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POLYMER STANDARDS FOR TESTING FOURIER TRANSFORM INFRARED SPECTROMETERS

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13. ABSTRACT (Maximum 200 words)

The use of commercially available stress relieved and extruded isotactic polypropylene (iPP) samples was evaluated as a potential photometric standard for Fourier transform infrared (FT-IR) spectrometers. The parameters of polymer film dichroism, temperature sensitivity, sample thickness, and sample positioning were investigated as a function of spectral band position, width, and absorbance. The spectral band at 841 wavenumbers for iPP exhibited a Lorentzian band shape at spectral resolutions of 4 reciprocal centimeters or higher. This band allowed an experimental determination of spectrometer resolution at 4 reciprocal wavenumbers or lower with the iPP samples. The iPP samples also permitted evaluation of the spectrometer responsivity (i.e., band height and position) once the iPP film spectra were assessed as a function of polymer sample temperature.

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PREFACE

The work described in this report was authorized under Contract No. DAAD05-96-P-2192. This work was started in March 1996 and completed in May 1997.

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1. INTRODUCTION

An ideal sample that is useful for monitoring the photometric performance of Fourier transform (FT-IR) spectrometers should be a self supporting solid that is stable over a period of several years. An isotropic polymer film of the appropriate thickness mounted between two windows to minimize the effect of interference fringing and to prevent the sample from being oxidized by the atmosphere would appear to have properties approaching the optimum. The polymer spectrum should contain at least one isolated (ideally Lorentzian) band with an absorbance of between 0.2 and 2 absorbance units (AU). The band should be broad enough that it can be readily measured with a resolution parameter, ρ[1,2] (i.e., the ratio of the resolution to the full width at half height of the band) of 0.2 or less, but narrow enough that it is separated from the other bands in the spectrum by at least 4 times its full width at half height (to allow it to be measured at a variety of different spectrometer resolutions).

Preliminary studies in our laboratory indicated that isotactic polypropylene films may fulfill these criteria. One particular band, at 841 cm^{-1}, in the spectrum of isotactic polypropylene (iPP) seemed exceptionally promising as an FT-IR standard. We have, therefore, studied the temperature, polarization and resolution dependence of the center wavenumber and peak absorbance of this band. This investigation also indirectly includes a study of the reproducibility of the spectra and the algorithms for measuring the band centers.

2. EXPERIMENTAL METHODS

Two types of iPP were used in this investigation. The first type was a 50 μm thick stress relieved material acquired from Transilwrap (Chicago, IL). The polymer chains in this material are fairly (but not totally) unoriented so the spectrum exhibited a small amount of dichroism. The second type was a 6 μm thick extruded material acquired from Chemplex (Tuckahoe, NY). This material is more ordered and the spectrum exhibited greater dichroism.

It was determined that the window of choice would be BaF_2 because of the index matching between the window material and the polypropylene sample. When 4-mm thick windows were used, it was noted that the cut off of the BaF_2 window gave rise to a problem as the baseline near 841 cm^{-1} sloped excessively. This problem was overcome by simply using a thinner (2-mm) BaF_2 window (International

Crystal Laboratories, Garfield, NJ).

Spectra were obtained using a Bomem MB-100 FT-IR spectrometer with a deuterated triglycine sulfate (DTGS) detector that was known to produce a linear response. The sample was placed in a variable-temperature sample cell (Harrick Scientific, Ossining, NY) with a Fisher Isotemp refrigerated circulator to maintain and control the temperature.

3. RESULTS AND DISCUSSION

3.1 SAMPLE DICHROISM

Because of the properties of the materials used in the fabrication of beamsplitters, the beam in every FT-IR spectrometer is polarized to some extent. Thus any dichroism exhibited by a polymer film will reduce its desirability for use as a photometric standard for FT-IR spectrometry. In practice, both iPP samples that were tested exhibited some level of dichroism.

As expected, the stress-relieved isotactic sample studied first had the lowest dichroism. A series of spectra was measured as the polarizer was rotated through 90°. The absorbance at 841 cm^{-1} varied by about ±4.5% for this sample, see Figures 1 and 2. When the same experiment was performed using the extruded iPP, the absorbance varied by more than a factor of 2 as the polarizers was rotated through 90°. To minimize the effect of dichroism, 2 layers of the sample were mounted so the orientation of the polymer chains in each layer were mutually perpendicular. In this case, the absorbance at 841 cm^{-1} varied by about ±1.2%, as shown in Figures 3 and 4. This method of mounting the sample appears to be the most promising means of eliminating the effect of chain orientation.

3.2 REPRODUCIBILITY OF BAND CENTER ESTIMATION

The position, full-width at half height (FWWH) and peak absorbance of a band can vary significantly as a function of temperature. Obviously, the bands in an ideal sample will exhibit no significant change in the center wavenumber, full-width at half-height (FWHH) and peak absorbance of analytically useful bands over a wide temperature range. Three methods are commonly used for the determination of the center of a band. In the first the center of mass (gravity) is calculated.[3] The second involves fitting an entire band or band multiplet to one or more synthetic bands with well defined shapes; this method is usually known as curve fitting. In the third method, known as either the cubic spline or peak-fitting methods, a cubic equation is fitted to the points around the top of the peak and the second derivative is calculated; the wavenumber at which the second derivative is zero is the maximum value of the peak. Different algorithms are typically recommended by different spectrometer manufacturers. The center-of-mass and curve fitting methods, as incorporated in GRAMS/32 supplied by Galactic Industries Corporation, were tested in this study, with the center-of-mass algorithm typically having twice as good reproducibility as the curve-fitting algorithm.

To test the temperature dependence of the 841-cm^{-1} band of iPP, spectra were measured every 5°C from 10°C to 50°C. Spectra of the stress relieved iPP sample were measured at 2-cm^{-1} resolution (unapodized); the standard deviation of the peak center determined by the center-of-mass algorithm was 0.011 cm^{-1}. Typical results are shown in Figures 5 and 6. The same procedure used with the two-layer extruded iPP sample gave a standard deviation of 0.005 cm^{-1}, see Figures 7 and 8.

The standard deviation of the band center for the series of spectra of the stress relieved iPP samples measured between 10 and 50°C obtained by curve fitting using a mixed Lorentzian/Gaussian band shape was 0.022 cm^{-1} which was twice that of the center of mass operation, see Figure 9. The corresponding standard deviation for the extruded iPP sample was 0.017 cm^{-1}, see Figure 10. Thus it was concluded that the center-of-mass method gave more reliable results. Of more importance, perhaps was the fact that the actual value of the peak center reported using the two algorithms were different by about 0.2 cm^{-1}, possibly because of a small peak asymmetry. Thus to obtain consistent results, the same algorithm should always be used.

Two factors can affect the value of the peak position reported by the software, the reproducibility of the placement of the sample in the beam, discussed in *d* below, and the number of interpolated data points between each independent datum; in FT-IR spectrometers, the latter is usually determined by the extent of zero filling applied to the interferogram.

3.3 INTERPOLATION

In principle, zero-filling[4,5] allows band centers to be measured more accurately than for non-interpolated data because there are more data points located near the peak center. This would be expected to become particularly important if the spectrum is measured with a resolution numerically greater than the FWHH of the band of interest. By changing the number of data points used for the calculation, however, it is possible that the band center shifts from the value calculated using no zero filling. Surprisingly, however, the standard deviation for the temperature dependent series was 0.011 cm^{-1} for non-zero-filled spectra and 0.015 cm^{-1} after zero filling. It can also be seen that there is a wavenumber shift of about 0.2 cm^{-1} between the zero filled and non-zero-filled data, Figure 11.

3.4 PLACEMENT OF SAMPLE AND REPRODUCIBILITY

Small changes in the position at which the sample cell is mounted in the sample chamber can have even larger effects on the calculated band center if the diameter of the sample is smaller than the diameter of the beam in the sample chamber (i.e. if *vignetting* occurs).[6] This effect can be seen in Figure 12, where the sample cell was bumped between the measurements of 30 and 35°C by an amount that was just enough to cause the discontinuity in the series. Ideally, the diameter of the sample should be large enough to avoid vignetting. The cell used for our measurements did not allow vignetting. The cell used for our measurements did not allow us to avoid vignetting, however. This leads to the question of how reproducible are the series from run to run instead of with in the series it self. As can be seen from Figures 13 and 14, there is difference from run to run using the same sample, and that sample position reproducibility is an important factor.

