

# Near-Infrared Spectra of Polyamide 6, Poly(vinyl chloride), and Polychlorotrifluoroethylene

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**ABSTRACT:** The near-infrared spectra (NIR) of polyamide 6 (PA 6), poly(vinyl chloride) (PVC), and polychlorotrifluoroethylene (PCTFE) were measured. The tentative assignment of the overtone and combination frequencies was made with curve fitting calculations and local mode theory. Anharmonicity correction and mechanical frequency were determined from a Birge–Sponer plot. Tentative assignments of stretch overtone frequencies of CH<sub>2</sub>, NH, and CO functional groups of PA 6 and CH<sub>2</sub>, and CH functional groups of PVC were made. Anharmonicity corrections of 55, 61, and 20 cm<sup>-1</sup> were obtained for CH<sub>2</sub>, NH, and CO stretch modes of PA 6, respectively, and of 60 and 66 cm<sup>-1</sup> for CH<sub>2</sub> and CH stretch modes of PVC, respectively. The local mode model seems to be adequate to interpret the origin of the bands observed in NIR spectra of PA 6 and PVC. Anharmonicity corrections of 33, 19, and 16 cm<sup>-1</sup> were obtained, respectively, for CF, asymmetrical CF<sub>2</sub>, and symmetrical CF<sub>2</sub> stretch of PCTFE functional groups. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 199–208, 2002

**Key words:** near-infrared; polyamide 6; poly(vinyl chloride); polychlorotrifluoroethylene; spectroscopy; FTIR; fluoropolymers; polyamides

## INTRODUCTION

Near-infrared (NIR) radiation was discovered by Frederic William Herschel in 1800. However, the use of NIR spectroscopy as an analytical tool only began in the 1980s. Nowadays, the increasing interest observed in NIR spectroscopy occurs not only because of the technological progress in microelectronics, optics, and materials used in the faster and more reliable spectrometers, but also because of its unique technical characteristics, like rapid spectra acquisition, little or no sample preparation, no sample destruction, and the possibility to obtain much information from a single spectrum.

Probably NIR spectroscopy would not be such a successful tool in agriculture, astronomy, biology,

biomedical, textile, chemistry, foods, pharmaceuticals, and petrochemical industries without fast computers and the sophisticated multivariate calibration techniques of chemometrics.<sup>1</sup>

The basic difference between NIR and mid-infrared (MIR) spectroscopy is that bands in the MIR region, 400–4000 cm<sup>-1</sup>, are due to molecular fundamental vibrational bands whereas those in the NIR region, 4000–12 800 cm<sup>-1</sup>, are primarily due to overtone and combination bands.<sup>2, 3</sup> Overtone and combination bands are not allowed within the harmonic oscillator approximation; in fact, they are observed experimentally because the molecular motions are not harmonic but instead they have a certain degree of mechanical and electrical anharmonicity.<sup>4–6</sup> Indeed, overtone and combination bands of CH, OH, NH, and SH stretch modes are easily observed in NIR spectra, although higher overtone stretch or bending modes of other functional groups can also absorb in this region.<sup>7</sup>

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Another characteristic of the NIR region is the too weak absorption compared with the MIR range. But this effect can contribute as an advantage because for NIR transmission spectroscopy, thicker sample path lengths can be used.<sup>8, 9</sup>

MIR spectra are very sensitive to chemical and structural properties of a material. In the same way, NIR spectra can also be affected by the chemical and structural factors providing relevant structural information.<sup>8, 10</sup>

NIR spectroscopy can be used as an adequate tool in qualitative and quantitative polymer investigation, and when band assignment is available, a correlation between structure and polymer properties can be obtained.

Several polymer properties, such as molar mass, residual monomer content, degree of cure, crystallinity, and composition of polyolefins, polyurethanes, nylon, and epoxy resins have been studied by NIR spectroscopy coupled with chemometrics methods.<sup>1, 5, 6</sup>

Polyamide 6 (PA 6), poly(vinyl chloride) (PVC), and polychlorotrifluoroethylene (PCTFE) are polymers that have large industrial and technological applications. PA 6 is an engineering plastic used in home furnishings, apparel, and in the automotive industry. PVC is a commodity plastic used mainly in pipe and fittings, films and sheet, flooring materials, wire and cable insulation, automotive parts, adhesives, and coatings. Both polymers are nowadays largely recycled. PCTFE is a high-performance plastic that presents chemical stability, low solubility, high softening point, and electric and mechanical properties appropriate to several applications.<sup>11</sup>

It was our main goal in this work to perform a tentative assignment of the NIR spectra of these polymers using the local mode theory, a mathematical treatment of the spectra with curve fitting calculation, and the Birge–Sponer plot to obtain the anharmonicity correction and mechanical frequency of the functional groups belonging to those polymers. The local mode model was introduced by Hayward and Henry,<sup>12</sup> in 1975, to study high energy vibrational overtone spectroscopy in gases and liquids. A Birge–Sponer plot of  $\Delta E/v$  versus  $v$ , gives the anharmonicity correction and mechanical frequency of the vibrational mode. The transition energies  $\Delta E$  (in  $\text{cm}^{-1}$ ) of a particular vibrational mode can be described by the following formula:

$$\Delta E = (\omega_e - \omega_e\chi_e)v - \omega_e\chi_e v^2$$

**Table I Optical Configuration of Bomem DA3 used to Obtain the NIR Spectra**

Wavenumber Range ( $\text{cm}^{-1}$ )	Source	Beam Splitter	Detector
3500 to 5500	Globar	KBr	DTGS
4500 to 9000	Quartz/Halogen	Visible	MCT
8500 to 12500	Quartz/Halogen	Visible	Si

where  $\omega_e$  is the mechanical frequency,  $\omega_e\chi_e$  is the anharmonicity correction,  $\chi_e$  is the anharmonicity constant, and  $v$  is the vibrational quantum number.

