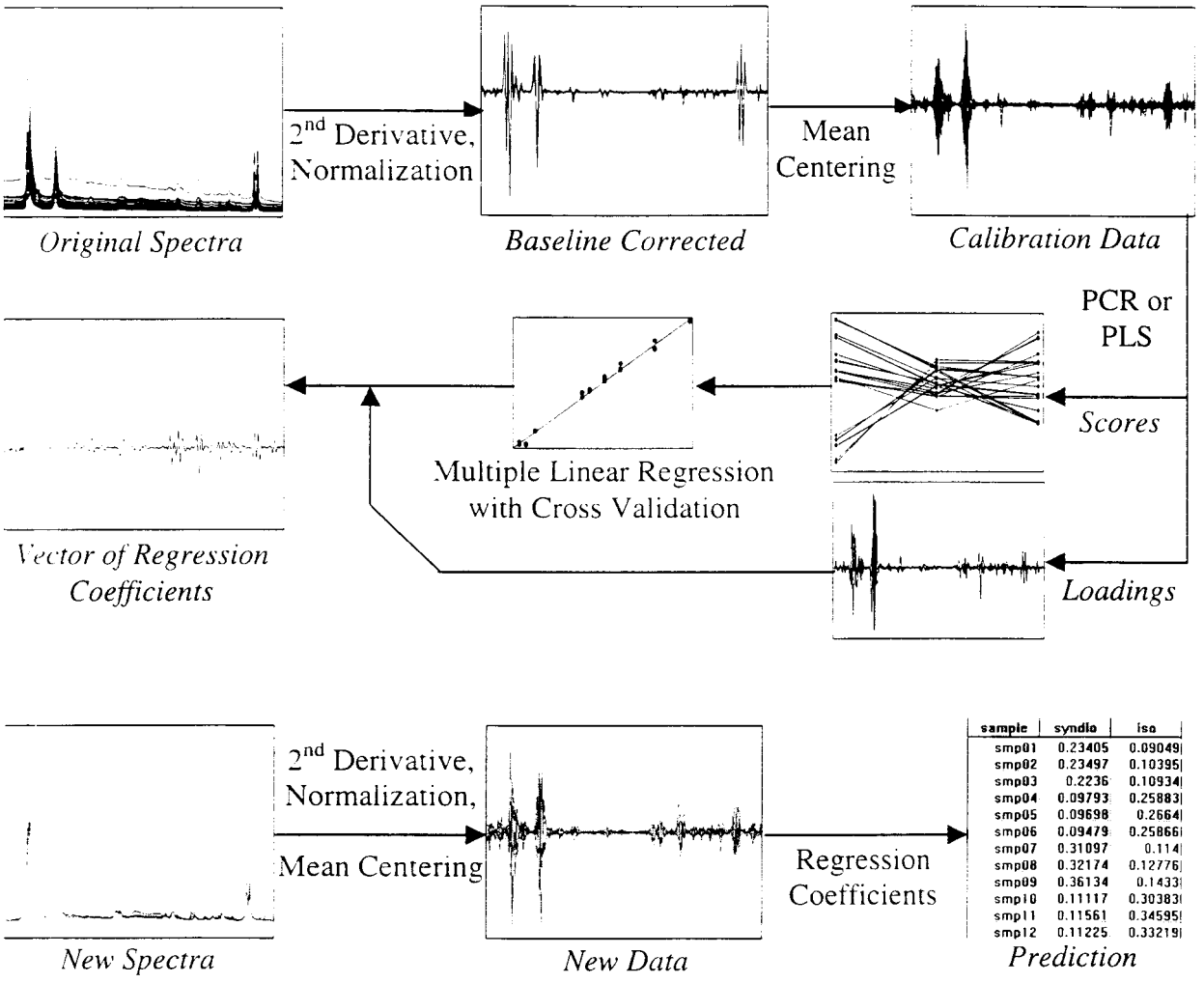

Figure 1 Schematics of multivariate calibration with factor-based analysis for the FTIR data.

NMR tube. The samples were then analyzed on a 500-MHz Bruker equipment (Bruker Instruments, Billerica, MA) at 125°C with 10-s relaxation time and 400 signal accumulations.