3.5 VARIATION OF BAND WIDTH, HEIGHT AND AREA WITH TEMPERATURE

The fact that the center wavenumber changes by considerably less than 0.1 cm^{-1} as the temperature is varied by 40°C suggests that the 841-cm^{-1} band is a good one to use as a standard for testing the performance of FT-IR spectrometers. We were also interested in whether iPP could be used as a photometric standard for commercial FT-IR spectrometers. To be a good photometric standard, the height and width of the band should also remain constant as the temperature of the sample is changed. In practice, this is much more difficult to achieve as the FWHH of most samples increases with temperature. The width of the band, as estimated by curve-fitting a spectrum measured at 2 cm^{-1} resolution, is approximately 3.3 cm^{-1} and increases from 3.1 to 3.5 cm^{-1} as the temperature is increased from 10 to 50°C, see Figure 16. As expected for such a narrow band, the measured width is dependent on spectral resolution, as shown in Figures 16-23, although the widths measured at 1 and 2 cm^{-1} are essentially identical (as they should be for unapodized spectra measured with a resolution parameter less than 0.5). When the iPP spectrum is measured at 8 and 16 cm^{-1}, the shape of the 841-cm^{-1} band changes from largely Lorentzian to that of the sinc function corresponding to the instrument line shape (ILS) function of the spectrometer.[7] (None of these spectra are apodized). For low resolution spectra, the measured FWHH is approximately equal to maximum optical path difference times 0.61, i.e., the width is about the same as the FWHH of the sinc ILS function of an unapodized spectrum. For such spectra, the 841-cm^{-1} band shows very strong side-lobes, as expected, see Figure 16. The FWHH of this band increases with temperature, changing from about

3.1 cm^{-1} at 10°C to 3.5 cm^{-1} at 50°C in the spectrum of extruded iPP when measured with $\rho<1$ without apodization, see Figures 16, 17 and 18. The band in the spectrum of the (less oriented, and hence probably less crystalline) stress-relieved iPP is about 4.3 cm^{-1}, with very slightly less temperature dependence than the extruded polymer, see Figures 19, 20, 21, 22, and 23.

As would be expected, the peak absorbance of the band decreases with temperature, as shown for extruded iPP in Figures 24-26 and for stress-relieved iPP in Figures 27-31. Surprisingly, the band area varies quite significantly with temperature, as shown in Figure 32 for stress relieved iPP and Figure 33 for the extruded polymer. If one assumes that the temperature of most laboratories is held between 68 and 72°F (20-22°C), it is probable that the greatest variance in FWHH, peak height and band area will come from the amount by which the sample is heated by the infrared beam in the sample compartment.

The biggest difficulty with using polymer films as photometric standards is the sample-to-sample variation in their thickness. It is possible that the film thickness can be measured prior to mounting them between the BaF_2 windows either from the interference fringes in the spectra of the unsupported films or from the small signature in the interferogram. (Both of these phenomena originate from internal reflection in the film.) We propose to investigate the feasibility of this during the final period of this cooperative agreement.

4. CONCLUSIONS

Stress relieved isotactic polypropylene is a reasonable choice for a performance standard. However this requires two films to be mounted at 90° to each other to avoid the effects of dichroism.

For the calculation band centers, there appears to be a statistical advantage in using the center of mass algorithm over peak fitting methods. This gives the additional advantage that the center-of-mass algorithm is more easily automated.

At least a 4x zero fill is required to determine the band center with any degree of statistical accuracy at resolutions of 2 cm^{-1} through 8 cm^{-1}. Because of the sharpness of the 841-cm^{-1} band (~3 cm^{-1} FWHH) the spectra measured at a 8 cm^{-1} resolution using a boxcar truncation function do show the effects of side lobes (see, for example, Figure 15) and an appropriate apodization function should be applied.

The reproducibility of sample position appears to be more important than the effect of band shift due to temperature. Thus either the sample must have significantly larger diameter than the beam or great care must be taken during positioning to guarantee reproducibility from run to run.

Both the width and height of the 841-cm^{-1} band of isotactic polypropylene are somewhat temperature dependent. Nonetheless, this band has many of the properties that are desirable for a wavenumber and photometric standard.