We used the local mode model for solid-state polymer samples to obtain the normal mode anharmonicity constant and thus to describe the spectrum in terms of the components of anharmonically coupled modes.

## EXPERIMENTAL

### Material

The plates ( $\sim 1$  cm of thickness) of PA 6 (type 9200 D) used were obtained by injection molding in an injection machine SEMERARO S 100, and kindly given by Radiciplastics.

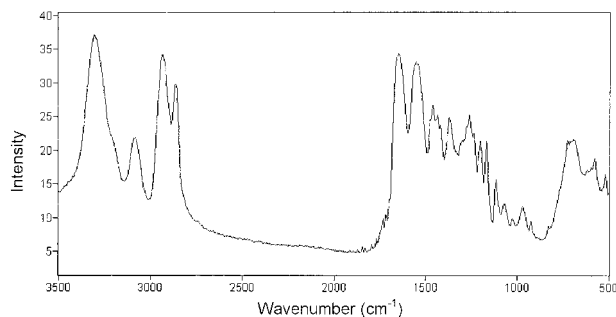
Films (0.1–0.9 mm of thickness) of PVC (Solvay) were prepared by casting from tetrahydrofuran solution. A mass of 3 g of powder PVC was dissolved in 30 mL of tetrahydrofuran (Merck).

Samples of commercial PCTFE (Chemplast Inc.) of high molar mass in the pellet form were used to record the NIR spectra, and a hot-pressed, 0.7-mm thick film produced with this material was used to obtain the MIR spectrum.

### NIR Instrumentation

The NIR spectra of the PA 6 and of PCTFE were recorded on a Bomem Fourier transform infrared (FTIR) spectrometer model 154 S, with a germanium detector, tungsten lamp, and diffuse reflectance accessory, at  $8 \text{ cm}^{-1}$  resolution. NIR transmittance spectra of PVC were also obtained with this equipment.

The NIR spectra of PVC were recorded on a Bomem FTIR spectrometer model DA3, at  $4 \text{ cm}^{-1}$  resolution, using the optical configuration given in Table I.



**Figure 1** MIR photoacoustic spectrum of the PA 6: (A)  $1549\text{ cm}^{-1}$ , (B)  $1653\text{ cm}^{-1}$ , (C)  $2863\text{ cm}^{-1}$ , (D)  $2935\text{ cm}^{-1}$ , (E)  $3086\text{ cm}^{-1}$ , and (F)  $3304\text{ cm}^{-1}$ .

The MIR photoacoustic IR spectrum of PA 6 was recorded on a Bomem FTIR, model DA3, with KBr beam splitter and detection through an photoacoustic cell MTEC model 200. Active coal was used as reference and all the measurement were accomplished after a purge with gaseous He through the photoacoustic cell compartment of samples for  $\sim 1$  min.

The MIR transmittance IR spectra of PVC and PCTFE were recorded on a Bomem FTIR spectrometer, model DA3 with KBr beam splitter and DTGS detector, at  $4\text{ cm}^{-1}$  resolution.

The curve fitting calculation was performed by using the Grams 386 software.

## RESULTS AND DISCUSSION

In this work we recorded the NIR spectra of solid-state polymer as film for transmission or as pellet for diffuse reflectance mode. The band intensity of the NIR spectrum profile decreased with increasing vibrational quantum number, and to increase the absorbance of higher energies, the sample thickness was increased appropriately to obtain the higher overtone region spectra.

The MIR transmittance spectra of PVC and PCTFE or photoacoustic spectrum of PA 6 were recorded to get the fundamental vibrational frequencies of several functional groups related to solid-state polymers studied in this work.

### Polyamide 6

The formula of the constitutional repeating unit of PA 6 is  $-\text{[NH}-\text{C}(\text{C}=\text{O})-(\text{CH}_2)_5]-$ . The MIR photoacoustic spectrum of PA 6 is shown in Figure 1. PA 6 has  $\text{CH}_2$ , NH, and CO functional

**Table II** MIR Vibrational Bands and Assignments for PA 6<sup>a</sup>

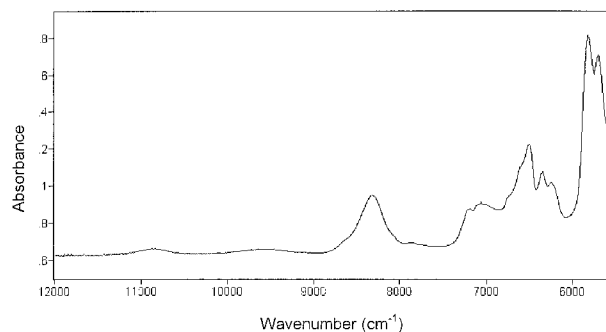
Assignment	Band ( $\text{cm}^{-1}$ )
Amide II (NH in plane bending + CN stretch)	1549
Amide I (CO stretch)	1653
$\text{CH}_2$ symmetrical stretch	2863
$\text{CH}_2$ asymmetrical stretch	2935
First overtone of amide II	3086
NH stretch	3384

<sup>a</sup> Reference 6.

groups with characteristic vibrational frequencies that can be identified in the IR spectrum. These groups absorb in different frequency regions, so the spectral profile is very simple in the region above  $1500\text{ cm}^{-1}$ , as can be seen in Figure 1. The wavenumber corresponding to the most strong bands marked in this spectrum have been assigned according to literature data<sup>6</sup> to the vibrational modes presented in the Table II.