FTIR

A 20-mg sample of a mixture of the polymers in the appropriate proportions and 20 mg of polyethylene were dissolved under argon atmosphere, in a system previously purged for 30 min, in 3 mL of tetrachloroethylene at 110°C, with the minimum heating time possible. Ten drops of this solution were dripped onto a KBr tablet and the solvent was vacuum-dried overnight, giving a thin film of the PP–PE blend. Table I gives the composition of each sample prepared. The infrared spectra of the samples were obtained with a Bomem MB-100 Series equipment, in the range of 4000 to 400 cm^{-1}, with 4 cm^{-1} resolution and 16 signal accumulations, automatic signal gain, and cosine apodization.

Data Treatment

Only the 1550–640 cm^{-1} region of the spectra was used for calibration, given that, in many samples, the bands between 3030 and 2760 cm^{-1} were saturated. Before calibration, data were submitted to pretreatment, as shown in Figure 1: Savitsky–Golay second derivatives[22] of the spectra were taken, with a window width of 7 points, to correct the baseline drift; normalization was done to compensate differences in intensities of the spectra.[23] Data were also mean centered.[23] PCR and PLS models were built using the soft-

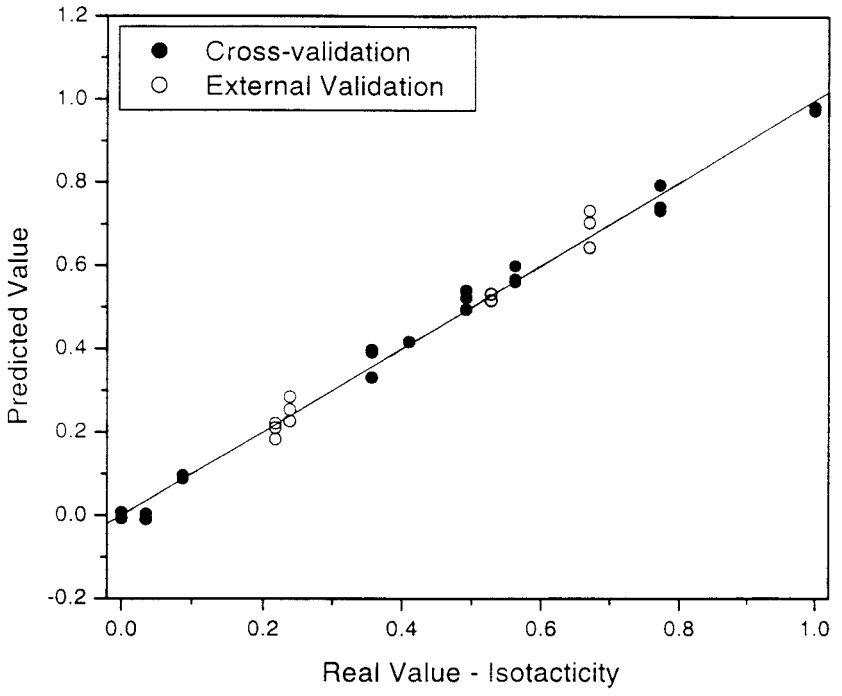

Figure 2 Predicted versus real values for isotacticity, calculated by PCR with 4 PC.

ware Pirouette 2.02 (Infometrix Inc.), choosing the best number of principal components by leave-one-out cross-validation.[23] All calibrations were done with respect to isotactic and syndiotactic PP content in the blends because these are the values proportional to the intensities of the bands in the spectra, and then divided by the PP fraction in each blend to yield PP tacticity values. The optimal number of principal components was chosen by leave-one-out cross-validation. Prediction errors were estimated using a set of independent samples of known tacticity.

RESULTS AND DISCUSSION

Nine blends of different compositions were used to build the regression model. Samples were prepared in triplicate, giving a total of 27 calibration points. Because of its high crystallinity, PP alone would not give films with enough transparency when deposited from the tetrachloroethylene solution. To increase the transparency, the PP samples were blended with polyethylene, which was chosen because it has only a few bands that overlap with PP in the 1500–600 cm^{-1} region.

Several models were tested, calculating the standard error of cross-validation, both with PCR and PLS. The optimal number of principal components (PC) was chosen by cross-validation of the different models. The best models obtained used 4 PC for PCR and 3 PC for PLS, both for isotacticity and syndiotacticity. However, standard errors of cross-validation can provide a somewhat optimistic value of real prediction errors. To have more realistic estimates, standard errors of prediction for an independent set of samples were measured (external validation). Cross-validation and external validation were also applied to the classical FTIR calibration methods,[2,3] to compare the prediction errors and correlation coefficients.