Figure 1

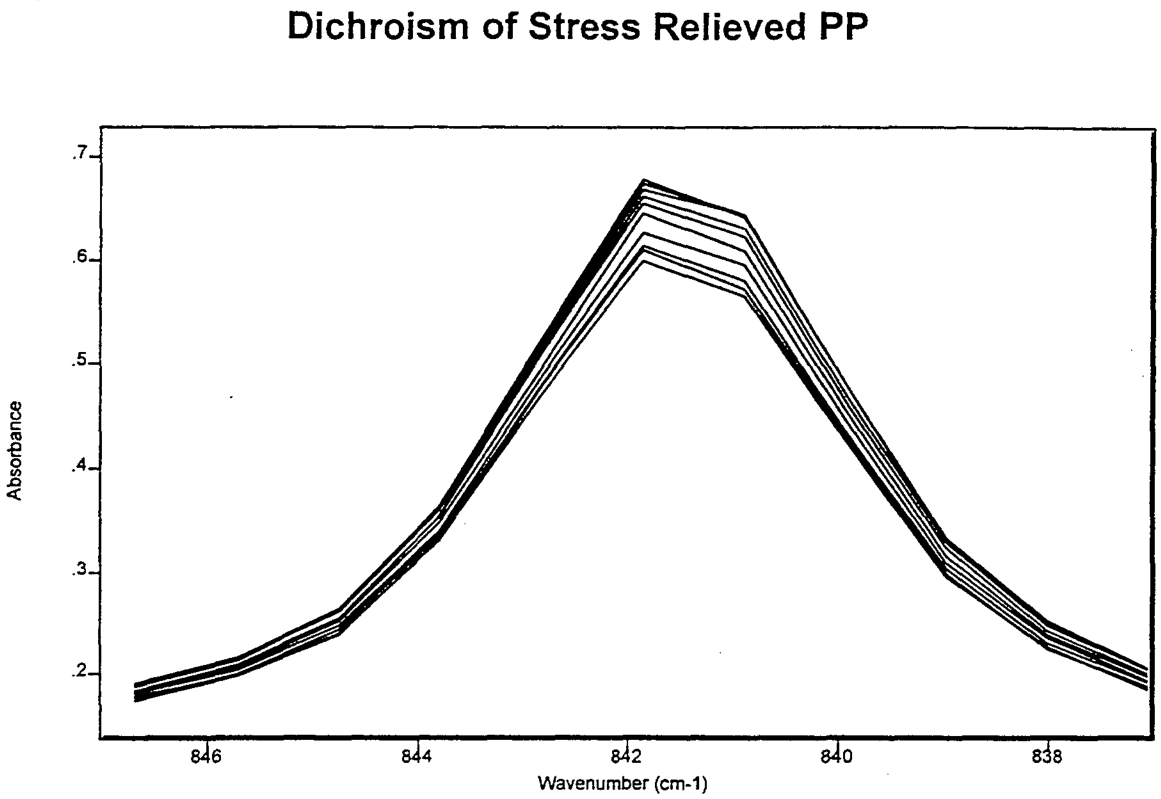


Figure 2

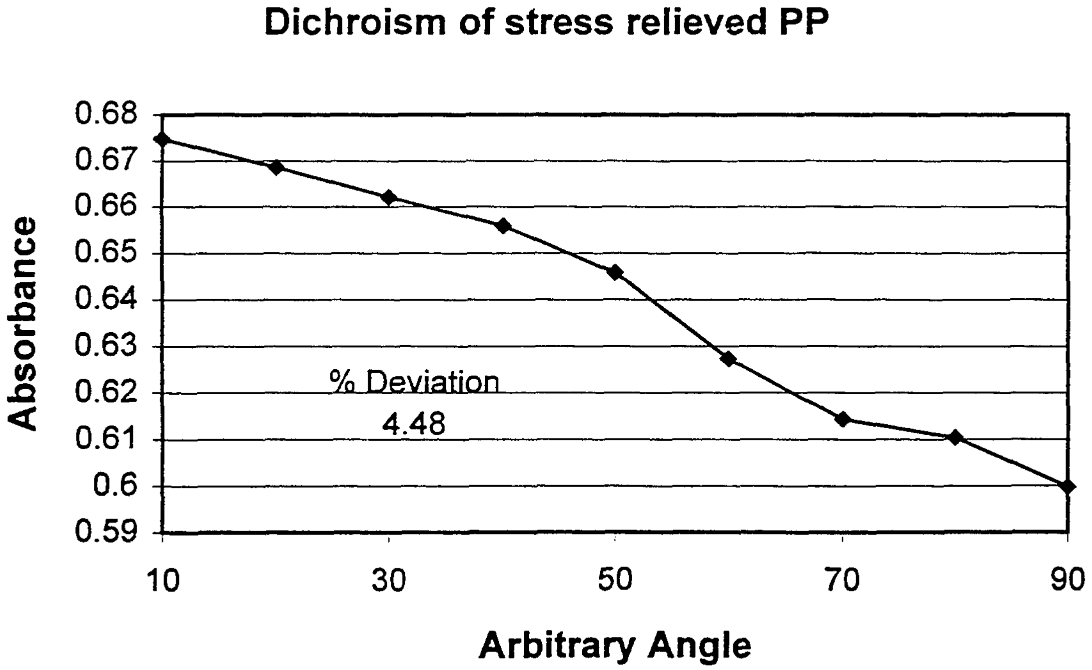
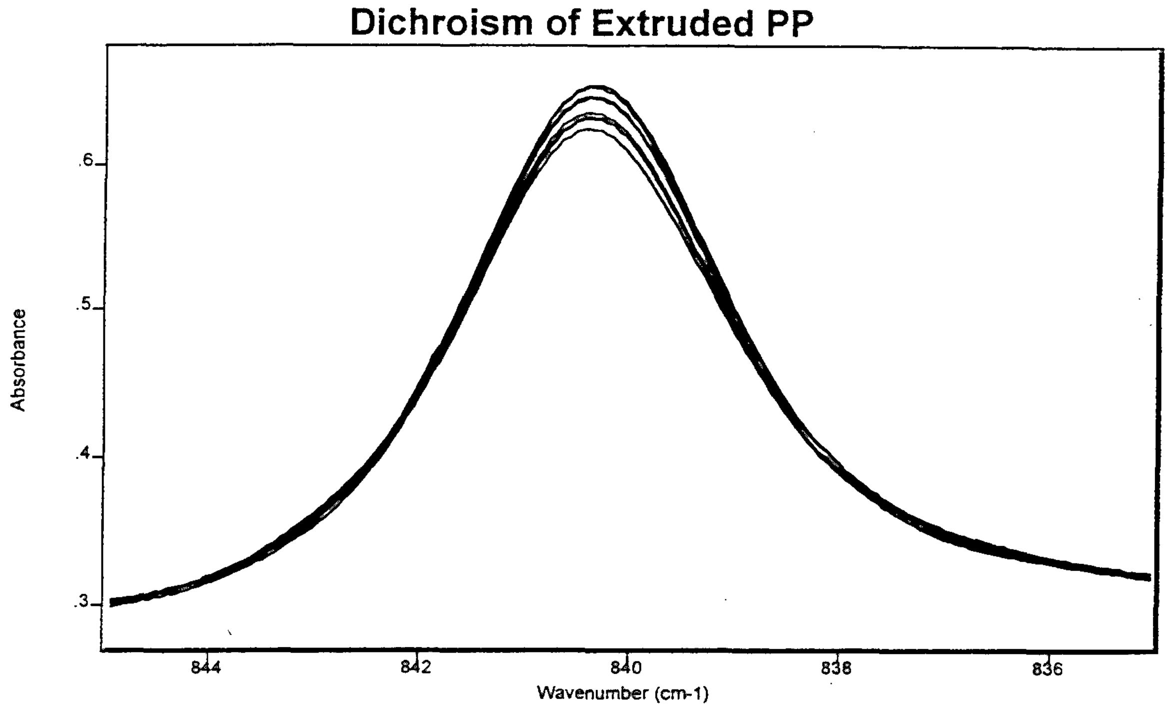


Figure 3



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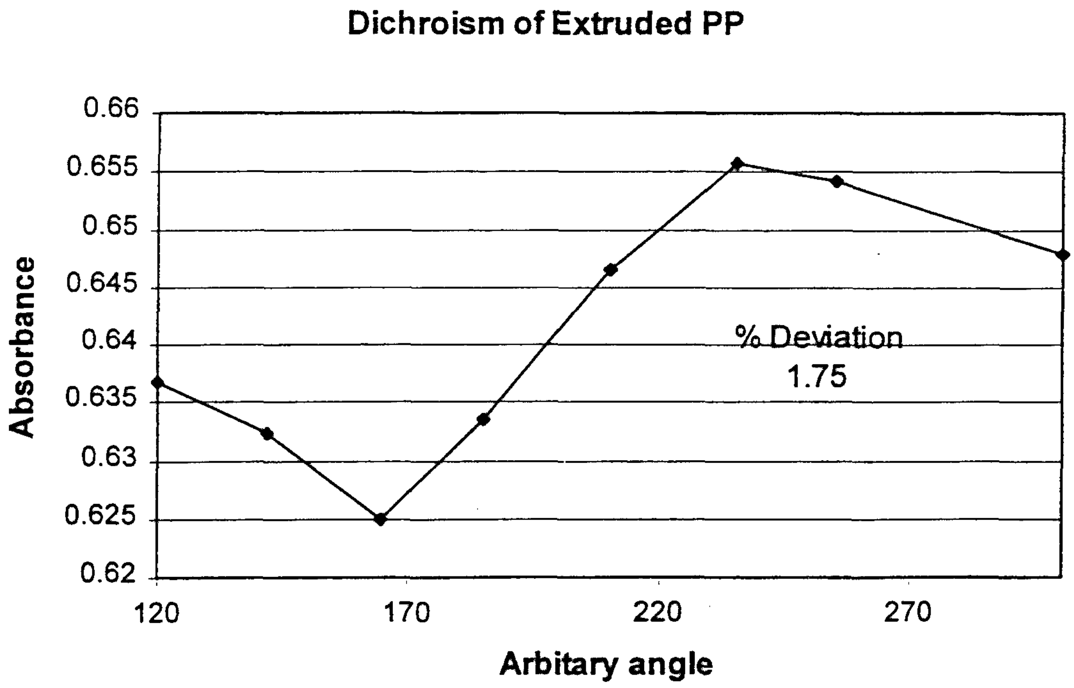

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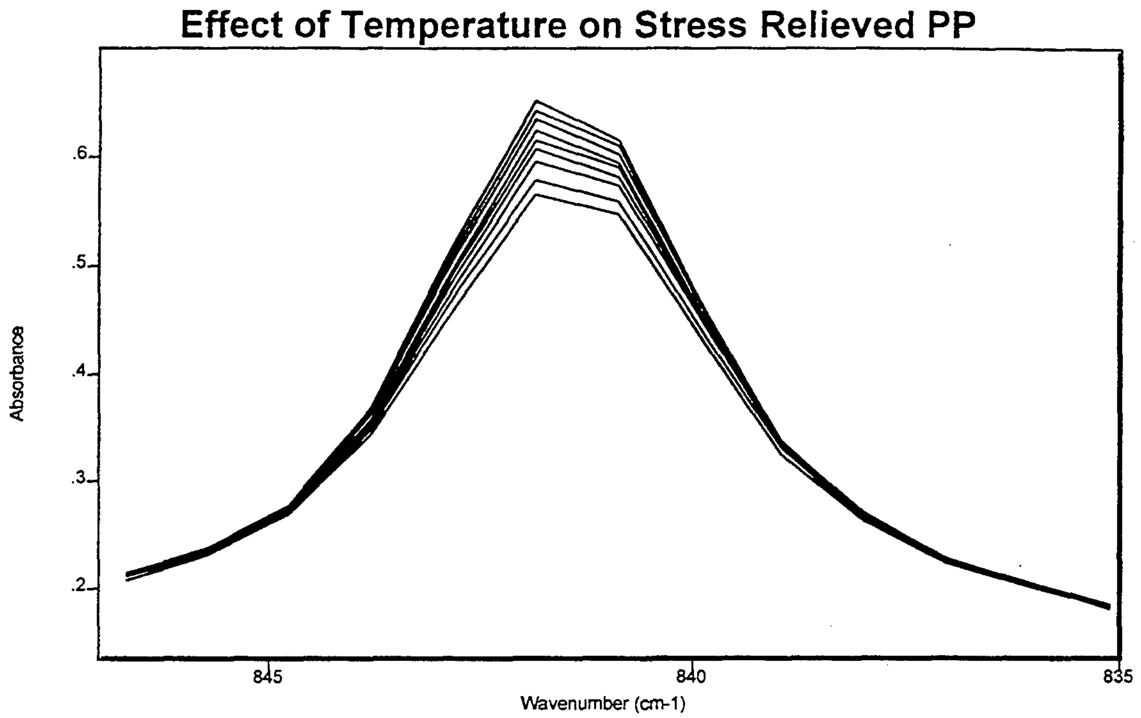

