Analysis of Polyolefin Compositions Through Near Infrared Spectroscopy

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ABSTRACT: In this work, NIRS is employed to provide compositions of α-olefin copolymers, allowing for evaluation of the effects of certain key process variables on the final NIR spectral responses of obtained polymer materials. This work also introduces a new temperature programmed analytical technique, which combines NIRS measurements with partial fractionation of α-olefin copolymers. The new proposed technique can be used for evaluation of polyolefin compositions, as presented here for poly(propene/1-butene) copolymers. Besides, preliminary results obtained from thermal fractionation experiments indicate that this new proposed experimental technique can be employed for characterization of comonomer sequence distributions of α-olefin copolymers. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40127.

INTRODUCTION

Near infrared spectroscopy (NIRS) has been widely used for analytical control and quality assurance in several applications, both in academia and in industry. For this reason, the field has been reviewed by different authors.[1–3]

NIR-based techniques present substantial advantages when compared to other conventional analytical techniques. For instance, NIR instruments can provide confident real-time information about the process behavior; NIR data can be obtained at high sampling rates; NIR technologies allow for simplification of process monitoring, minimization of sample handling steps and maximization of sample throughput; among other advantages. Consequently, NIR-based techniques provide opportunities for improvement of product quality and analyses of complexes samples, such as slurries and solid materials. For all these reasons, NIR-based technologies can lead to reduction of production costs and of time delays at plant site.[1]

Techniques based on the near infrared spectroscopy (NIRS) are extensively used for quantitative characterization of polymer properties, due to the fact that they are nondestructive and provide real-time structural and kinetic information with simple hardware and software tools. NIR spectroscopy can be used as a powerful tool in qualitative and quantitative polymer investigations. NIR spectroscopy has been employed for the *in situ* determination of structural and kinetic data of polymers.[4] Several properties, such as molar mass, monomer conversion, composition of latexes, bulk viscosity, residual monomer content, degree of crystallinity, color, average particle size, antibiotic content in pharmaceutical products, and chemical compositions have been determined by NIR spectroscopy.[5–22] Interesting polymer applications include real-time monitoring and control of particle size,[23,24] control of copolymer composition,[25] additive concentration and polymer bulk density[26,27] in suspension polymerizations; and detection of the formation of the core-shell structure[28] in suspension/emulsion polymerization processes, as a result of reflection, refraction and random scattering at the surface of the particles. In this case, the larger scattering/absorption ratios, usually regarded as a disadvantage for spectroscopic analyses, constitute a major advantage for analysis of the morphological characteristics of heterogeneous systems, as in usual polymerization reaction media.[1]

In recent years, de Faria Jr. et al. employed NIR-based techniques for the in-line process monitoring and control of bulk density (BD), cold plasticizer absorption (CPA), and the average particle diameter (Dp) of poly(vinyl chloride) microparticles during suspension polymerizations of vinyl chloride. It was shown that process variables such as the agitation speed and the
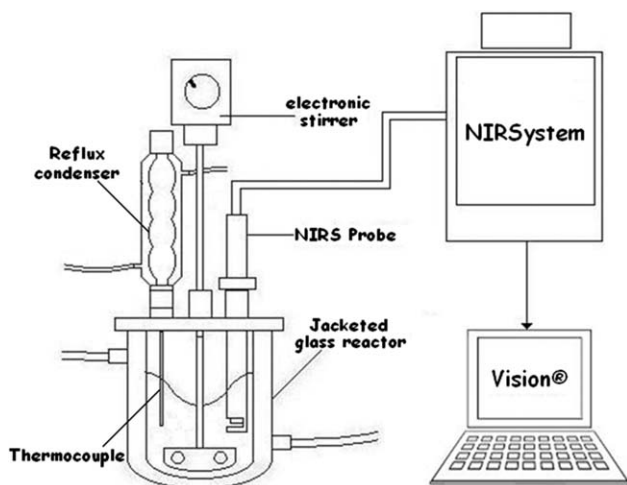
Figure 1. Scheme of the experimental setup used for fractionation experiments.

suspending agent concentration can be successfully manipulated to control the morphological properties (BD, CPA, and Dp) of the poly(vinyl chloride) particles by using NIRS-based model predictions as references.[26,27]

More recently, Pereira et al.[25] showed that NIRS can be used successfully to monitor monomer and copolymer compositions in vinyl acetate/acrylic acid suspension copolymerizations performed in batch. It was shown that calibration models based on the standard partial least squares (PLS) regression are useful for monitoring both the copolymer composition and the monomer concentration profiles during the batch reactions.

NIRS can also be used to monitor the morphology, the mechanical properties and the dispersion of fillers in polymer–clay nanocomposites prepared by melt-mixing using batch mixers or extruders.[29–32] Barbas and coauthors used NIRS for the in-line monitoring of polypropylene/montmorillonite clay nanocomposites, focusing on the characterization of the clay dispersion (agglomerated, intercalated or exfoliated, based upon the delamination degree of montmorillonite (MMT) layers, given by the wavelength shift of the vibrational spectroscopy spectra in two specific peaks located at 1050 and 1080 cm^{-1}) when the polymer–clay nanocomposites had been prepared in a batch mixer[29] and a twin screw extruder.[30] It was shown that NIRS predictions based on a PLS regression model were able to describe in real time the dynamic evolution of the clay dispersion in the process.

Fischer et al.[31] employed NIRS for the real time monitoring of morphological and mechanical properties of polyamide 6 (PA6)/MMT and polypropylene/MMT nanocomposites prepared by extrusion. The capacity of exfoliation of different modified MMT nanofillers was evaluated and associated to rheological and morphological properties of the final polymer–clay nanocomposites. According to the authors, it is possible to observe different degrees of exfoliation as a consequence of the extruder operating conditions.

In particular, the microstructure of polyolefins is normally evaluated with help of programmed temperature techniques, includ-

ing temperature rising elution fractionation (TREF), crystallization analysis fractionation (CRYSTAF), solid state and solution differential scanning calorimetry (DSC), and size exclusion chromatography (SEC). These techniques can provide information about chemical composition distributions (CCD), short chain branching (SCB), and long chain branching (LCB) distributions and molecular weight distributions (MWD) of semicrystalline polymer materials.[33–41]

For example, Albrecht et al.[42] evaluated the CCD of different ethylene-vinyl acetate (EVA) copolymers through CRYSTAF, TREF and high temperature interactive liquid chromatography (HT-HPLC). According to the authors, although all analyzed techniques are able to detect chemical composition heterogeneities in EVA copolymers, HT-HPLC provide more detailed information about the distribution of the chemical units and is faster than CRYSTAF and TREF. Despite that, the analytical time (including sampling, sample preparation and analysis) can be regarded as long for the three analyzed techniques, which can also be regarded as expensive and labor demanding.