The NIR spectrum of PA 6 is shown in the Figure 2. As can be seen, overtone and combination absorption due to distinct vibrational modes are observed. An assignment based only on the approach of multiples of the fundamental frequency (two or three times to determine the overtones bands) and the sum or differences of the distinct bands (to determine the combination bands) are presented in Table III. The fifth overtone of the CO stretch expected at  $\sim 9918\text{ cm}^{-1}$  was not observed because the intensity of the overtone bands decrease with increasing the overtone order.

The detection of two overtone bands corresponding to the symmetrical  $\text{CH}_2$  and asymmet-



**Figure 2** NIR diffuse reflectance spectrum of the PA 6.

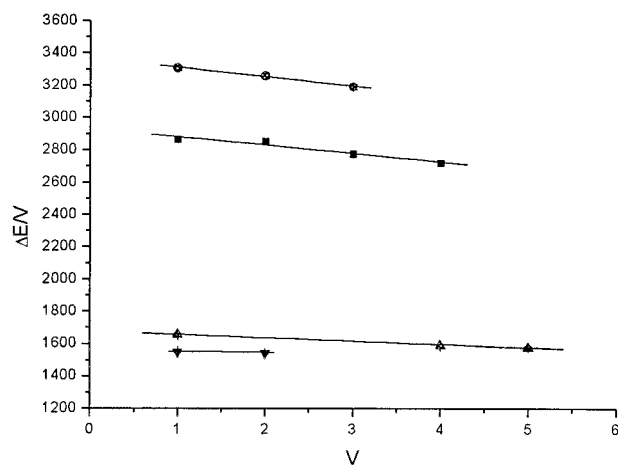
**Table III** Initial Tentative Assignment of the NIR Spectrum of the PA 6

Assignment	Band ( $\text{cm}^{-1}$ )
$\Delta v = 2$ CH <sub>2</sub> symmetrical stretching	5703
$\Delta v = 2$ CH <sub>2</sub> asymmetrical stretching	5823
$\Delta v = 4$ CO stretch	6352
$\Delta v = 2$ NH stretch	6511
$\Delta v = 5$ CO stretch	7869
$\Delta v = 3$ NH stretch	9562

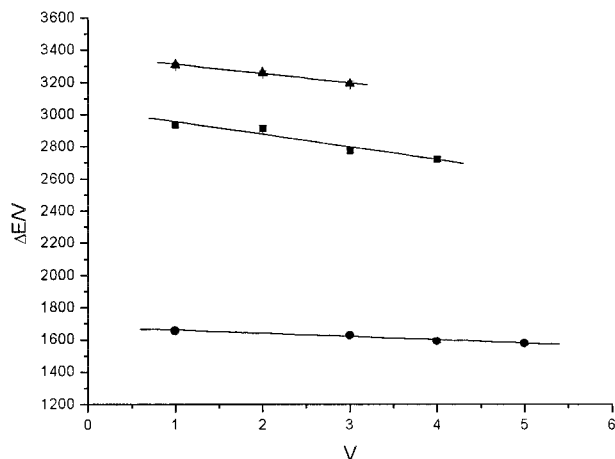
rical CH<sub>2</sub> stretching modes in the higher overtone region could be expected. However, the spectrum of PA 6 (Fig. 2) show only single bands at 8316 and 10846  $\text{cm}^{-1}$  that probably correspond, respectively, to the second and third CH<sub>2</sub> stretch overtone. No evidence of doublet bands corresponding to symmetrical CH<sub>2</sub> and asymmetrical CH<sub>2</sub> stretch overtones in those regions was observed.

The local mode theory establishes that in the higher overtone region ( $v > 3$ ), only an oscillator type is present. Snively and Dubsy,<sup>10</sup> in a study of polyethylene, determined an anharmonicity correction of 57  $\text{cm}^{-1}$  (in module) from a Birge-Sponer plot for the CH stretch overtone progression (fundamental, first overtone, second overtone, etc.), considering the wavenumber that correspond to the bands maxima observed in the NIR spectrum.

Using this approach, Figure 3 presents the straight line of linear regression obtained for the



**Figure 3** Birge-Sponer plot. The transitions values used are reported in the text (where SD = standard deviation). Key: (●) NH stretch (SD = 0.5); (■) CH symmetrical stretch (SD = 1.5); (▲) C=O stretch (SD = 0.6); (▼) amide II (SD = 0).