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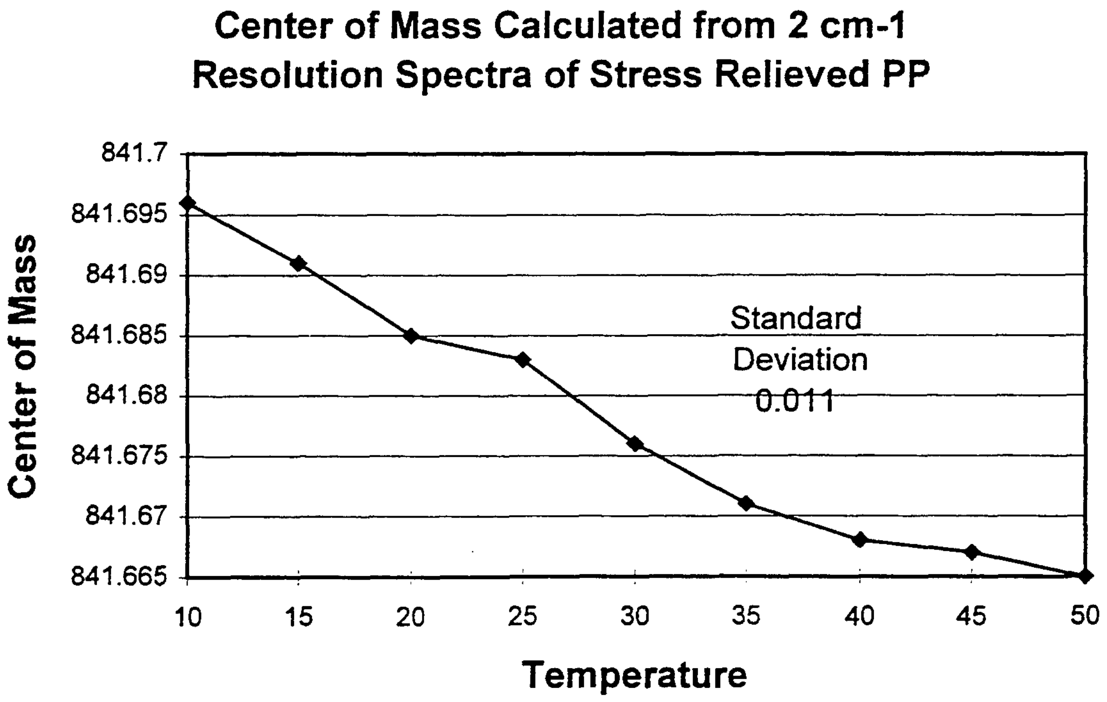

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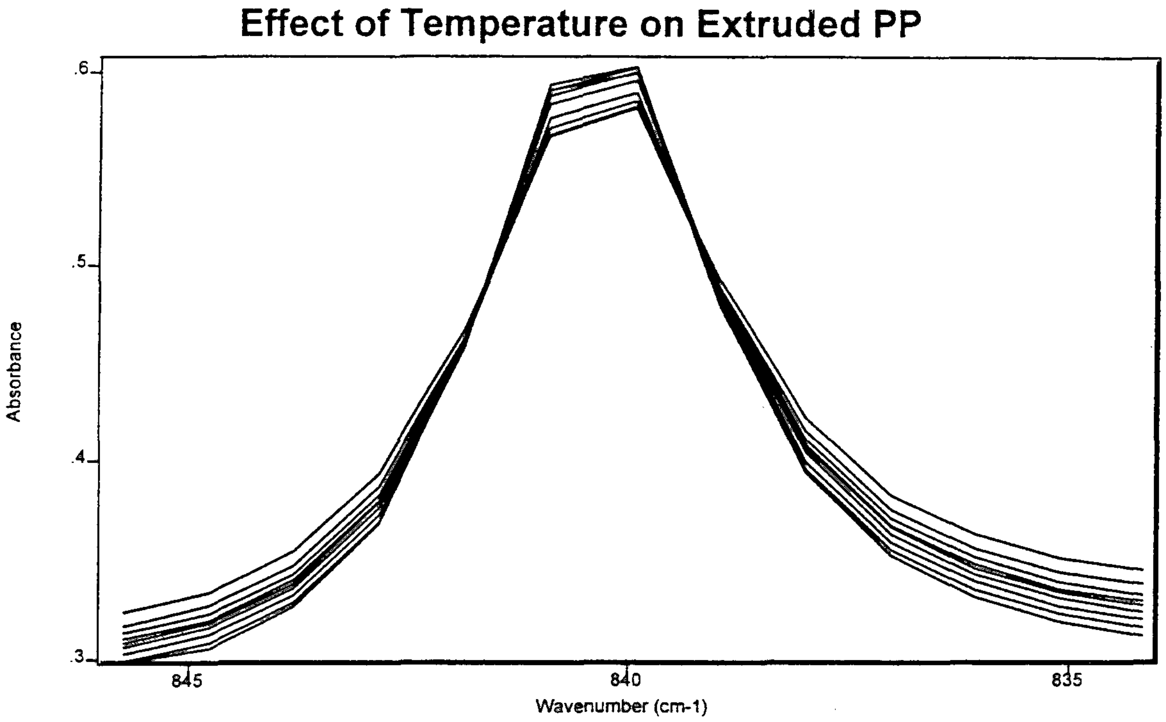

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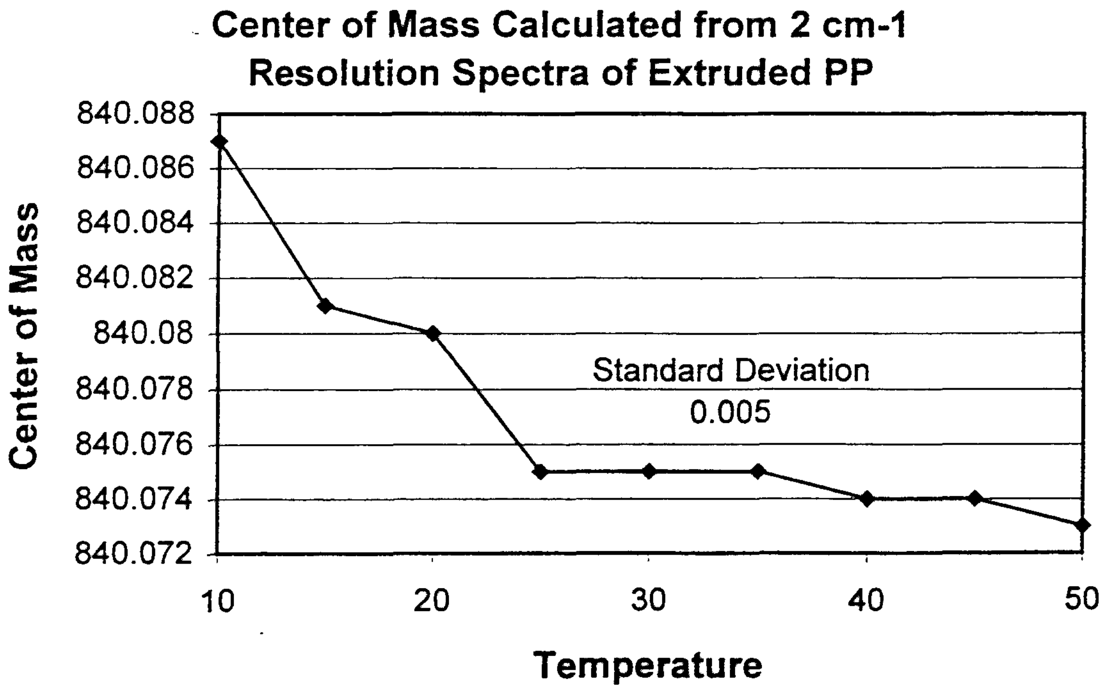

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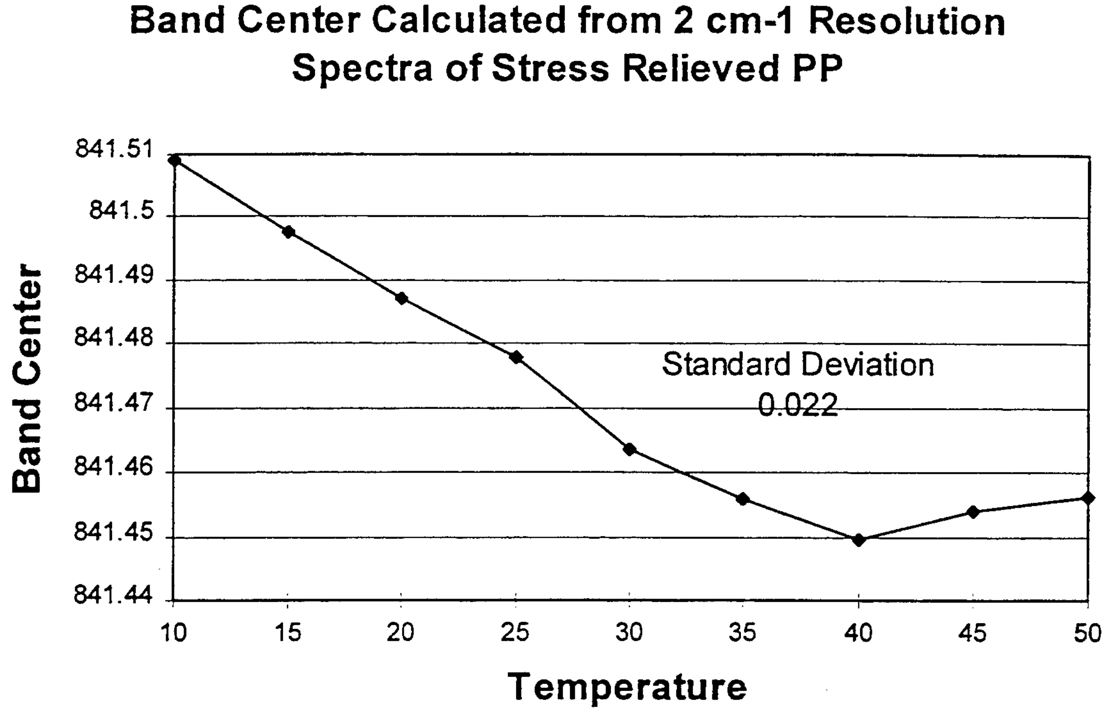