Graef et al.[43] employed CRYSTAF, DSC, and SEC-FTIR (size exclusion chromatography coupled to a Fourier transfer infrared detector) for evaluation of chemical heterogeneity in ethylene copolymers. It was observed that the three analyzed techniques are appropriate for determination of chemical heterogeneity in ethylene copolymers containing 1-decene, 1-tetradecene, and 1-octadecene. Composition distributions of ethylene/1-olefin copolymers were also studied by Tso and DesLauriers[44] using TREF (equipped with three detectors, 3D-TREF) and SEC-FTIR. According to these authors, although both techniques are suitable for characterization of chemical distributions in ethylene copolymers, the use of 3D-TREF is more advantageous when the analyzed materials present similar molecular weight

Table I. Three-level Factorial Design for Evaluation of the Spectral Response to the Process Variables

Process variable	Level		
	Low (−1)	Intermediate (0)	High (+1)
Copolymer concentration (wt %)	0.5	1.0	1.5
Medium temperature (°C)	140	160	180

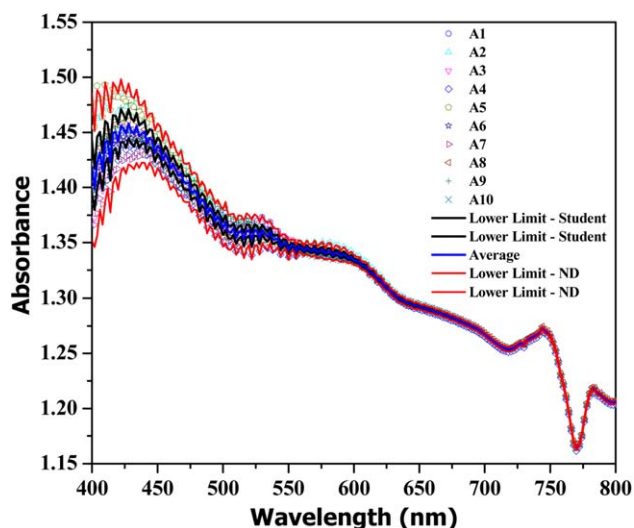| Run	Copolymer concentration	Medium temperature
1	−1	−1
2	−1	0
3	−1	+1
4	0	−1
5	0	0
6	0	+1
7	+1	−1
8	+1	0
9	+1	+1

Figure 2. NIRS Spectra of 0.5 wt % poly(propylene/1-butene) solution in the range of 400–800 nm (visible region). Spectra from A1 to A10 are replicas. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

distributions. Once again, it is important to emphasize that the analytical time (including sampling, sample preparation, and analysis) required by all analyzed techniques can be regarded as long and that the proposed analytical procedures can be regarded as expensive and labor demanding.

It can be generically agreed that programmed temperature techniques contribute with the enhanced understanding of the microstructural aspects of semicrystalline thermoplastic polymer chains. In spite of that, as usually recognized in the field, these analytical techniques can be regarded as time-consuming, expensive and require the implementation of complex fractionation apparatus, leading to costly equipment investments. In
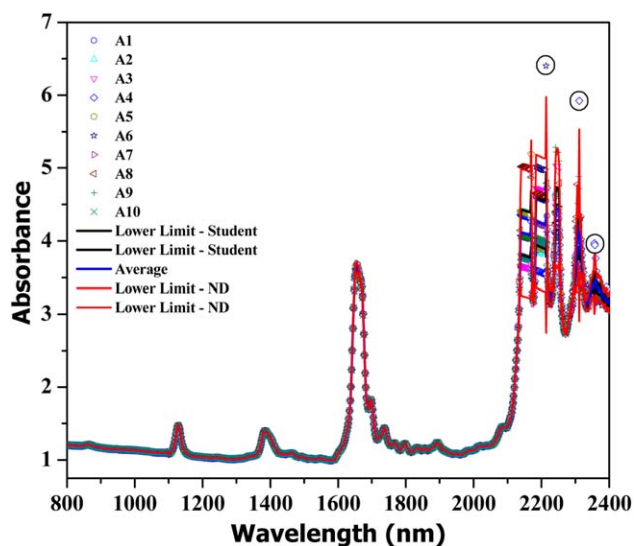

Figure 3. NIRS spectra of 0.5 wt % poly(propylene/1-butene) solution in the range of 800–2500 nm (near infrared region). Spectra from A1 to A10 are replicas. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
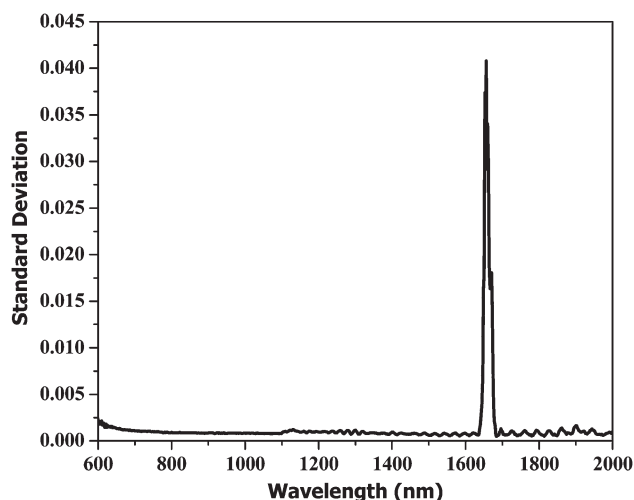

Figure 4. Standard deviation calculated at each particular wavelength.

comparison, NIRS can provide very fast characterization of polymer materials with relatively low costs. Therefore, the development of NIR-based progammed temperature techniques sounds appealing.

On the basis of the previous discussions, this article introduces a new NIR-based technique that can be used for identification of the composition of α-olefin copolymers. This new technique can be used successfully for fractionation and characterization of semicrystalline polymers, such as polyolefin resins based on ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, and other α-olefins. Analyses based on NIRS can present several advantages, when compared to analyses based on more traditional techniques, including CRYSTAF and TREF. For instance, there is no need to transfer the sample from the crystallization vessel to the sensor; the analytical time can be much shorter; the acquisition of experimental data is easier and well-established; it is possible to minimize sample handling and to reduce the investment in costly pieces of equipment. In
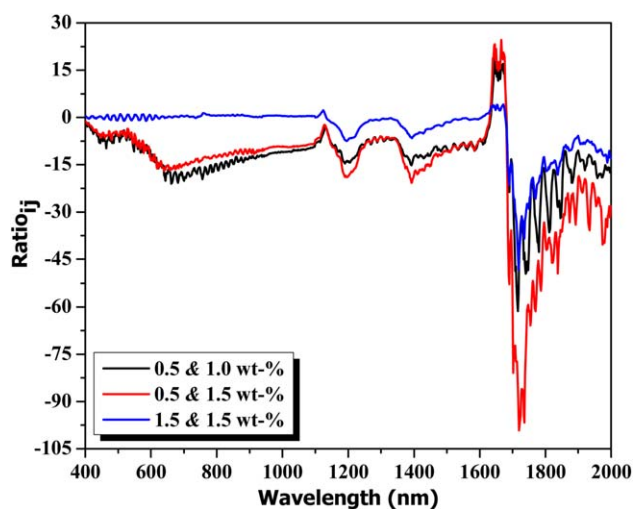