**Figure 4** Birge-Sponer plot. The transitions values used are reported in the text (where SD = standard deviation). Key: (▲) NH stretch (SD = 0.5); (■) CH asymmetrical stretch (SD = 2.3); (●) C=O stretch (SD = 0.9).

following progression: symmetrical CH<sub>2</sub> stretch [2863 ( $\Delta v = 1$ ), 5703 ( $\Delta v = 2$ ), 8316 ( $\Delta v = 3$ ), and 10 846  $\text{cm}^{-1}$  ( $\Delta v = 4$ )], NH stretch [3304 ( $\Delta v = 1$ ), 6511 ( $\Delta v = 2$ ), and 9562  $\text{cm}^{-1}$  ( $\Delta v = 3$ )], CO stretch [1653 ( $\Delta v = 1$ ), 6352 ( $\Delta v = 4$ ), and 7869  $\text{cm}^{-1}$  ( $\Delta v = 5$ )] and amide II [1549 ( $\Delta v = 1$ ) and 3086  $\text{cm}^{-1}$  ( $\Delta v = 2$ )]. In the same way, Figure 4 present the straight line of linear regression obtained for the following progression: asymmetrical CH<sub>2</sub> stretch [2935 ( $\Delta v = 1$ ), 5823 ( $\Delta v = 2$ ), 8316 ( $\Delta v = 3$ ), and 10 846  $\text{cm}^{-1}$  ( $\Delta v = 4$ )], NH stretch (same before), and CO stretch [1653 ( $\Delta v = 1$ ), 4870 ( $\Delta v = 3$ ), 6352 ( $\Delta v = 4$ ), and 7869  $\text{cm}^{-1}$  ( $\Delta v = 5$ )]. The anharmonicity correction and mechanical frequencies obtained from the Birge-Sponer plots (Figs. 3 and 4), are presented in the Table IV.

The frequency at 4870  $\text{cm}^{-1}$  observed in the NIR spectrum of PA 6 (not shown) fitted the straight line of linear regression, indicating that the assignment of this frequency to the second overtone of CO stretch should be correct.

The values presented in Table IV for symmetrical CH<sub>2</sub> stretch, NH stretch, and CO stretch are close to the values presented in the literature<sup>13-15</sup> obtained in the investigation of the NIR spectra of several organic molecules. However, the anharmonicity correction of asymmetrical CH<sub>2</sub> stretch (81  $\text{cm}^{-1}$ ) is too high and it has not been reported in the literature for CH stretch mode of polymer.

As we know, curve fitting is a mathematical tool to separate and identify bands in regions



**Table IV Anharmonicity Correction and Mechanical Frequency in (cm<sup>-1</sup>) of PA 6<sup>a</sup>**

Assignment	Figure 3		Figure 4	
	$\omega_e\chi_e$	$\omega_e$	$\omega_e\chi_e$	$\omega_e$
CH <sub>2</sub> asymmetrical stretching			81 (± 14)	3035
CH <sub>2</sub> symmetrical stretching	52 (± 9)	2930		
NH stretching	58 (± 5)	3365	58 (± 5)	3365
CO stretching	20 (± 2)	1676	20 (± 2)	1676
Amide II	6 (± 0)	1555		

<sup>a</sup> The values in parentheses are the standard deviations.

where occur overlapping. The curve fitting considering a Gaussian function of the spectrum of the PA 6 between 5000 and 7500 cm<sup>-1</sup> didn't show any additional bands other than those presented in the spectrum (Fig. 2). In the mathematical treatment of the second overtone region, a shoulder in lower frequency and another in the higher frequency can be identified. In the third overtone region, the shoulders are not observed.

The band narrowing of the third overtone region when compared with the second, the disappearance of the shoulders, and the smaller number of bands determined by the mathematical treatment suggest that in the frequencies of the third overtone region, the CH<sub>2</sub> stretch overtone mode has a higher local mode character than that at second overtone region. The values of the frequencies observed by the curve-fitting treatment of the second and third overtone region of the CH<sub>2</sub> stretch are presented in Table V.

Because of the anharmonicity correction, bands from nonequivalent oscillators must be further separated from one another at each higher overtone.<sup>16</sup> Analyzing the set of frequencies obtained by curve-fitting calculations in the second and third overtone region of CH<sub>2</sub> stretch (Table V), the best progression that fits the straight line in Birge-Sponer plot are 2863, 5701, 8316, and 10

827 cm<sup>-1</sup> for symmetrical CH<sub>2</sub> stretch and 2935, 5822, 8599, and 10 983 cm<sup>-1</sup> for asymmetrical CH<sub>2</sub> stretch.

Plotting these wavenumber progression in Birge-Sponer plot (Figure 5), the value of 55 and 2934 cm<sup>-1</sup> were obtained for anharmonicity correction and mechanical frequency, respectively, of symmetrical CH<sub>2</sub> stretch, and 61 and 3018 cm<sup>-1</sup> for asymmetrical CH<sub>2</sub> stretch. There is a better agreement between these values and that data reported in the literature<sup>10, 13-15</sup> than the anharmonicity correction and mechanical frequency values obtained previously for CH<sub>2</sub> stretch considering the frequencies without the curve-fitting calculation.