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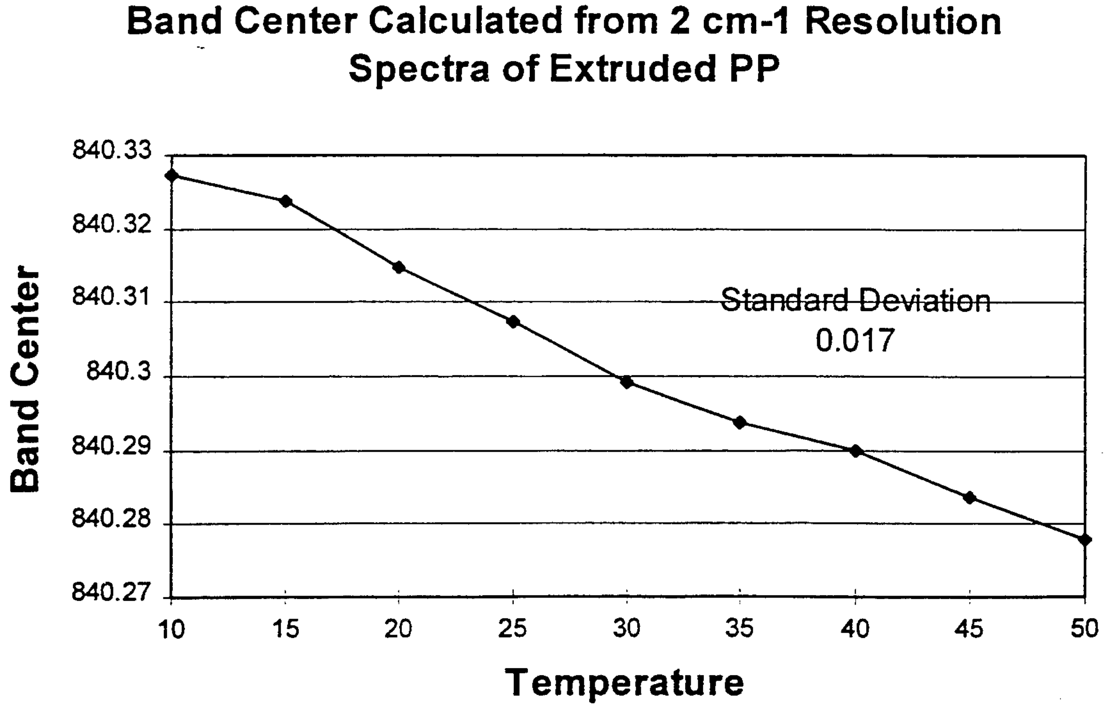

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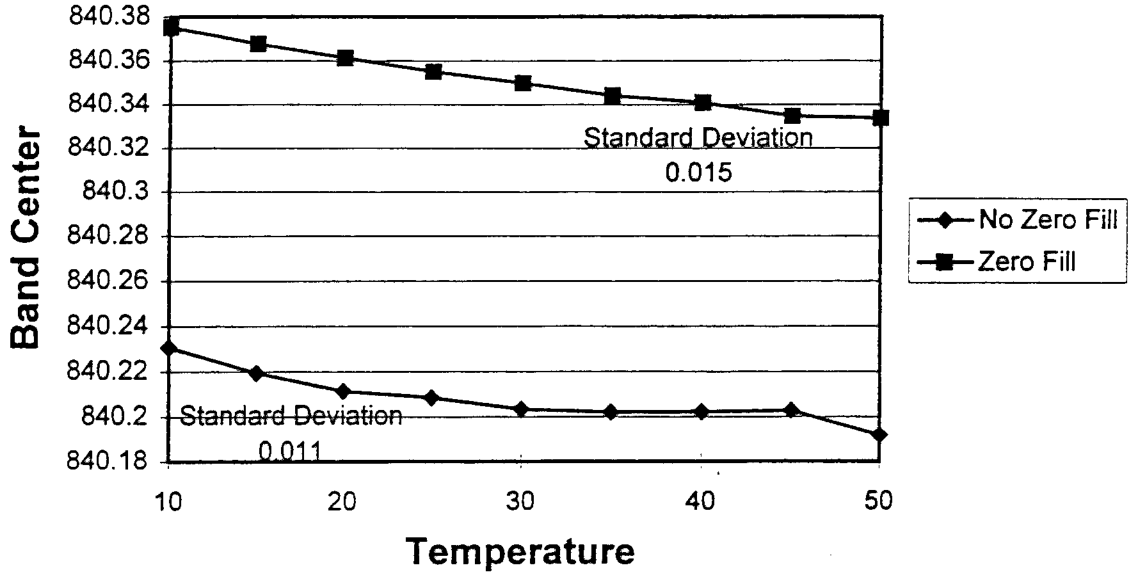

Band Center Calculated from 4 cm-1 Resolution Spectra of Extruded PP

Figure 12

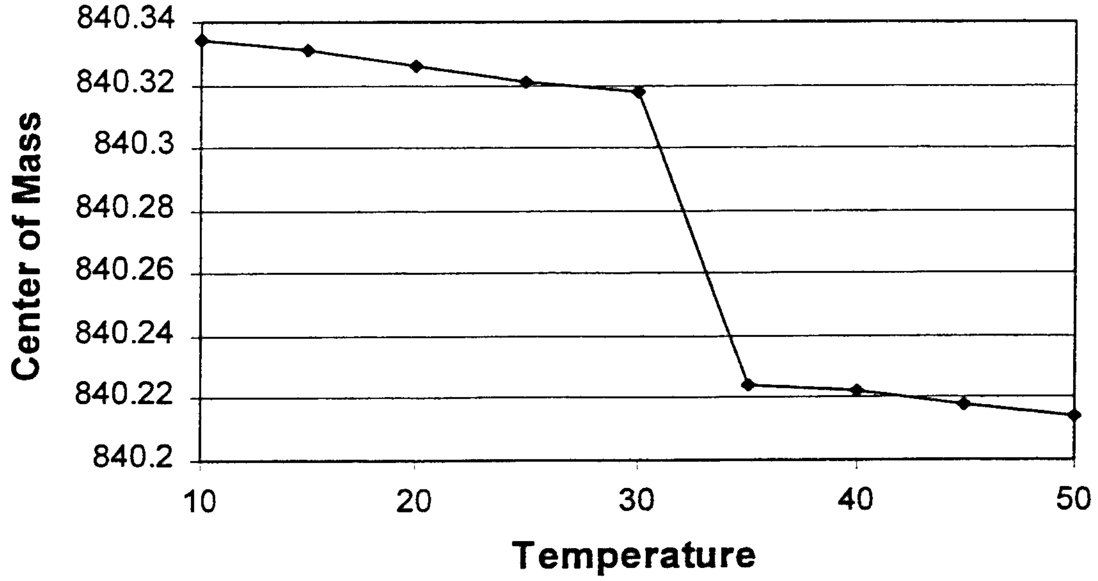
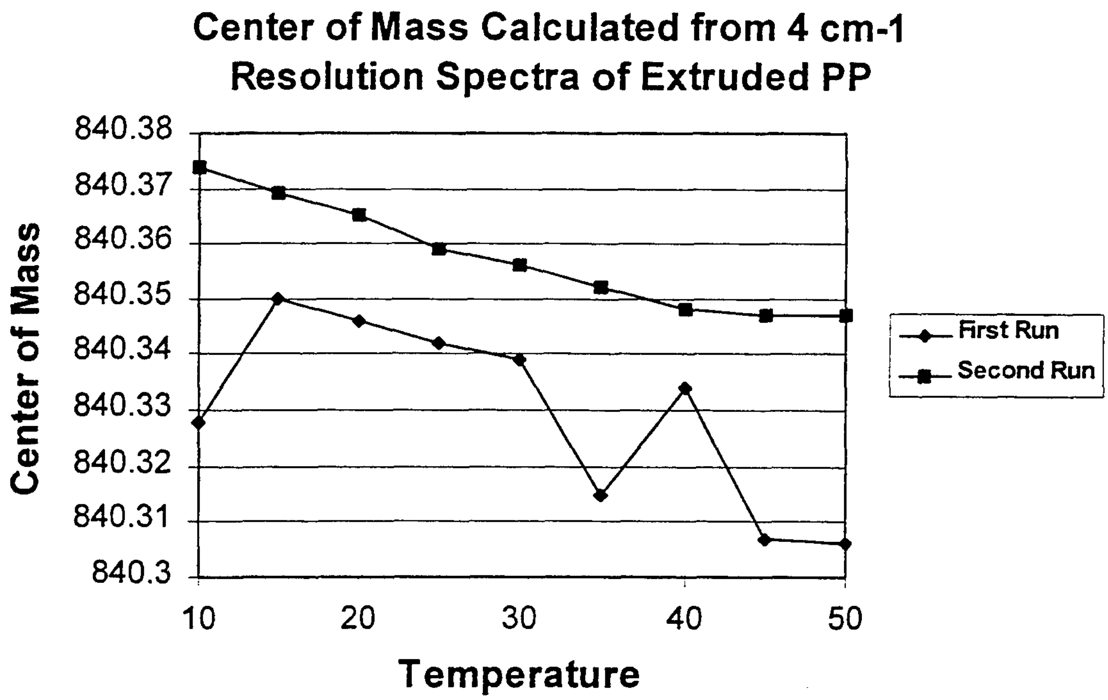