Figures 2 and 3 show the plots of predicted value versus real value of the PCR and PLS models for isotacticity, for both cross-validation and external validation. It can be seen that, although both models give good precision and accuracy, PLS uses one less principal component. As an example, for samples B1–B3 (isotacticity 0.529), PCR predicted 0.516, 0.532, and 0.516; and PLS predicted 0.517, 0.529, and 0.513, respectively.

Figure 4 shows the same results for the univariate regression. Comparing this figure with the earlier ones, it is possible to see that the prediction errors for the multivariate methods are significantly lower than those for the univariate

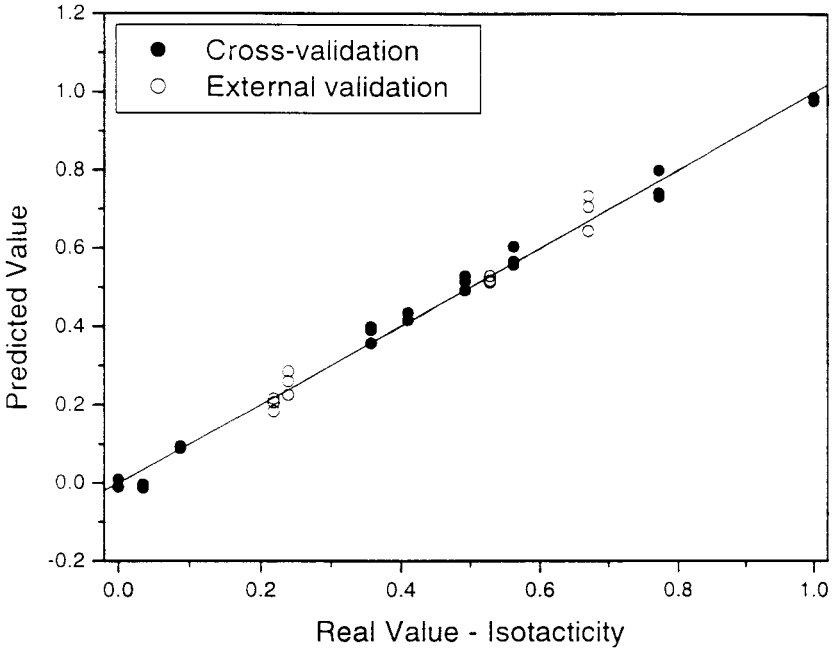

Figure 3 Predicted versus real values for isotacticity, calculated by PLS with 3 PC.

method. Also, the univariate method shows poor reproducibility in the replicates and false values are obtained for some samples: For the same samples B1–B3, the classical method gave predictions of 0.570, 0.754, and 0.582. The poor reproducibility of the univariate model can be attributed to the low intensity of the bands used for calibration, which can be easily obscured by interference. These bands are also heavily dependent on the crystallinity of the polymer[7] and can be affected