Figure 5. Spectral difference between poly(propylene/1-butene) solutions ranged from 0.5 to 1.5 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
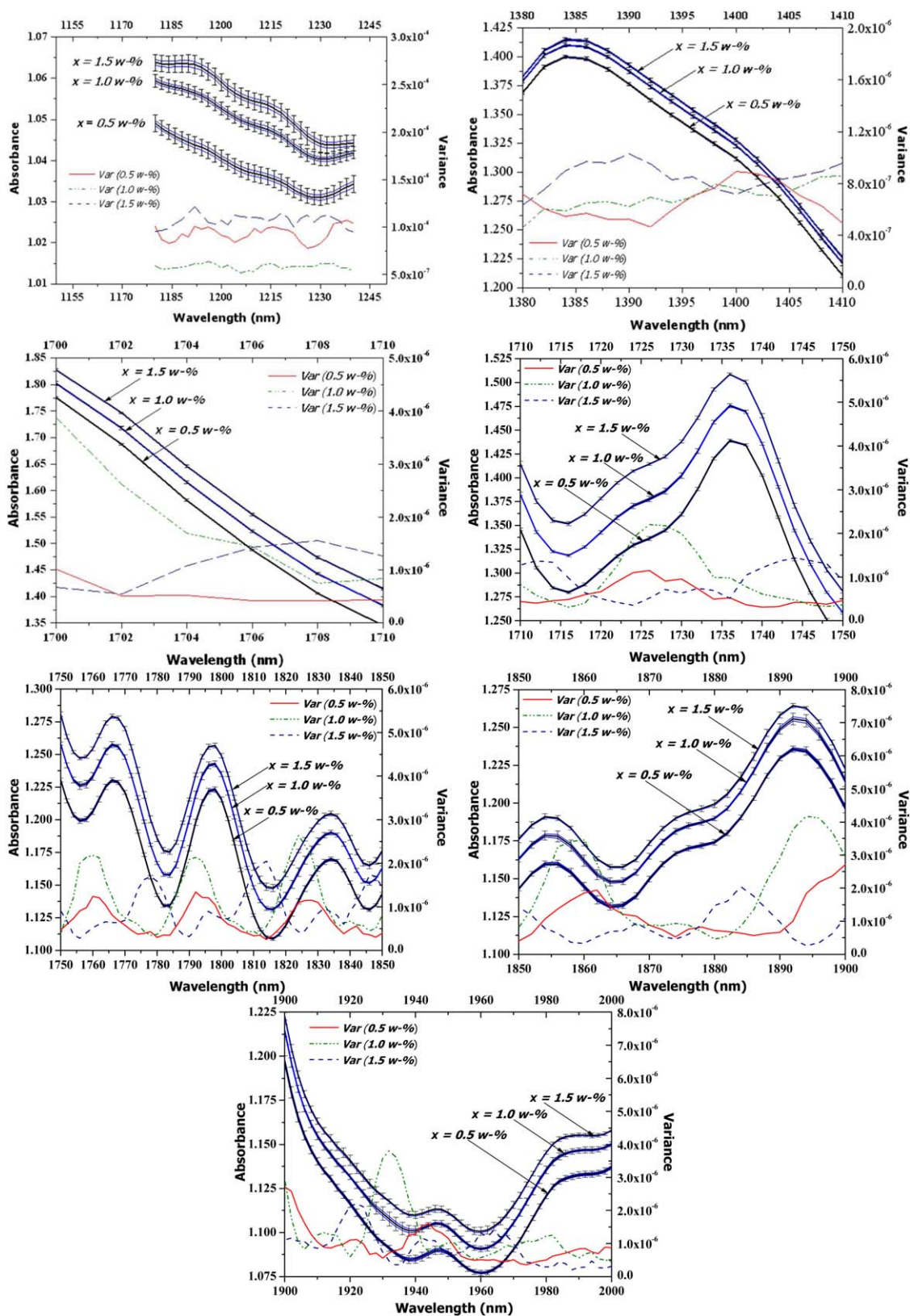
Figure 6. Analyses of mean and variance of absorbance at different wavelength for poly(propylene/1-butene) solutions ranged from 0.5 wt to 1.5 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
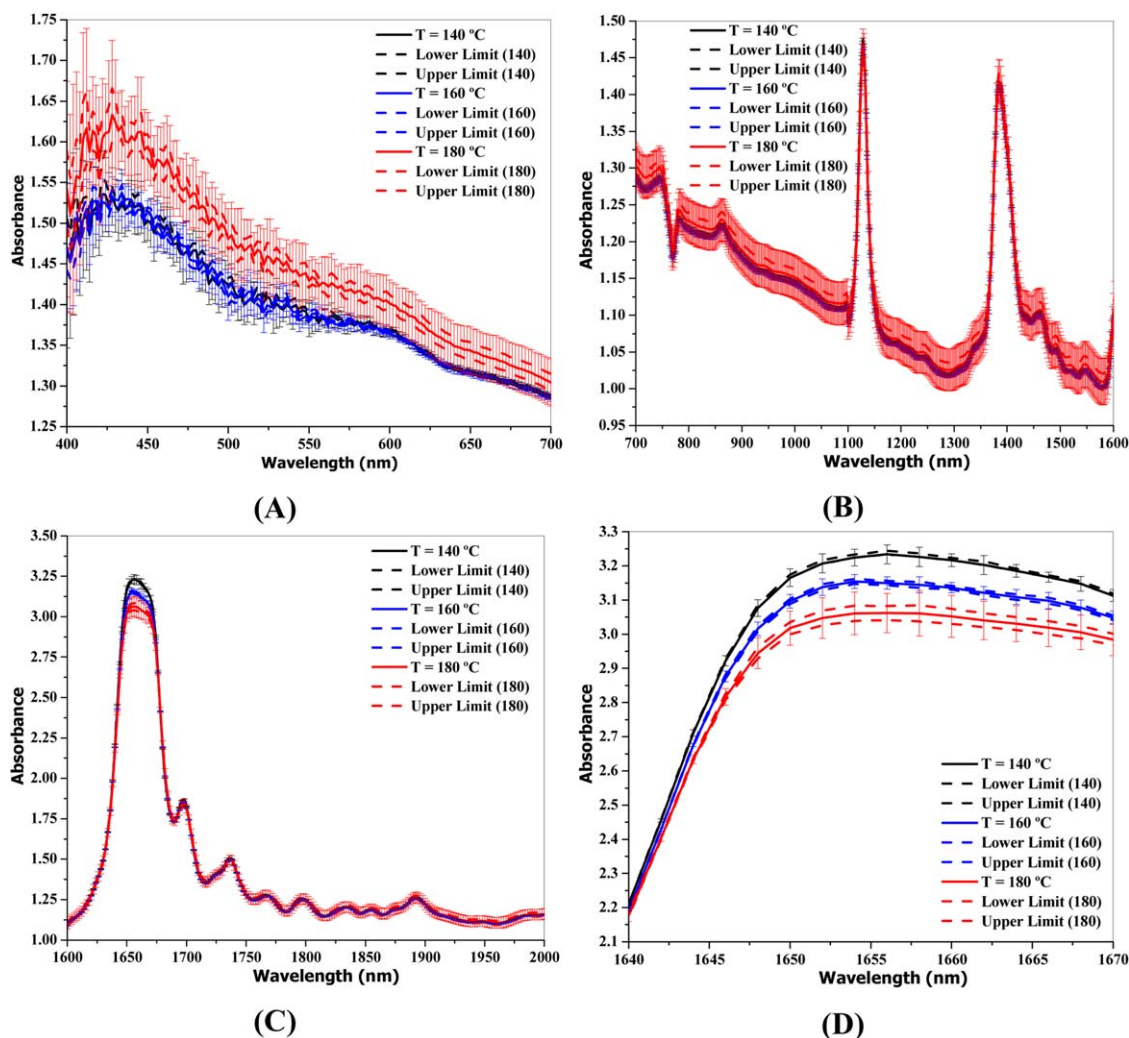
Figure 7. Effect of the temperature on the NIRS spectral response. Experiments carried out with 1.5 wt % poly(propylene/1-butene) solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

addition, combination of NIRS with programmed temperature analyses can eliminate the need for preparation of fractionation columns, preventing problems associated to fabrication, maintenance, and blocking of columns.