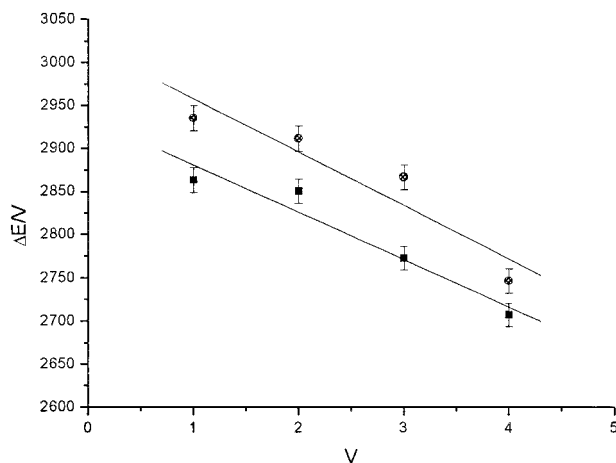
The curve-fitting figures (not shown) in the second and third CH<sub>2</sub> overtone regions show a high intensity for the band assigned to symmetrical CH<sub>2</sub> stretch compared with the intensity of the band assigned to the asymmetrical CH<sub>2</sub> stretch. Also, the dispersion of data in the Birge-Sponer plots is lower in the straight line regression of symmetrical CH<sub>2</sub> stretch than in the asymmetrical CH<sub>2</sub> stretch, so the symmetrical CH<sub>2</sub> stretch mode may have a large contribution in the local mode picture in these regions.

Although it is difficult to assign the overtone bands of angular deformation mode because of complex bands superposition (not shown) between 4000 and 5500 cm<sup>-1</sup>, comparison of the NIR spectrum of PA 6 with the NIR spectrum of polyethylene<sup>10</sup> suggests that the band at 7199 cm<sup>-1</sup> could be a higher overtone of CH<sub>2</sub> angular deformation mode, whose fundamental frequency is observed at 1464 cm<sup>-1</sup>, and that bands observed close to 7199 cm<sup>-1</sup> could be originated from combinations bands.<sup>13</sup>

A possible tentative assignment of the NIR spectrum of PA 6 is presented in the Table VI.

**Table V Bands Observed by Curve-Fitting Treatment of the Spectrum of PA 6**

CH <sub>2</sub> Second Overtone Range (cm <sup>-1</sup> )	CH <sub>2</sub> Third Overtone Range (cm <sup>-1</sup> )
8088	10686
8316	10827
8466	10983
8599	—



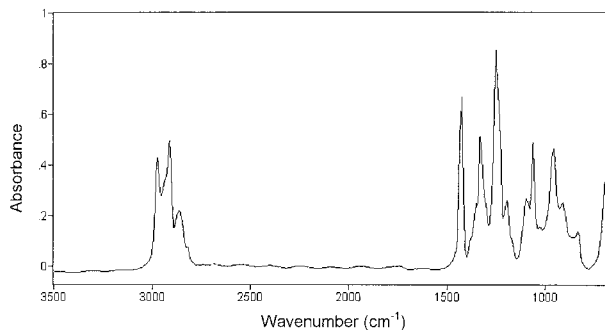
**Figure 5** Birge–Sponer plot. The transitions values used are described in the Table V (case B) (where SD = standard deviation). Key: (■) CH symmetrical stretch (SD = 22.1); (●) CH asymmetrical stretch (SD = 35.0).

### Poly(vinyl chloride)

The formula of PVC is  $-\text{[CHCl-CH}_2\text{]}-$ . Two types of nonequivalent CH functional groups can be identified:  $\text{CH}_2$  and  $\text{CHCl}$ . The stretching modes of these groups absorb in different regions, as can be seen in the Figure 6. The bands assignment in the fundamental region are based on literature data.<sup>17, 18</sup>

**Table VI** Tentative Assignment of the NIR Spectrum of the PA 6

Assignment	From Curve-Fitting (cm <sup>-1</sup> )
$\Delta v = 3$ CO stretch	4870
$\Delta v = 2$ $\text{CH}_2$ symmetrical stretching	5701
$\Delta v = 2$ $\text{CH}_2$ asymmetrical stretching	5822
	6250
$\Delta v = 4$ CO stretch	6352
$\Delta v = 2$ NH stretch	6511
Combination	6604
Combination	6752
—	7065
$\Delta v = 5$ $\text{CH}_2$ angular deformation	7199
$\Delta v = 5$ CO stretch	7869
Combination	8088
$\Delta v = 3$ $\text{CH}_2$ symmetrical stretching	8316
$\Delta v = 3$ $\text{CH}_2$ asymmetrical stretching	8599
$\Delta v = 3$ $\text{CH}_2$ stretch	9562
$\Delta v = 4$ $\text{CH}_2$ symmetrical stretching	10927
$\Delta v = 4$ $\text{CH}_2$ asymmetrical stretching	10983