Center of Mass Calculated from 8 cm-1 Resolution Spectra of Extruded PP

Figure 13



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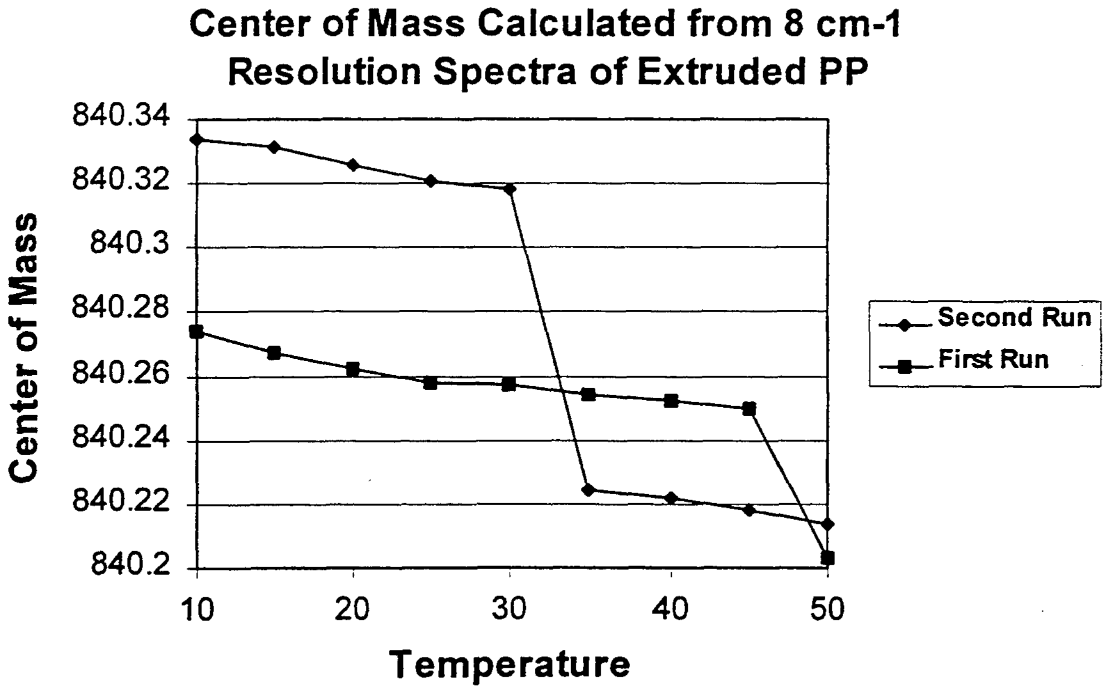


Figure15

Effect of Boxcar Truncation Function on Bands Measured at Resolutions Greater Than Their FWHH

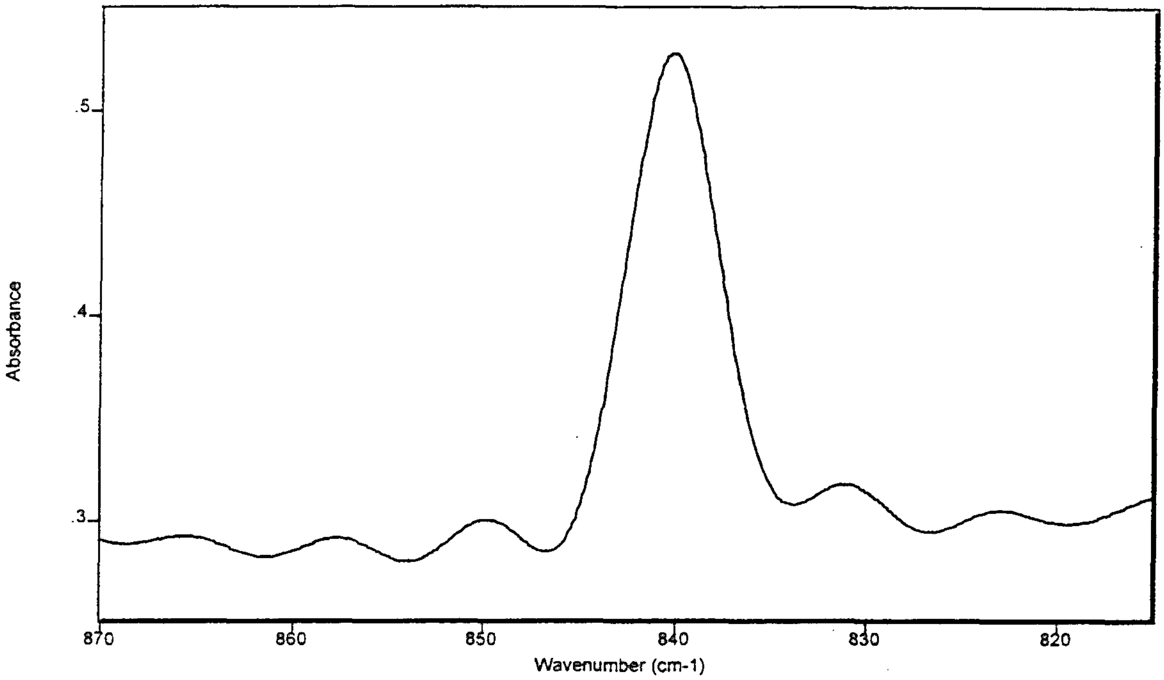
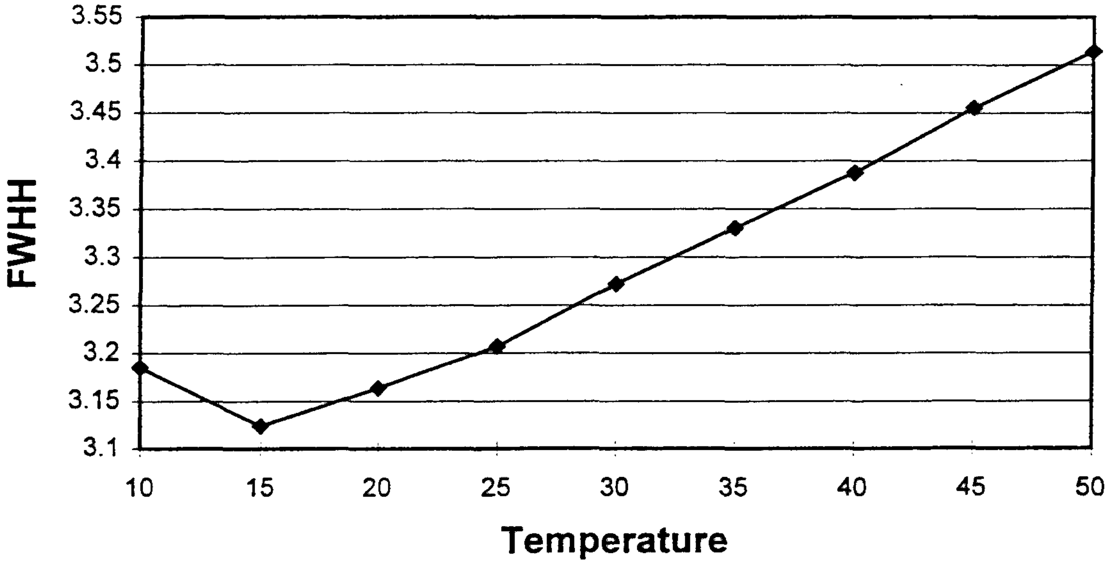