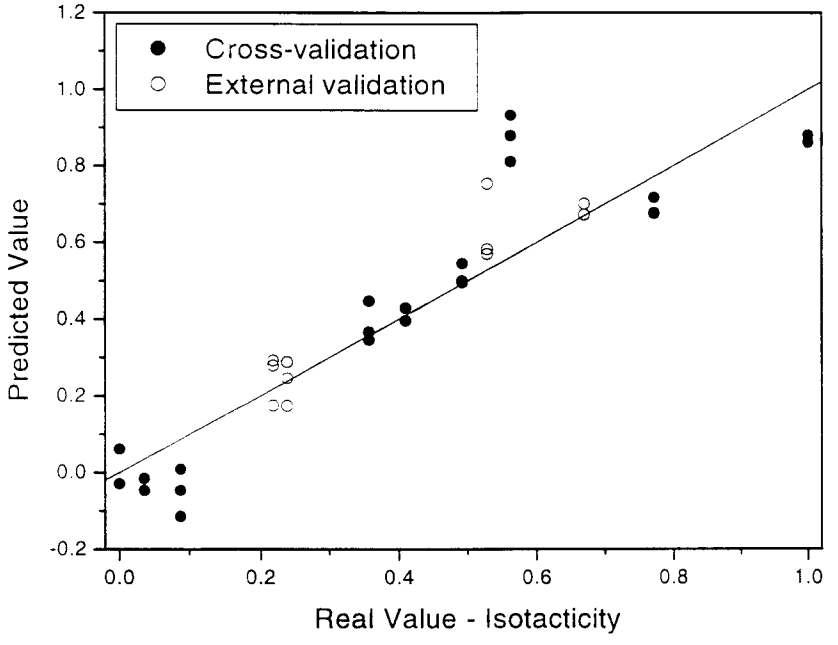

Figure 4 Predicted versus real values for isotacticity, calculated by linear regression with the ratio of the bands at 998 and 972 cm^{-1}.

Table II Standard Prediction Errors and Correlation Coefficients for Determination of Isotacticity with Univariate and Multivariate Calibration

	PCR (4 PC)	PLS (3 PC)	Univariate Calibration
Standard error			
Cross-validation	0.025	0.025	0.139
External validation	0.029	0.030	0.078
Correlation coefficient (r)	0.998	0.998	0.928

by sample preparation. The multivariate model, as will be seen later, does not primarily rely on these bands, and thus is less affected by these factors. Table II summarizes the prediction errors for both methods. The classical method shows a cross-validation error of 0.139, more than fivefold higher than the 0.025 obtained with PCR and PLS. With external validation this difference decreases to twofold higher, though it is still larger.

Industrial production of s-PP is relatively new, so its characterization is much less studied. Therefore, we repeated the same procedure to also evaluate syndiotacticity, comparing multivariate and classical methods. The results are shown in Figures 5, 6, and 7. PCR and PLS gave smaller prediction errors than did classical methods, as can be seen in the case of samples A1–A3 (0.483 syndiotacticity): the values predicted in the three replicates were 0.472, 0.473, and 0.450 for PCR and 0.471, 0.476, and 0.454 for PLS, whereas the classical model was again less accurate and reproducible, giving syndiotacticities of 0.635, 0.582, and 0.423. Table III summarizes the standard errors for both methods. The results are similar to the isotacticity determination as the cross-validation error was fivefold higher in the classical method than that in PCR and PLS and the external validation error was fourfold higher. Once again, the predictions obtained by PCR and PLS match closely, even with PLS using one less PC. As shown below, both models use basically the same information from the spectra. The univariate method of syndiotacticity determination by FTIR also uses bands that are basically dependent on the crystallinity of the sample, which leads to calibration curves that are much less reliable than those of multivariate regressions.

The PCR and PLS models are much more robust than the univariate regressions. How-

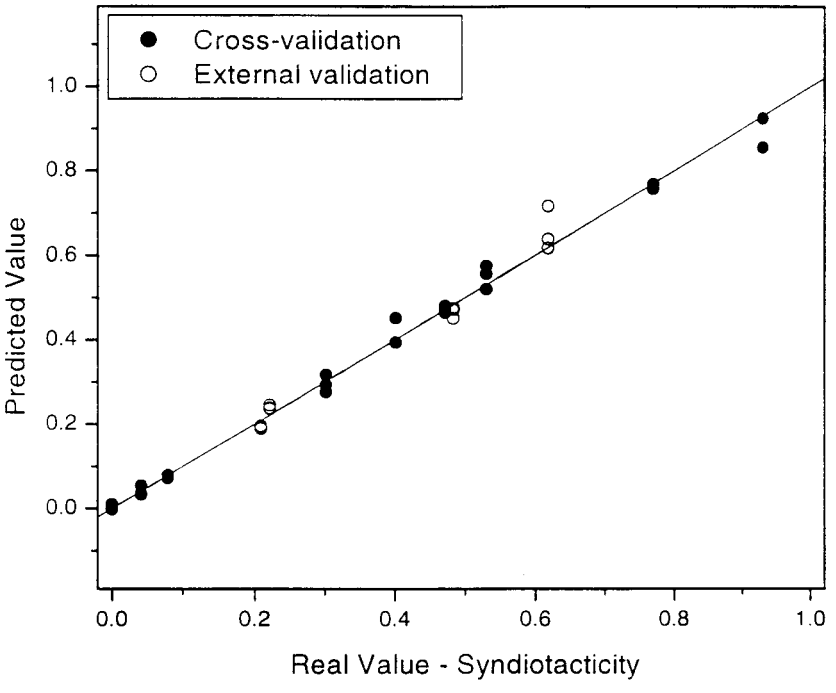

Figure 5 Predicted versus real values for syndiotacticity, calculated by PCR with 4 PC.