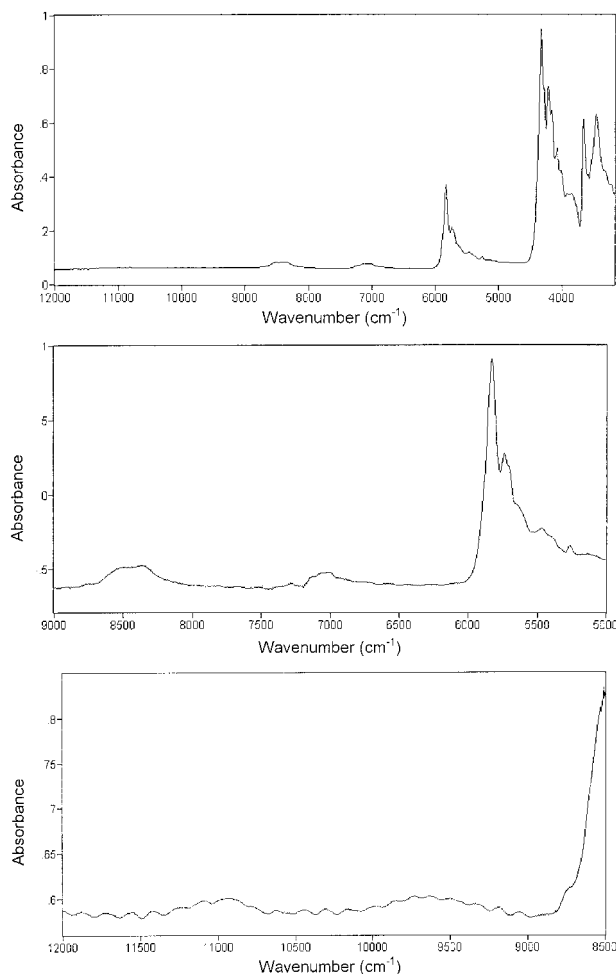
**Figure 6** MIR spectrum of PVC (thickness of the film, 0.02 mm).

The NIR spectrum of PVC is shown in Figure 7A. Films of larger thickness were used to obtain the NIR spectra presented in the Figures 7B (4 mm) and 7C (7 mm) in the regions 5000–9000 and 8500–12 000  $\text{cm}^{-1}$ , respectively. As can be seen in Figure 7B, in the first overtone region of CH stretch at  $\sim 5500$   $\text{cm}^{-1}$ , there are several bands superposed and no bands that could be assigned to the distinct  $\text{CH}_2$  stretch modes can be identified. In the same region, the first overtone of the CH stretch mode of  $\text{CHCl}$  functional group is also expected. A work published by Henry<sup>19</sup> on dihalomethanes suggests that the CH stretching of the  $\text{CHCl}$  group should present a large local mode character at the high overtone region.

The assignment of bands to the first overtone of CH stretch modes is not easy. The maxima of second and third overtone bands are not resolved in this region, as shown in Figures 7B and 7C, respectively. Additionally, the presence of interference fringes in the third overtone region, probably originated from the superposition of several films used to obtain the spectrum, makes the band resolution more difficult. The curve-fitting calculations considering a Gaussian function in the NIR spectrum in the first, second, and third overtone regions, show the occurrence of strong bands in those regions.

The fundamental frequency and frequencies calculated by curve fitting of the first, second, and third overtone regions of the NIR spectrum of PVC are presented in the Table VII.

The following wavenumber progressions, determined by curve fitting calculation were used in the Birge–Sponer plot presented in Figure 8: 2909, 5725, 8374, 10 929  $\text{cm}^{-1}$  for the  $\text{CH}_2$  stretching mode of the  $\text{CH}_2$  group and 2974, 5829, 8544, and 11 104  $\text{cm}^{-1}$  for the CH stretch mode of the  $\text{CHCl}$  group. The values of anharmonicity cor-



**Figure 7** (A) NIR spectrum of PVC (thickness of the film, 0.7 mm). (B) NIR spectrum of PVC (5000–9000  $\text{cm}^{-1}$ ; thickness of the film, 4 mm). (C) NIR spectrum of PVC (8500–12 000  $\text{cm}^{-1}$ ; thickness of the film, 7 mm).

rection (60 and 66  $\text{cm}^{-1}$ ) and mechanical frequency (2974 and 3043  $\text{cm}^{-1}$ ) were obtained for  $\text{CH}_2$  and CH stretch mode, respectively.

It can be seen in Figure 8 that the data are fitted to the straight line in the Birge–Sponer plot, suggesting that PVC presents a NIR spectrum with a large character of local mode model.

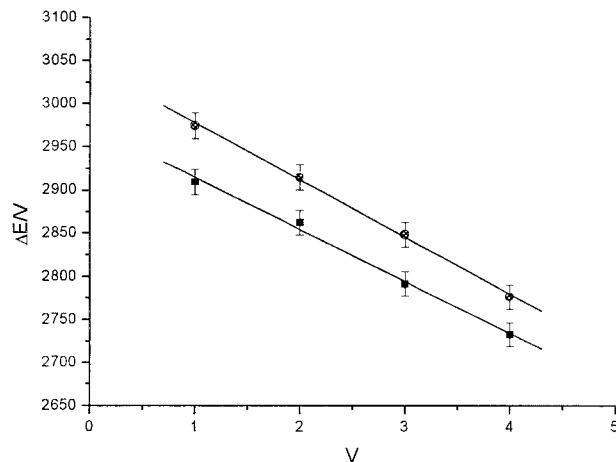
A tentative assignment based on aforementioned wavenumber is presented in the Table VII. Several unassigned frequencies (calculated by curve fitting) in Table VII should be assigned to combination bands. The tentative assignment of the bands observed between 5249 and 5505  $\text{cm}^{-1}$  by multiples or adds of the fundamentals mode didn't result in any assignment that seemed probable. The band observed around 9672  $\text{cm}^{-1}$  may also originate from combination band but having the contribution of the second overtone.