EXPERIMENTAL

Materials and Methods

Propylene with minimum purity of 99.5%, 1-butene with minimum of purity 99.0% and hydrogen with minimum purity of 99.9% were purchased from AGA S/A (Rio de Janeiro, Brazil). Heptane, obtained from VETEC, Rio de Janeiro, Brazil, was used for preparation of cocatalyst solution and catalyst system slurry after pretreatment on 3 Å molecular sieves (purchased from Spectrum Chemical, USA). The triethylaluminum (TEA) cocatalyst was provided by Akzo Nobel, São Paulo, Brazil. Cyclohexyl-methyl-dimethoxysilane (DMMCHS) was used as external electron donor. The 1,2,4-trichlorobenzene (TCB) was used as solvent in gel permeation chromatography (GPC), nuclear magnetic resonance (NMR), and crystallization analyses. Nitrogen purchased from AGA S/A (Rio de Janeiro, Brazil),
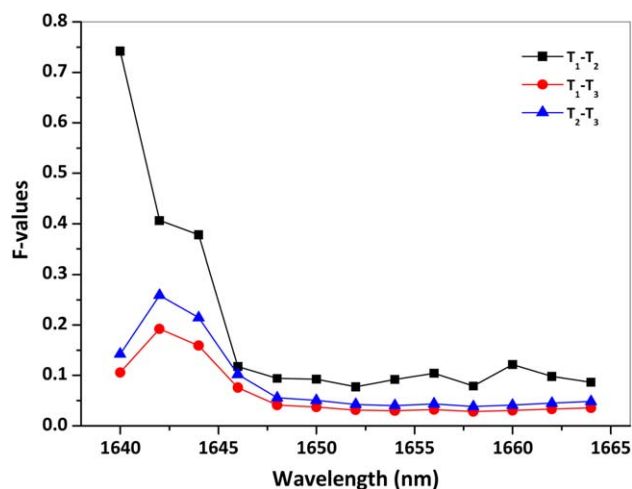

Figure 8. Statistic inference of the temperature effect based on the F-test. $T_1 = 140°C$, $T_2 = 160°C$, and $T_3 = 180°C$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
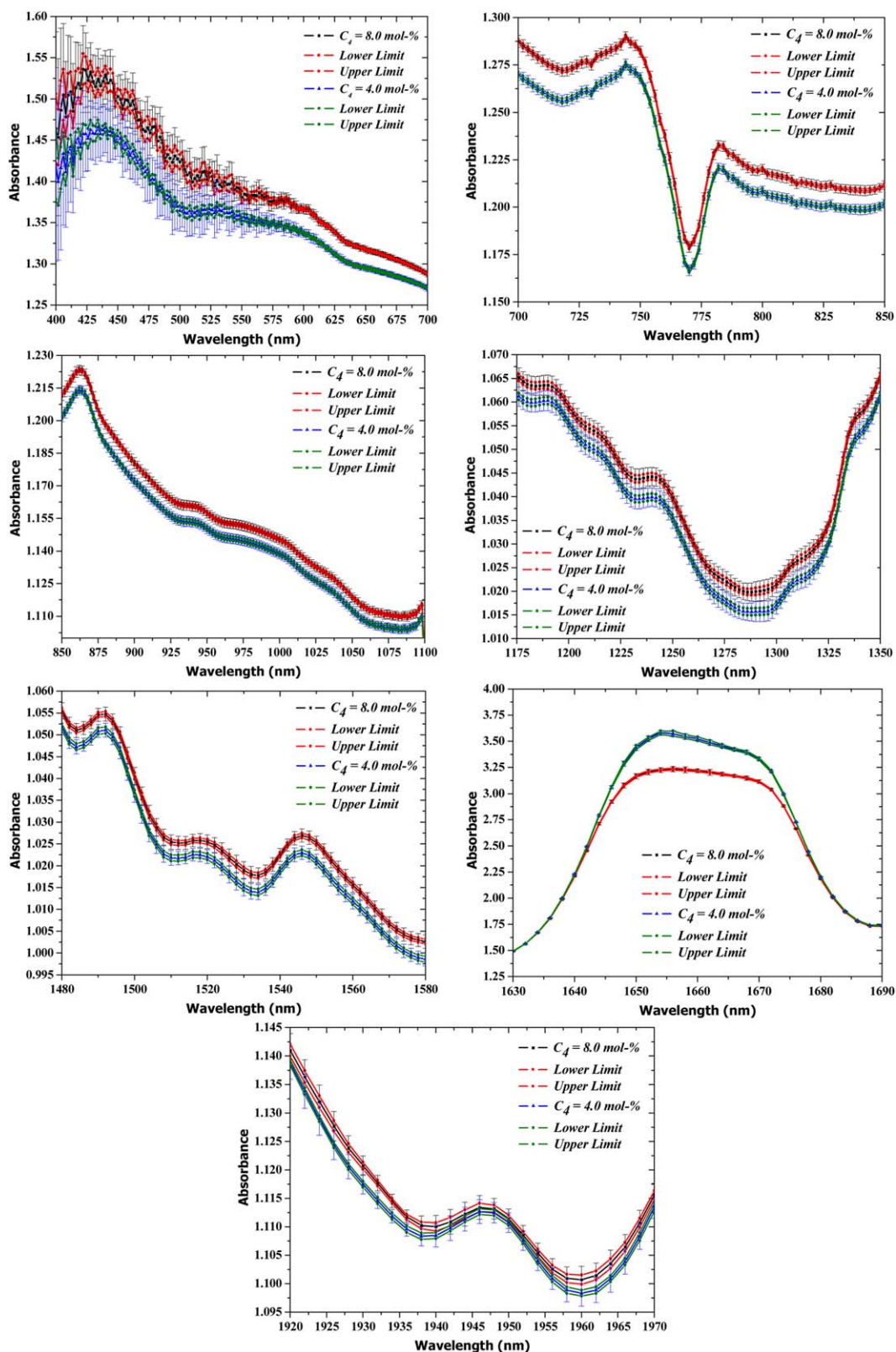
Figure 9. Effect of the copolymer composition. Experiments carried out with copolymer concentration of 1.5 wt % at 140°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
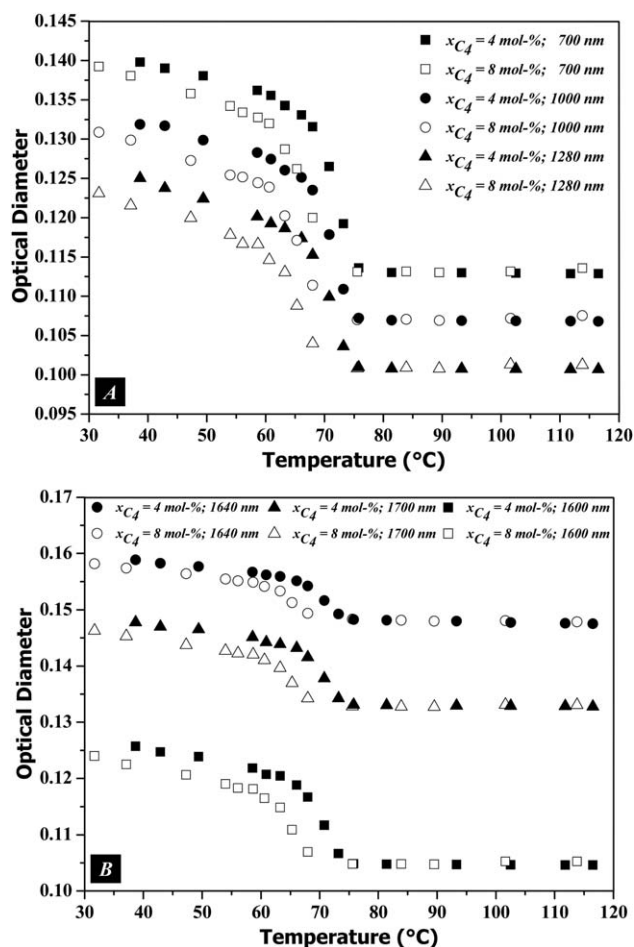
Figure 10. Thermal fractionation analysis of poly(propylene/1-butene) with 4.0 and 8.0 mol % of 1-butene at cooling rates of 0.023 °C · s^{-1}.