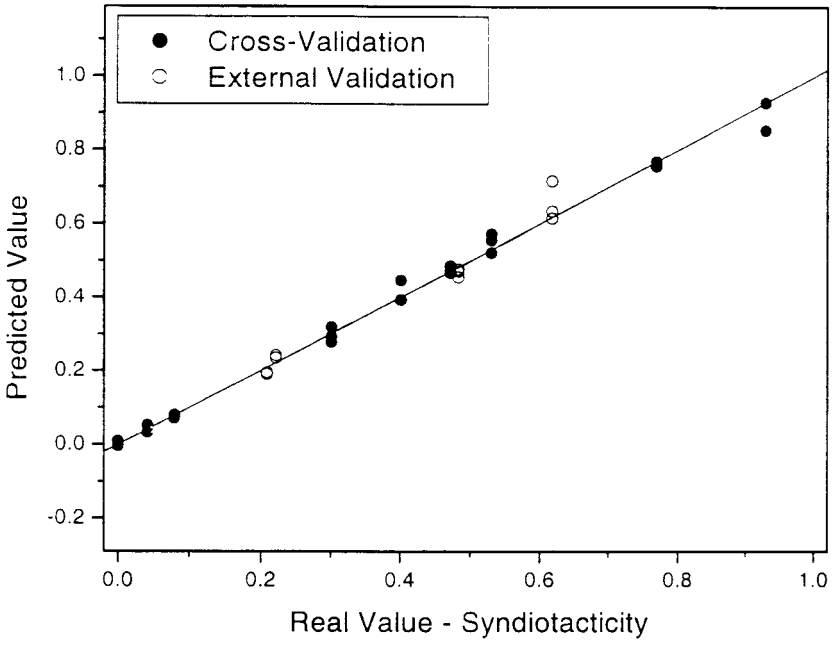

Figure 6 Predicted versus real values for syndiotacticity, calculated by PLS with 3 PC.

ever, it was observed during the first sample preparations that they can also be significantly affected by the presence of anomalous bands in the spectra. Some of the first samples of our study, prepared using longer heating times, had intense bands in the 1240–1280, 1150–990, and 840–760 cm^{-1} regions, as shown in Figure 8, which led not only to loss of reproducibility in the models but also, sometimes, to false results. These bands are thought to be from oligomers

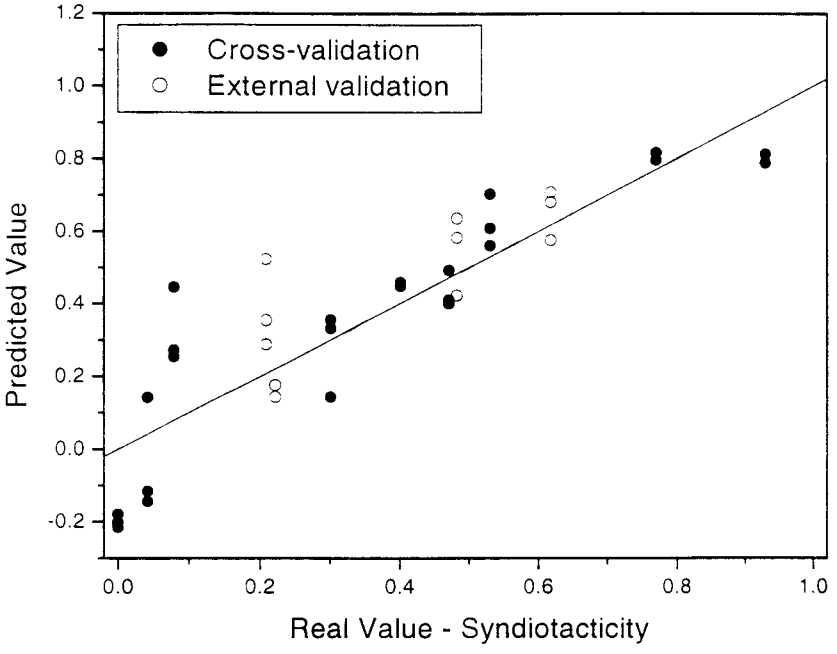

Figure 7 Predicted versus real values for syndiotacticity, calculated by linear regression with the ratio of the bands at 868 and 972 cm^{-1}.