**Table VII** MIR and NIR Vibrational Frequencies and Tentative Assignment of PVC

Assignment	From Curve-Fitting ( $\text{cm}^{-1}$ )
—	2816
—	2851
—	2872
$\text{CH}_2$ symmetrical stretch	2909
$\text{CH}_2$ asymmetrical stretch	2931
CH stretch	2974
$3 \times 1198$	3453
$3 \times 1254$	3668
—	4081
$3 \times 1426$	4212
—	4325
—	5249
—	5263
—	5403
—	5505
Combination	5630
$\Delta\nu = 2$ CH stretch	5725
$\Delta\nu = 2$ $\text{CH}_2$ stretch	5829
—	5838
—	8331
$\Delta\nu = 3$ CH stretch	8374
$\Delta\nu = 3$ $\text{CH}_2$ stretch	8544
—	8702
$\Delta\nu = 4$ CH stretch	10929
$\Delta\nu = 4$ $\text{CH}_2$ stretch	11104

### Polychlorotrifluoroethylene

The formula of the constitutional repeating unit of PCTFE is  $-\text{[CFCl-CF}_2\text{]}-$ . The following



**Figure 8** Birge–Sponer plot. The transitions values used are presented in the text (where SD = standard deviation). Key: (■)  $\text{CH}_2$  stretch (SD = 0.5); (●) CHCl stretch (SD = 0.3).

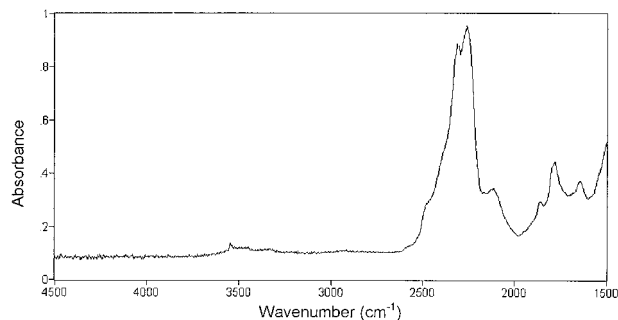


Figure 9 MIR spectrum of PCTFE.

functional groups were identified in PCTFE: CF, CCl, and CF<sub>2</sub>. The absorption bands corresponding to the stretching modes were assigned as follows:<sup>20</sup> 1285 cm<sup>-1</sup> (CF stretch), 1202 cm<sup>-1</sup> (asymmetrical CF<sub>2</sub> stretch), 1130 cm<sup>-1</sup> (symmetrical CF<sub>2</sub> stretch), and 937 cm<sup>-1</sup> (CCl stretch).

The MIR spectrum of a hot-pressed film of PCTFE of high molar mass and 0.74-mm thickness is presented in the Figure 9. In the region between 1600 and 2500 cm<sup>-1</sup> are the expected four bands corresponding to the first overtone of the distinct fundamental stretch modes, that can be identified as ~2840, 2310, 2263, and 1860 cm<sup>-1</sup>, respectively. The group of bands observed in the Figure 9 in this region, however, suggests that overtones of angular deformation or combination bands can also be present.

The NIR diffuse reflectance spectrum of PCTFE in pellet form is shown in Figure 10. In this spectrum, bands are observed in the region between 3000 and 4000 cm<sup>-1</sup> that appeared very weak in Figure 9, probably because of the low sample concentration. In this region, frequency that can be assigned to overtone of distinct fundamental frequency of stretching mode can also be expected, although the assignment based just

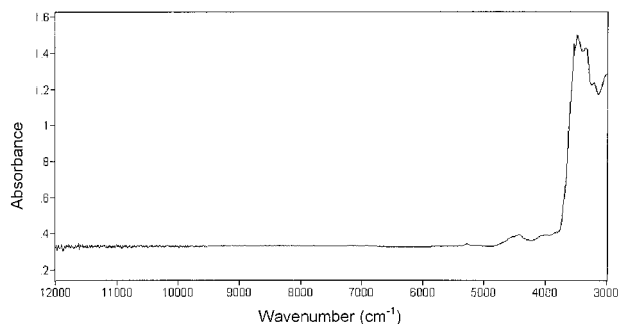


Figure 10 NIR diffuse reflectance spectrum of PCTFE.

Table VIII MID and NIR Vibrational Frequencies and Tentative Assignment of PCTFE

Assignment	From Curve-Fitting (cm <sup>-1</sup> )
CF <sub>2</sub> asymmetrical stretch	1202
CF <sub>2</sub> symmetrical stretch	1130
CF stretch	1285
Δv = 3 CF <sub>2</sub> wagging	1646
—	1783
Δv = 2 CCl stretch	1860
—	2125
Δv = 2 CF <sub>2</sub> symmetrical stretch	2255
Δv = 4 CF <sub>2</sub> wagging	2319
Δv = 2 CF <sub>2</sub> asymmetrical stretch	2349
Δv = 2 CF stretch	2484
—	3214
2125 + 1130	3255
Δv = 3 CF <sub>2</sub> symmetrical stretch	3328
—	3398
Δv = 3 CF <sub>2</sub> asymmetrical stretch	3486
2349 + 1202	3544
—	3565
Δv = 3 CF stretch	3619
—	3704
Δv = 4 CF <sub>2</sub> symmetrical stretch	4329
3486 + 937	4416
3544 + 937	4468
Δv = 4 CF <sub>2</sub> asymmetrical stretch	4568
Δv = 4 CF stretch	4749
—	5274
—	6926

on multiples of the fundamental frequency is difficult. The group of bands due to combinations among overtone with fundamental bands and/or combinations among overtone bands is also not satisfactory, and frequencies that can be assigned to overtone of angular deformation are not observed, probably because of the weak intensity of bands.