Figure 16

Band Width Calculated from 2 cm-1 Resolution Spectra of Extruded PP



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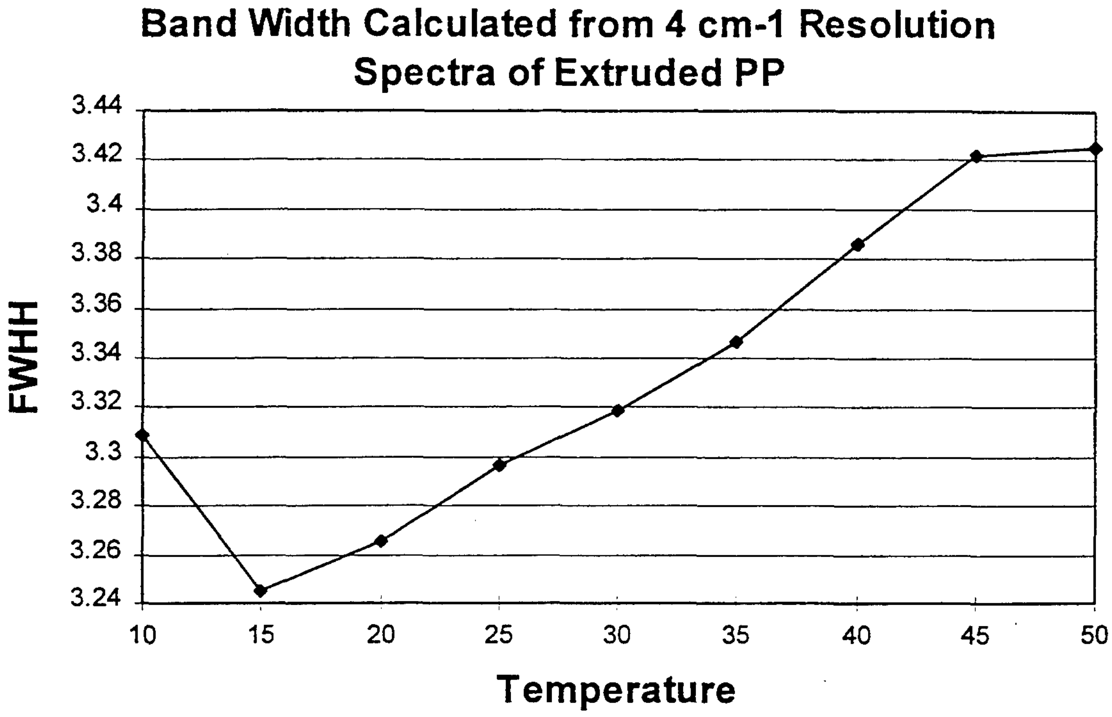

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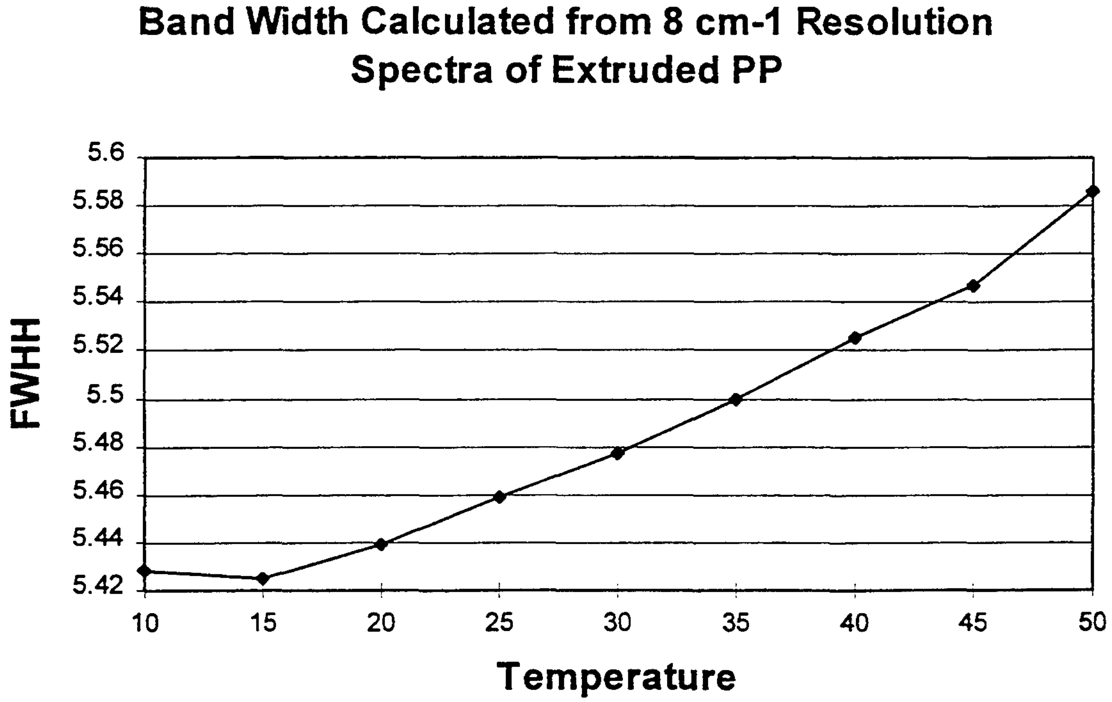

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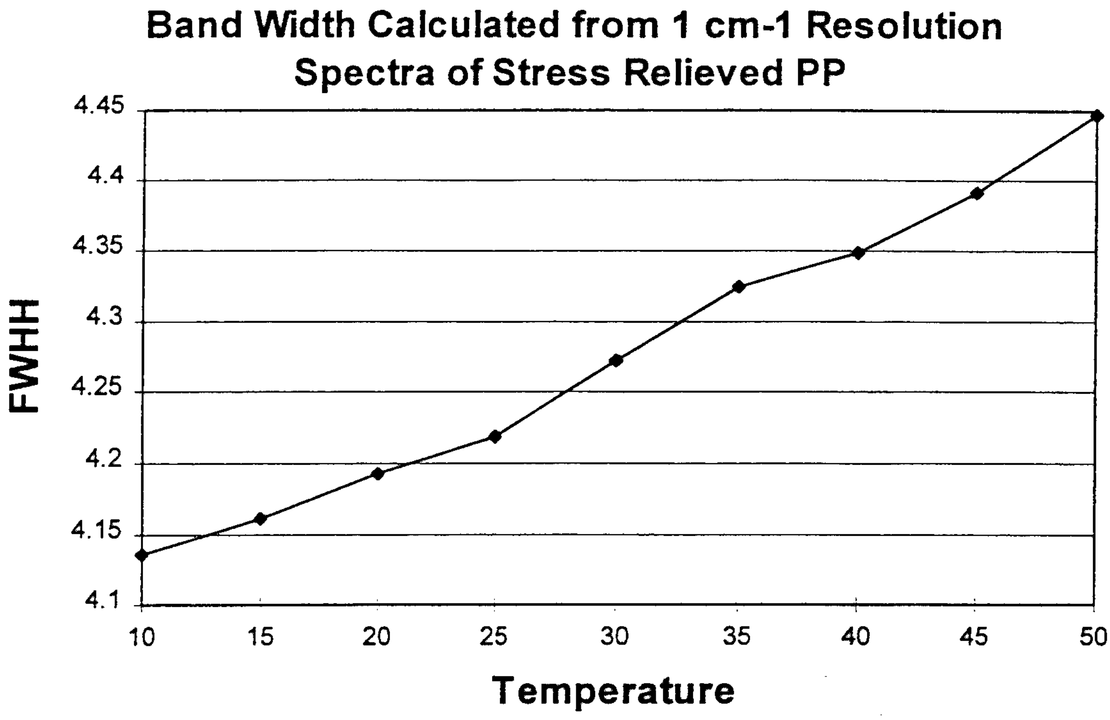