São Paulo—SP), and the experimental data acquired by using the software *ADPol 2.0*.[45] The experimental setup used to carry out the polymerization reactions was similar to the one described by Machado et al.[46] and the reader is referred to this publication for detailed information.

Thermal Fractionation Analysis and NIRS Measurements of Copolymer

NIRS measurements were carried out using a NIR spectrophotometer (Monochromator model 6500 supplied by NIRSystems, Silver Spring, MD) equipped with a stainless steel transflectance probe with a path length of 3 mm. The length of the probe was equal to 0.30 m and the diameter was equal to 19.05 mm. A 3-m long fiber-optics cable was used for light transmission. At each sampling time, with regular intervals of 1 min, 32 scan spectra were automatically collected and the average spectra were recorded and used for the analysis and data interpretation. This instrument has a wavelength range of 400–2500 nm, which comprises both the visible and the near infrared spectral regions. The Vision® spectral analysis software for Windows was used for data acquisition and spectral data treatment. Figure 1 illustrates the experimental apparatus used for fractionation analysis based on NIRS measurements.

with minimum purity of 99.0%, was used to keep the reaction environment free of oxygen. The 2,6-di-butyl-4-methylphenol (BHT) (Acros Organics, USA) with a purity of 99.0% was used as antioxidant in order to avoid oxidative degradation of polymer samples. Propylene and 1-butene were purified in successive beds of Cu catalyst and 3 Å molecular sieves. Other chemicals were used as received without additional purification. A commercial MgCl$_2$-supported TiCl$_4$ catalyst with catalyst titanium content of 3.0 wt % containing diisobutyl phthalate (DIBP) as internal donor, was used to perform the polymerizations.

Polymerization Reactions

Bulk reaction polymerizations were performed in a 450-mL mini bench top PARR 4562 reactor (Parr Instruments, Moline, IL). Along the reaction, the polymerization system was maintained under isothermal conditions at 60°C and constant stirring speed of 500 rpm. The gas feed was controlled by using a Brooks 5860 *i* mass flow meter (Brooks Instruments, Hatfield, PA). Both the reaction temperature and the gas feed flow rates were monitored in line with a microcomputer equipped with an AD/DA data acquisition system PCI-1710 (Advantech Brazil,

Figure 11. Thermal fractionation analysis of poly(propylene/1-butene) with 4.0 and 8.0 mol % of 1-butene at heating rates of 0.023 °C · s^{-1}.

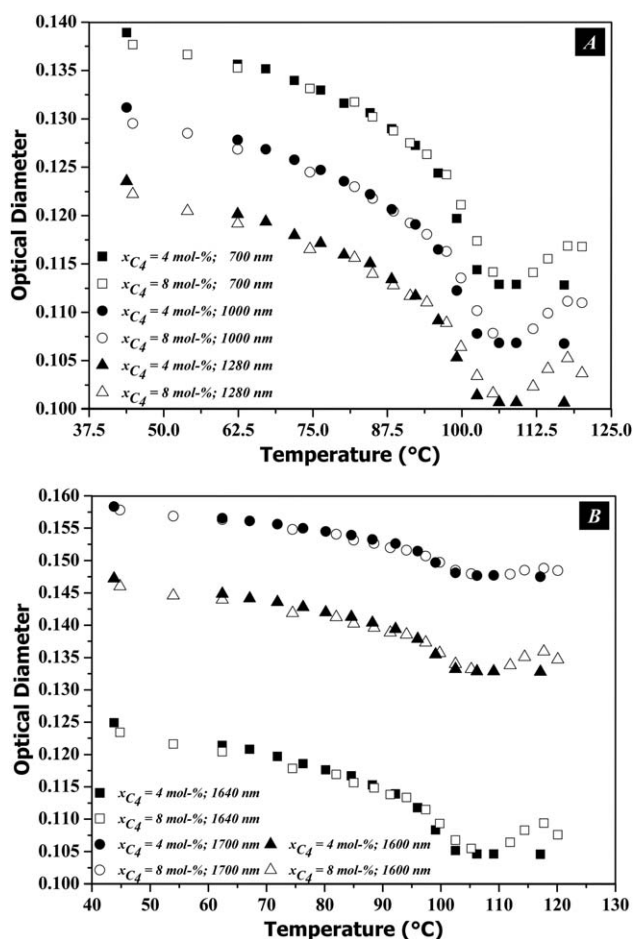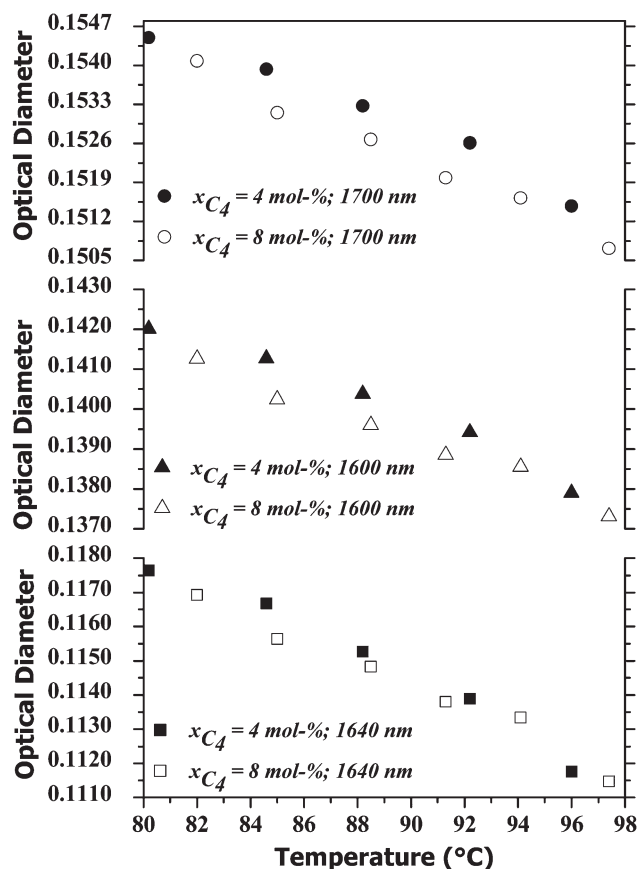**Figure 12.** Thermal fractionation analysis of poly(propylene/1-butene) with 4.0 and 8.0 mol % of 1-butene at heating rates of 0.023 °C · s^{-1} evaluated in the temperature interval ranged from 80 to 100°C.