The weak and nonresolved bands between 4000 and 5000 cm<sup>-1</sup> suggest behavior of the local mode model, where all the energy is concentrated on a single oscillator CF.

Expansion of the NIR spectrum (Fig. 10) reveals two narrow bands of very weak intensity, near the region of Δv = 5, ~5274 cm<sup>-1</sup> (fourth overtone) and Δv = 6, ~6926 cm<sup>-1</sup> (fifth overtone) with a local mode profile. The NIR spectrum of PCTFE in the higher overtone region shows a narrow band with increasing the spectral wavenumber.



In the region of  $\Delta\nu = 3$  ( $3000\text{--}3800\text{ cm}^{-1}$ ), the band profile and the respective curve-fitting calculation are consistent with the occurrence of symmetrical and asymmetrical  $\text{CF}_2$  stretching frequencies.

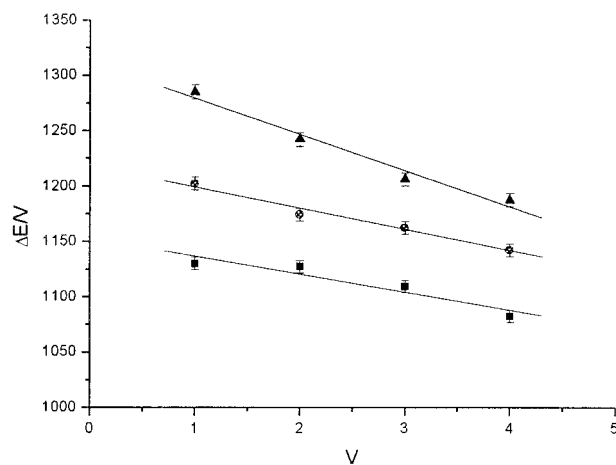
The MIR and NIR frequencies obtained from the curve-fitting calculation, considering a Gaussian function for the first, second, and third overtone region, are presented in the Table VIII. The spectral analysis and the Birge–Sponer plots of the several possibility of assignments for the overtone progression of CF stretch modes showed that the most probable progression is the following:  $1285, 2484, 3619, \text{ and } 4749\text{ cm}^{-1}$  for the CF stretch;  $1202, 2349, 3486, \text{ and } 4568\text{ cm}^{-1}$  for the asymmetrical  $\text{CF}_2$  stretch, and  $1130, 2255, 3328, \text{ and } 4328\text{ cm}^{-1}$  for the symmetrical  $\text{CF}_2$  stretch.

The Birge–Sponer plot obtained with those progressions is presented in Figure 11. The values of the anharmonicity correction and the mechanical frequency are presented in Table IX. As expected, the anharmonicity correction of the CF stretching modes should be smaller than that observed for CH functional groups primarily because of mass effect.

The tentative assignment of the MIR and NIR spectra of PCTFE are presented in the Table VIII.

## CONCLUSION

Tentative assignments of the vibrational frequencies in NIR region ( $4000\text{--}12\,800\text{ cm}^{-1}$ ) of PA 6



**Figure 11** Birge–Sponer plot. The transitions values used are presented in the text (where SD = standard deviation). Key: (■)  $\text{CF}_2$  symmetrical stretch (SD = 1.5); (●)  $\text{CF}_2$  asymmetrical stretch (SD = 0.8); (▲) CF stretch (SD = 1.4).

**Table IX** Anharmonicity Correction and Mechanical Frequency of PCTFE

Group	$\omega_e\chi_e$	$\omega_e$
CF stretch	$33 (\pm 4)$	1312
$\text{CF}_2$ asymmetrical stretch	$19 (\pm 2)$	1218
$\text{CF}_2$ symmetrical stretch	$16 (\pm 4)$	1152

and PVC were made. Because the bands superposition in several distinct  $\text{CH}_2$  stretch overtone regions, the vibrational frequencies were obtained by curve-fitting calculation, and the assignment was made according to the frequencies that gave the best fitting to straight line in the Birge–Sponer plot. The Birge–Sponer plot also gave the anharmonicity correction and the mechanical frequencies characteristic of each  $\text{CH}_2$  functional groups belonging to PA 6 and PVC. For PA 6, the parameters correlated with NH and CO stretch modes were also obtained. The NIR spectra of PA 6 and PVC were satisfactorily interpreted by the local mode theory approach.

Tentative assignments of MIR and NIR vibrational frequencies of PCTFE were also made, considering primarily the distinct CF stretch overtone regions of distinct CF functional groups of PCTFE. The vibrational frequencies were obtained by the curve-fitting calculation, and the tentative assignment was made by correlating the frequencies that gave the best fitting to straight line in the Birge–Sponer plot. The anharmonicity correction and mechanical frequencies of each CF functional group of PCTFE were obtained.

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