Table III Standard Prediction Errors and Correlation Coefficients for Determination of Syndiotacticity with Univariate and Multivariate Calibration

	PCR (4 PC)	PLS (3 PC)	Univariate Calibration
Standard error			
Cross-validation	0.023	0.023	0.145
External validation	0.033	0.032	0.126
Correlation coefficient (r)	0.999	0.999	0.910

formed by thermal cleavage of the PP skeleton[24]; thus those samples had to be discarded and sample preparation had to be redesigned to reduce heating time to a minimum and to be carried out in an inert atmosphere. When the intensities of these bands are lessened, they have very little interference on the multivariate models (but continue to affect the classical ones). In fact, an attempt to improve the model by removing from the calibration data the regions affected by the anomalous bands did not give any better results, with standard errors of validation of 0.027 for isotacticity and 0.023 for syndiotactic fraction, using PLS and 3 PC, equal to that obtained previously. It was necessary to discover whether the anomalous bands were interfering in the bands that were most important for the models, thus making them less reliable.

The regression vectors, presented in Figure 9 for PCR and in Figure 10 for PLS, show that the most important absorption for both multivariate models corresponds to the bending of the methyl side chains (around 1375 cm^{-1}). This band is very strong in the spectra of these polymers, being less prone to interference from contaminants in the sample and independent of the polymer crystallinity. Another important region corresponds to the bending of the methylene groups, which is around 1462 cm^{-1}, that is also a strong band and independent of crystallinity. It is interesting to note that this region is partially overlapped with PE bands, though the model can still extract information from it. Thus, anomalous bands from thermal decomposition do not obscure any region of high importance to the models. It is thought that the errors caused by these bands come from interference in the normalization of the spectra, attributable to their large area. Comparing both figures also shows that PCR and PLS give very similar regression vectors, which explains the similar results in the validations. Surprisingly, the multivariate models show a slight

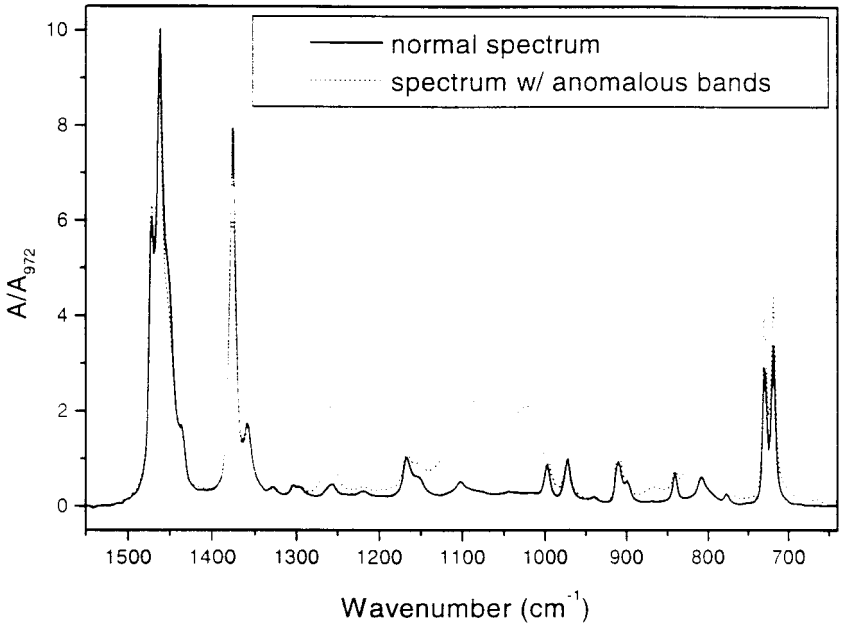

Figure 8 Spectra of two samples of PP–PE blends, one of which presents anomalous bands attributed to the presence of oligomers.