Polymer samples were dissolved in TCB stabilized with BHT to avoid oxidative degradation. In the fractionations experiments the medium temperature was increased and/or decreased at heating rates of 0.023 °C · s^{-1}. Fractionation experiments were carried out in a 1-L jacketed glass reactor (FGG Equipamentos Científicos, São Paulo, Brazil), with a total polymer fraction ranged from 0.5 to 1.5 wt %, under an inert nitrogen atmosphere in order to keep the reaction environment free of oxygen. Initially, the reactor was fed with TCB, containing the specified amount of polymer. The system was kept under a constant stirring speed of 150 rpm. The electronic stirrer (EUROSTAR power control-visc, Staufen Germany) was equipped with a blade-type impeller. The reactor was equipped with a reflux condenser, linked to a refrigeration bath (PolyScience KR30-TO, Niles, IL). A heating bath (Haake DC-3, Paramus, NJ) was used to maintain the temperature of the reactor medium at the desired setpoint value.

RESULTS AND DISCUSSION

Several analyses were performed in order to evaluate the NIR spectral response to the solution copolymer concentration, the system temperature and 1-butene composition into the copolymer samples. In the experiments, the copolymer concentration into the mixture was varied from 0.5 to 1.5 wt %, and the medium temperature was kept constant in the range of 140–

180°C. Two copolymer samples with 1-butene content of 4.0–8.0 mol % were analyzed.

Experimental Design

A three-level factorial design was employed to evaluate the reproducibility of the experimental procedure. In this particular case, a sample containing 8.0 mol % of 1-butene was utilized in the experiments. Table I shows how the process variables were changed and coded in accordance with the proposed 3^2 design.

It was assumed that experimental data were distributed normally and that the confidence level of 95% could be used for computation of confidence intervals of experimental measurements and the respective averages, with the help of the t-Student distribution. At each particular experimental condition, 10 spectra were collected and used for computations. The spectra were divided into the visible and near infrared spectral regions. The standard deviation and the mean of absorbance were calculated for each particular wavelength. Figure 2 shows the spectra in the visible region. It can be observed that there are no significant measurement fluctuations in the visible region. Figure 3 shows the spectral response in the near infrared region. As one can see, there are no important measurement fluctuations, except when one approaches the region above 2100 nm, as outliers were found at 2214, 2312, 2356, and 2358 nm, as shown in Figure 3. These results indicate that the experimental procedure is suitable for the qualitative and quantitative evaluation of the polyolefin composition. Similar results were obtained when the polymer concentration in the solution assumed value equal to 1.0 and 1.5 wt %, and were omitted to avoid repetition of experimental results.

Figure 4 shows the standard deviation calculated at each particular wavelength in the range of 400–2100 nm. As can be observed, the standard deviations are smaller than 0.045 (about 1% of the original average signal), indicating that this region can be used for characterization of the copolymer samples. It is very important to note that the standard deviation is more pronounced when the wavelength is in the range of ~1620–1690 nm, because of the more intense absorption of light in this region.

Effect of the Copolymer Concentration in the Solution

To detect significant differences of spectral responses to modification of the copolymer concentration, the following equation was used:

$$Ratio_{ij} = 2\left(\frac{R_i - R_i}{\sigma_i - \sigma_j}\right) \quad (1)$$

According to eq. (1) the spectral differences are more significant in the regions close to the wavelength at 1200 nm (1180–1240 nm), 1400 nm (1380–1410 nm), and 1700 nm (1700–2000 nm), as shown in Figure 5. On the other hand, the spectra can be truncated to 1100–2100 nm, an appropriate range for monitoring the polymerization process and polymer properties.

Based on the spectral changes in the near infrared region, and observing the maximum and the minimum (peaks and depressions) values of the absorbance for each copolymer concentration in the solution, it was observed that the spectra of absorbance present differences related to the copolymer
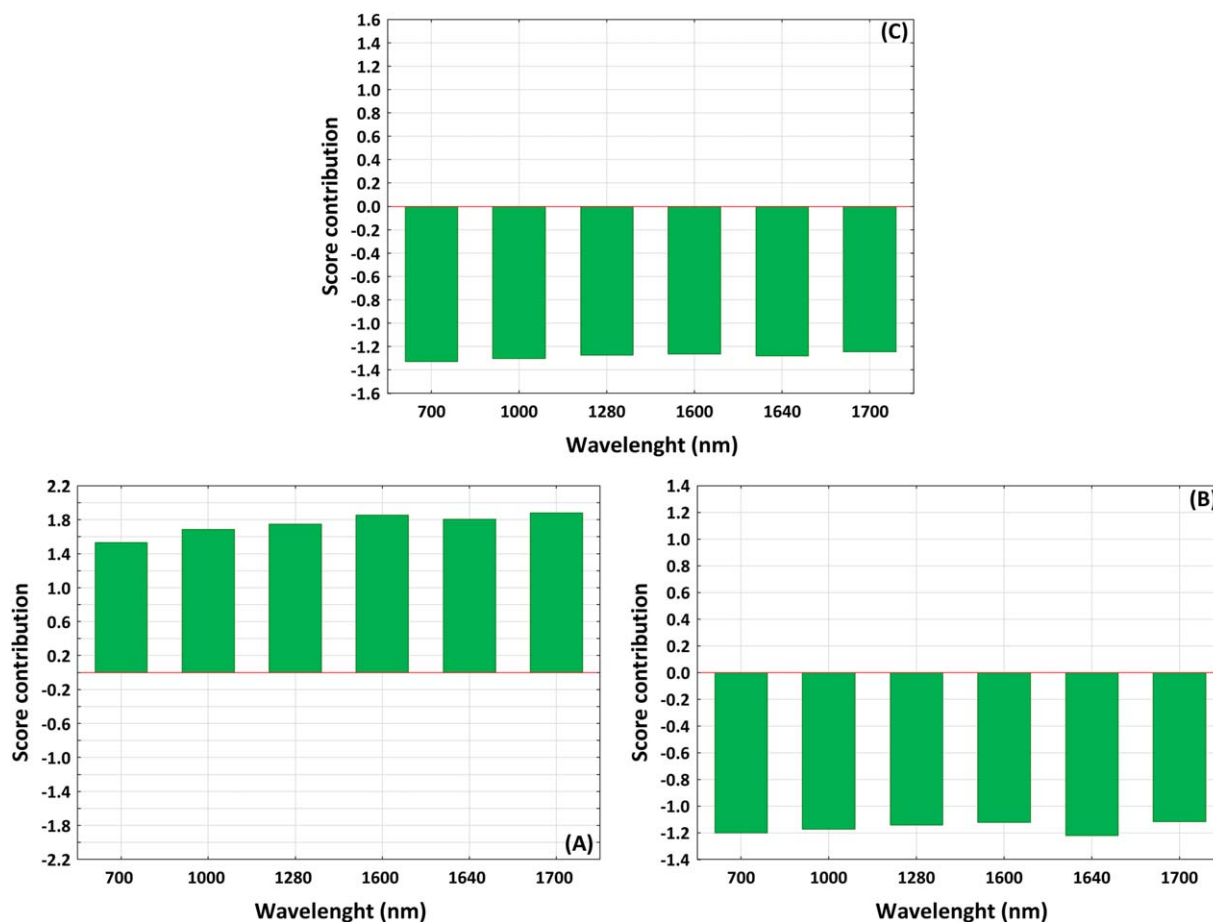
Figure 13. Score contribution plot (t_1) for (A) heating stage, (B) cooling stage, and (C) combination of heating and cooling experimental data. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

concentration at several spectral regions, for instance, at 1200, 1384, 1700, 1716, 1736, 1756, 1766, 1784, 1798, 1834, 1846, 1854, 1866, 1892, 1960, and 2000 nm. Figure 6 shows the mean of the absorbance with the true mean, the upper and lower limits calculated based on the t-Student distribution. The very small values of the variances indicate that the experimental technique is reproducible and that it can be employed for investigation of the copolymer composition of polyolefins.