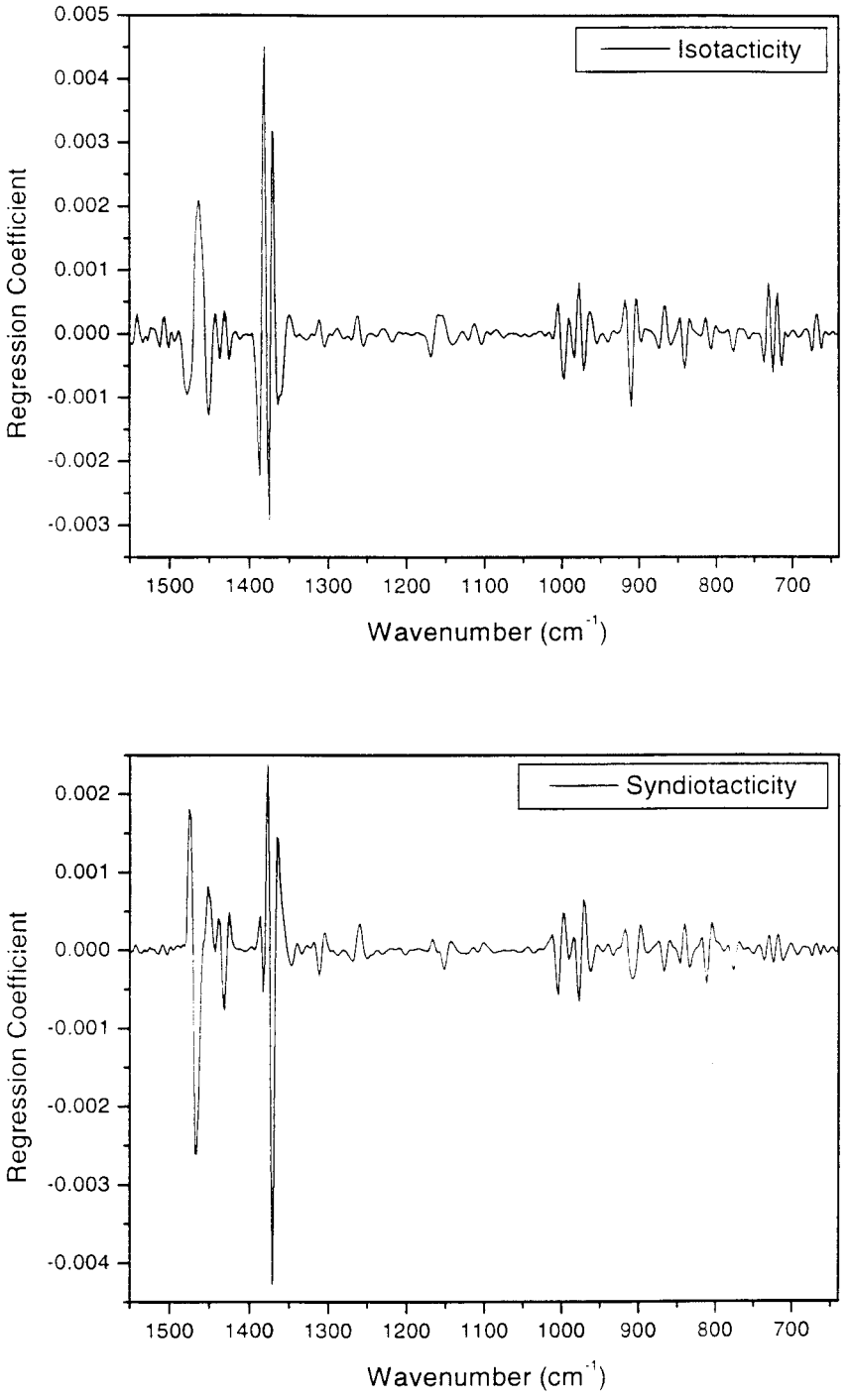

Figure 9 Regression vectors for the isotactic and syndiotactic PCR models.

contribution from the bands at 719 and 730 cm^{-1}, which are characteristic of methylene rocking in polyethylene, perhaps the result of data normalization, that could transfer variance from the intense bands to other regions of the spectra.

CONCLUSIONS

Polypropylene tacticity can be determined by FTIR with the application of the multivariate techniques, principal components regression (PCR) and partial least-squares regression (PLS).

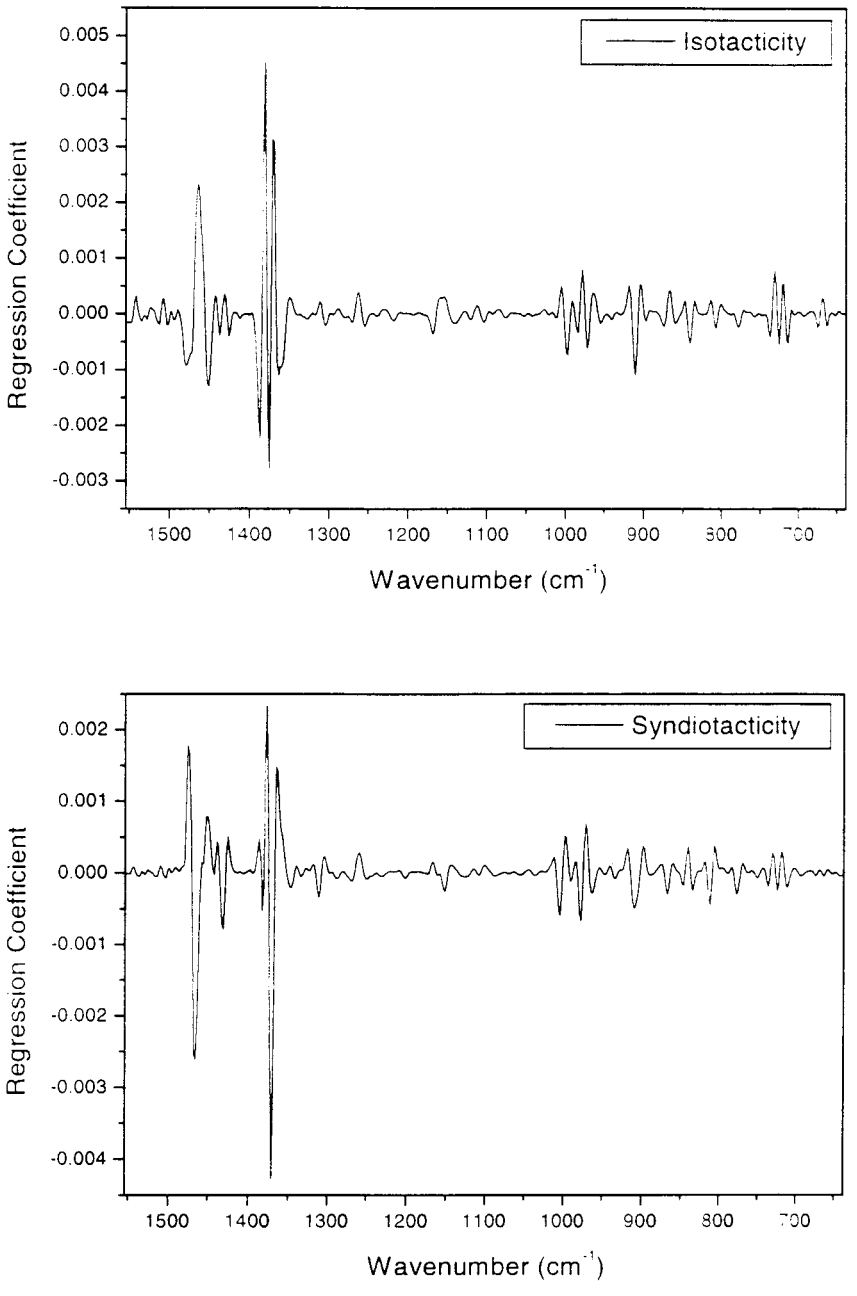

Figure 10 Regression vectors for the isotactic and syndiotactic PLS models.

These techniques give lower prediction errors than those given by classical univariate calibration and show a greater reliability, with less probability of prediction errors resulting from interferences in the spectra. The results obtained with PLS and PCR are very close, although PLS uses one less principal component. The regression vectors show that both models rely on the methyl and methylene bending bands, which are strong and unaffected by temperature or sample preparation; however, excessive thermal degradation of the polymer during sample preparation can generate bands that significantly hamper the results. This can be avoided by preparing the samples using a short heating time in an inert atmosphere.

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