Effect of the Medium Temperature
NIRS analyses were carried out at different temperatures to evaluate the spectral responses to variation on the medium temperature. Polymer samples containing 8 mol % of 1-butene were used for this study, with the copolymer concentration of 1.5 wt % in the solution of THB. Figure 7 shows the absorbance obtained as function of the medium temperature in the range of 700–2000 nm. It is observed that the temperature does not significantly affect the absorbance even in the large range of the temperature used in the experiments. Spectral changes were only observed in the wavelength range of 1640–1664 nm, as shown in Figure 7(B,C). Therefore, temperature effects can be disregarded in the present work, as there are no significant differences between the upper and lower limits of calculated means when temperature is changed. In spite of that, when a F-test is

applied (with 2 and 12 degrees of freedom and confidence interval equal to $0.02537 < F < 5.0959$) for three different temperatures (140, 160, and 180°C) it is concluded that all F values are within the test interval. Based on the F values represented in Figure 8, one can claim that the standard deviations of medium temperature are not different at the 95% confidence level, and that the medium temperature does not influence the system significantly in the analyzed range.

Effect of the 1-Butene Fraction in the Copolymer
NIRS analyses were performed in order to evaluate the sensibility of the absorbance spectra to the 1-butene content in the copolymer. In the experiments, copolymer concentration of 1.5 wt % was used, at a temperature of 140°C. Figure 9 illustrates the spectral variation in response to the 1-butene content in the copolymer in the wavelength range of 700–2000 nm. Spectral changes can be seen in the spectral ranges from 600 to 750 nm and 790 to 860 nm. It was observed that the difference in the absorbance is more significant at 1646 and 1674 nm, as shown in Figure 9. This wavelength region is very similar to the one observed in the experiments performed to observe the temperature effect (see Figure 7) and where the standard deviation assumed higher values. In spite of this, it seems that the temperature does not significantly affect the absorbance in the wavelength regions that
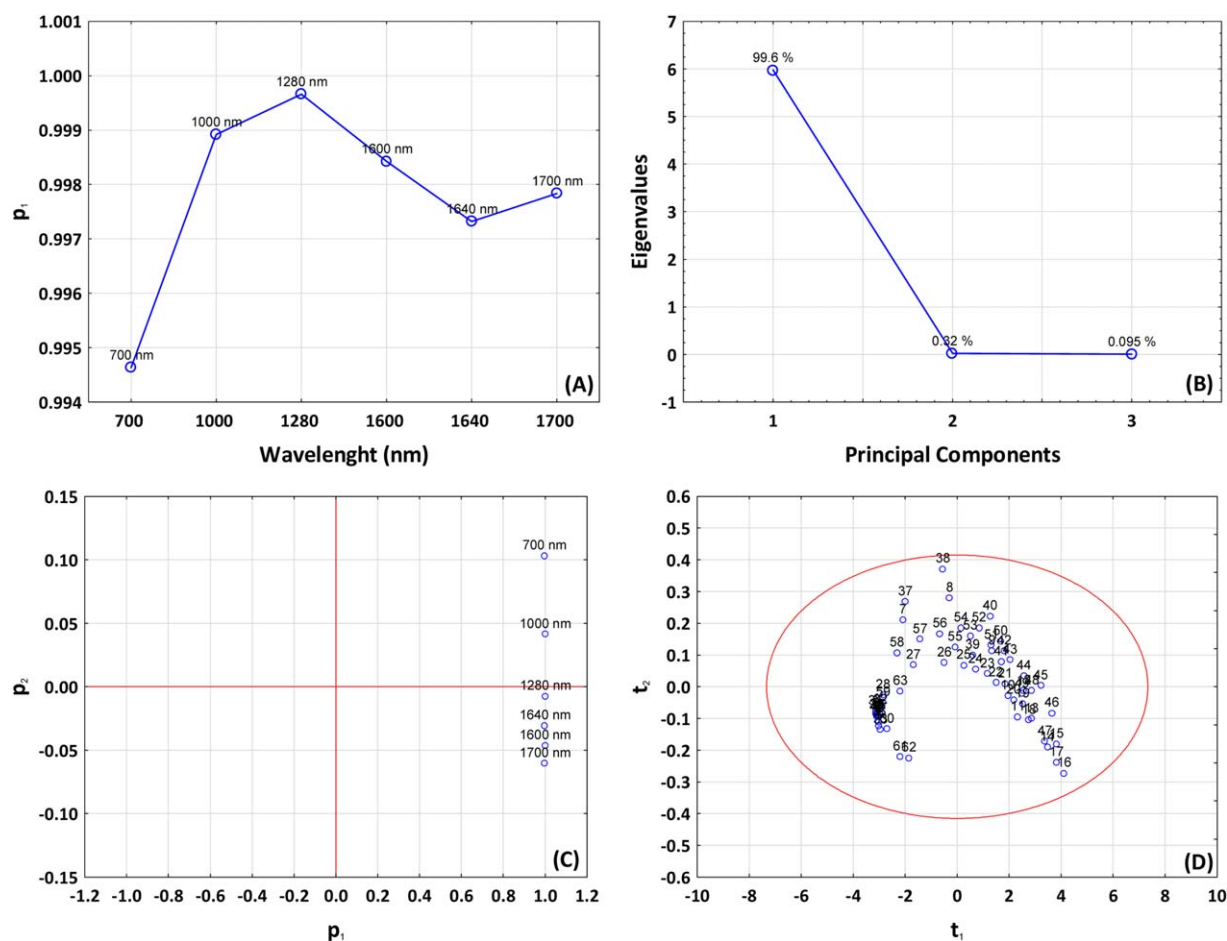
Figure 14. Principal component diagnostic based on the (A) loading line plot for p_1, (B) eigenvalues scree plot, (C) loading scatterplot for p_1 and p_2, and (D) score scatterplot for t_1 and t_2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

correspond to the spectral changes of poly(propylene/1-butene) samples, when the copolymer composition is varied.

Thermal Fractionation Analysis

Thermal fractionation associated with NIRS measurement was used for qualitative identification of the comonomer distribution in α-olefin copolymers. This new crystallization technique can be successfully used for fractionation and characterization of semicrystalline polymers.

Figure 10 illustrates the spectral variation that can be related to the monomer sequence distribution of two polymer samples, containing 4.0 and 8.0 mol % of 1-butene, when medium temperature was decreased at cooling rates of 0.023 °C · s^{-1}. As the signal changes, polymer fractions precipitate and affect the amount of light scattered by the samples. The smooth variation of the signal indicates that polymer precipitation takes place continuously until attainment of a plateau, where one can assume that precipitation ceases. Figure 10(A) shows the spectral changes at specific wavelengths of 700, 1000, and 1280 nm. Similar behavior can be observed when the spectra are analyzed in the spectral regions at 1600, 1640, and 1700 nm, as shown in Figure 10(B). It can be assumed that the NIRS is sensitive to variation of the monomer sequence distribution because the signal response is

very nonlinear during the crystallization of the polymer chains, as the medium temperature is decreased. Initially, the signal response increases slowly, due to the existence of small fractions of insoluble material (containing small amounts of comonomer); afterwards, the signal decreases steeply, as the solubility of the chains with the average comonomer content is reduced; finally, the signal response is stabilized, as the chains containing higher amounts of comonomer precipitate. This analysis is supported by the fact that the signal profiles of samples containing higher amounts of comonomer are shifted towards lower temperatures.

The NIRS performance was also evaluated in experiments where the medium temperature was increased at heating rates of 0.023 °C · s^{-1}. Figure 11(A,B) show the spectral variations at specific wavelengths ranged from 700 to 1700 nm. In general, the overall performance is very similar to the ones described in the previous paragraph and can be interpreted in similar terms. It can be seen that the spectral variation are more pronounced when the medium temperature is increased beyond the temperature required to solubilize the samples completely. In spite of this, there are appreciable spectral changes when the temperature of the medium is in the range of 80–100°C at the wavelength of 1600, 1640, and 1700 nm, as shown in Figure 12. In this particular interval of temperature, the copolymers
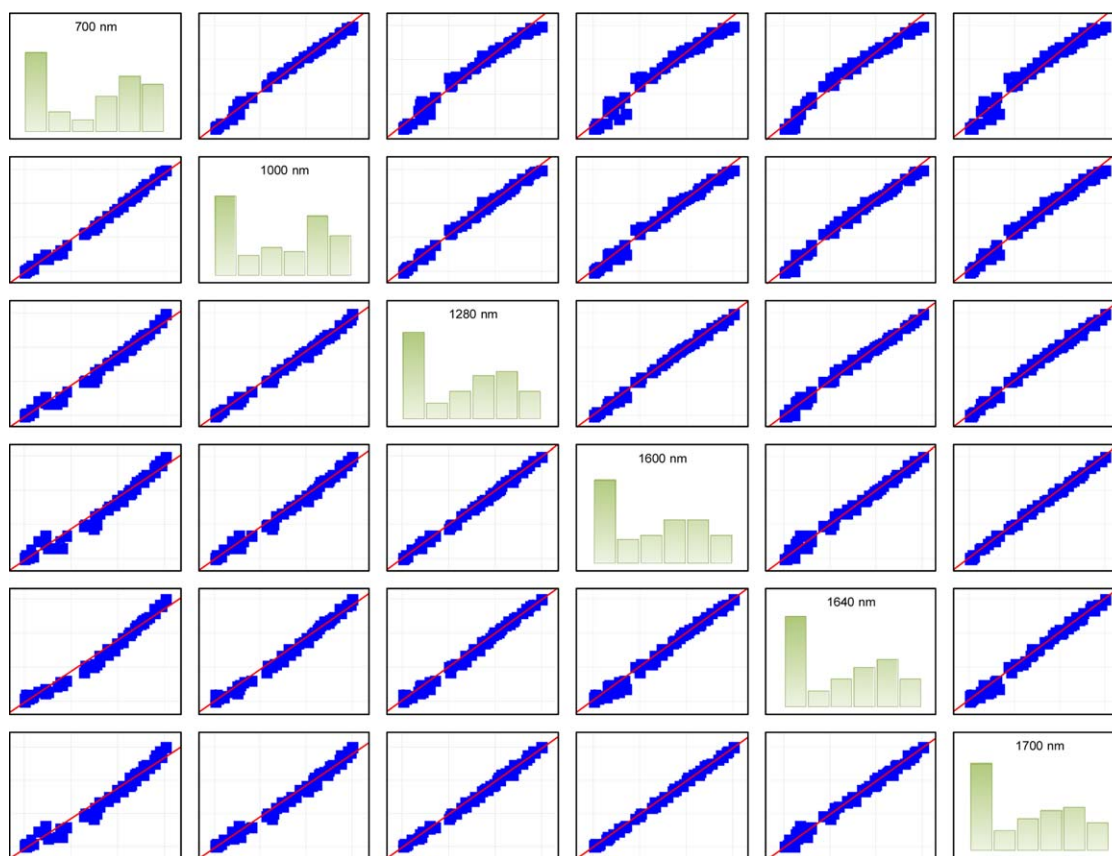
Figure 15. Linear correlation between the wavelengths. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

presenting different composition can also be distinguished through the proposed NIRS technique.

Principal components analysis (PCA) can be employed for process diagnosing, allowing to explore the role of the main analyzed process variables.[47,48] In the particular case analyzed here, the PCA was applied to the whole set of available spectral data, for polymer samples containing different 1-butene contents (4.0 and 8.0 mol % of 1-butene) and analyzed at different temperatures.

As depicted in Figure 13, the score contribution plot can be used for data interpretation, taking into account the influence of both the heating and the cooling stages on the spectral responses. When the heating and cooling stages are analyzed individually, it can be observed that the specific wavelengths at 700, 1000, 1280, 1600, 1640, and 1700 nm contribute almost equally to the scores. This is a clear indication that, although the intensity of the obtained spectra changes during the experiments, the relative intensities of the collected spectra remain essentially the same. This can be expected when the overall system composition is not changed significantly and scattering controls the modification of the intensities of light transmission, as in the analyzed case.

Although the spectral profiles obtained during the heating and cooling experiments reveal important changes in the copolymer concentration, it seems that the observed effects are more pronounced during precipitation (cooling), allowing for better discrimination of copolymer compositions, probably because mass transfer effects is more pronounced during dissolution (heating). The scores presented in Figure 13 seemingly confirm this interpretation, although copolymer composition can also be discriminated when heating is performed, as illustrated in Figures 10–12.

Figure 14 presents the line plot of the p-loadings for the principal component (PC) 1, indicating that all evaluated wavelengths are important to explain the observed spectral changes, as discussed previously, with negligible gap between the least important wavelength (700 nm) and the most influential wavelength (1280 nm), as can be seen in Figure 14(A). The eigenvalues scree plot of the principal components is shown in Figure 14(B). It is important to emphasize that only the first two principal components are statistically significant, concentrating 99.9% of the observed variability. This can be interpreted in terms of the overall change of the intensity of the collected spectra (as already discussed, as the system is controlled by scattering and the overall composition remains constant during an experimental run) and the slighter spectral changes that can be related to the different copolymer compositions. The dominant principal component (PC equal to 1) concentrates 99.6% of the total variability, while the second most important component concentrates 0.3% of the variability. In spite of that, copolymer composition can be detected because spectral changes can be observed at different temperatures, as shown in Figures 10–12.

The loading scatterplot for the two first components p₁ and p₂ are shown in Figure 14(C) and indicate that the variables are correlated. This behavior can also be noticed when the scatterplot of all variables are generated, showing strong linear correlations between the wavelengths, as presented in Figure 15. The scatterplot of the scores for PC 1 and PC 2 is illustrated in Figure 14(D). The absence of outliers can be observed, as all t scores fall inside the ellipsis. Again, the data seem to confirm the proposed interpretation of the observed phenomena.

CONCLUSIONS

Different experiments were performed to evaluate NIR spectral responses to changes of polyolefin compositions and temperatures in solutions of poly(propylene-co−1-butene) in TCB. It was observed that NIRS can be used successfully to determine the average composition of this particular α-olefin copolymer. A new technique based on the combination of NIRS measurements and thermal fractionation of α-olefin copolymers was also introduced in this work. This new technique can constitute a useful tool for identification of the composition of α-olefins copolymers and analysis of composition distributions. Experiments performed in conditions of increasing and/or decreasing temperatures indicated that the collected NIR spectra can be sensitive to modification of the comonomer sequence distribution. Particularly, it was shown that although the overall changes in intensity of the spectra during the experiments, the relative intensities of the collected spectra remained essentially the same, which indicates that the system is controlled by the intensity of light transmission.

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