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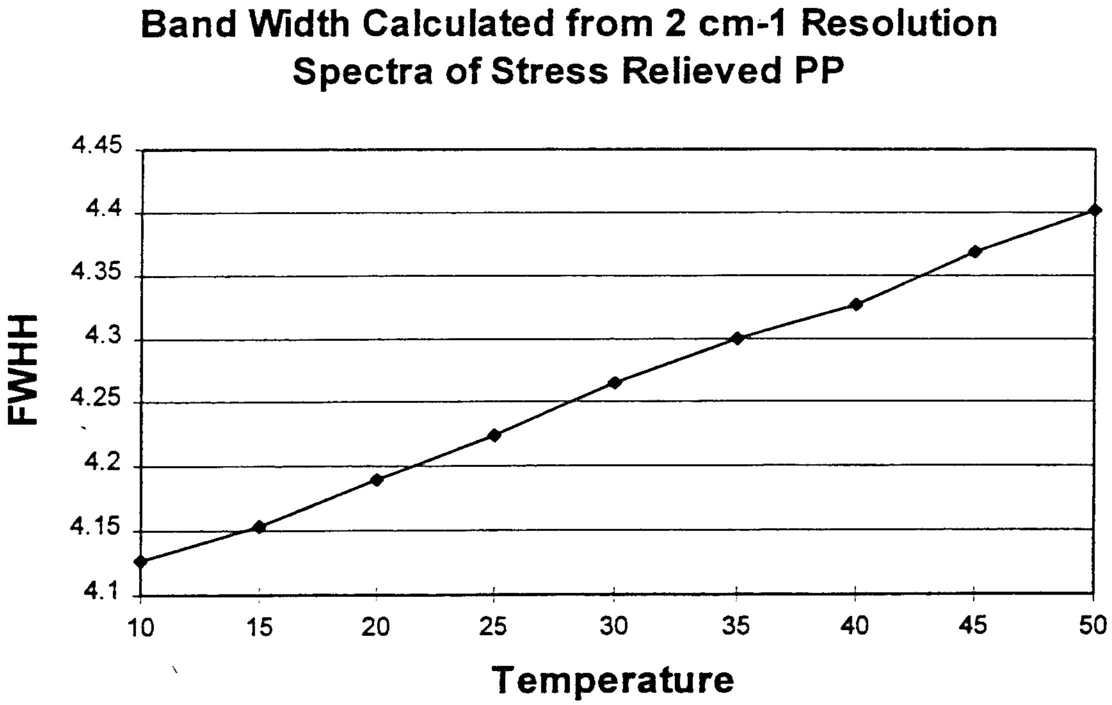


Figure 21

Band Width Calculated from 4 cm-1 Resolution Spectra of Stress Relieved PP

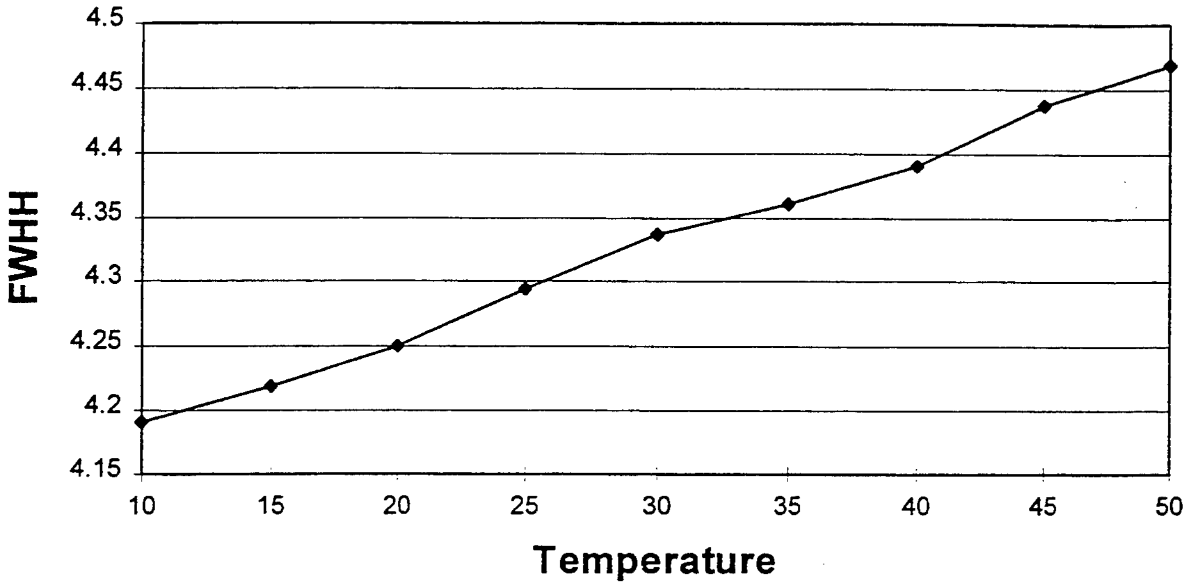
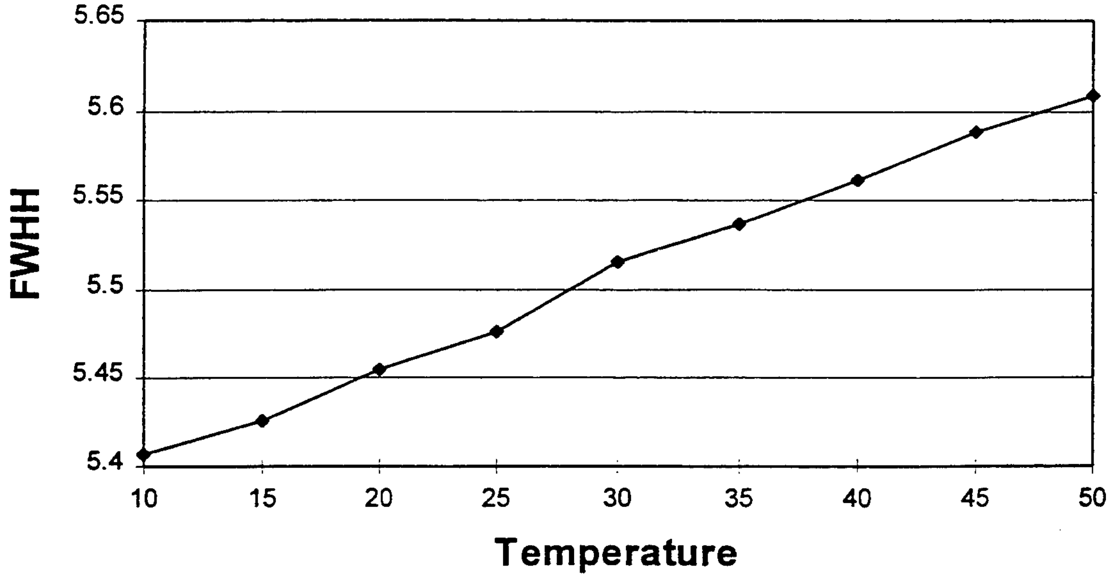


Figure 22

Band Width Calculated from 8 cm-1 Resolution Spectra of Stress Relieved PP



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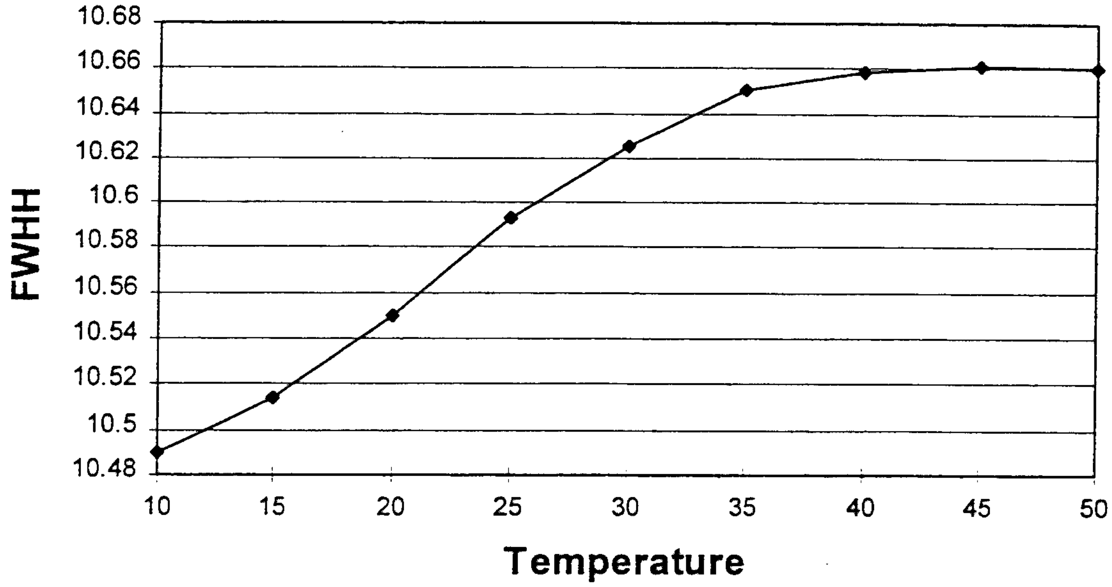

Band Width Calculated from 16 cm-1 Resolution Spectra of Stress Relieved PP

Figure 24

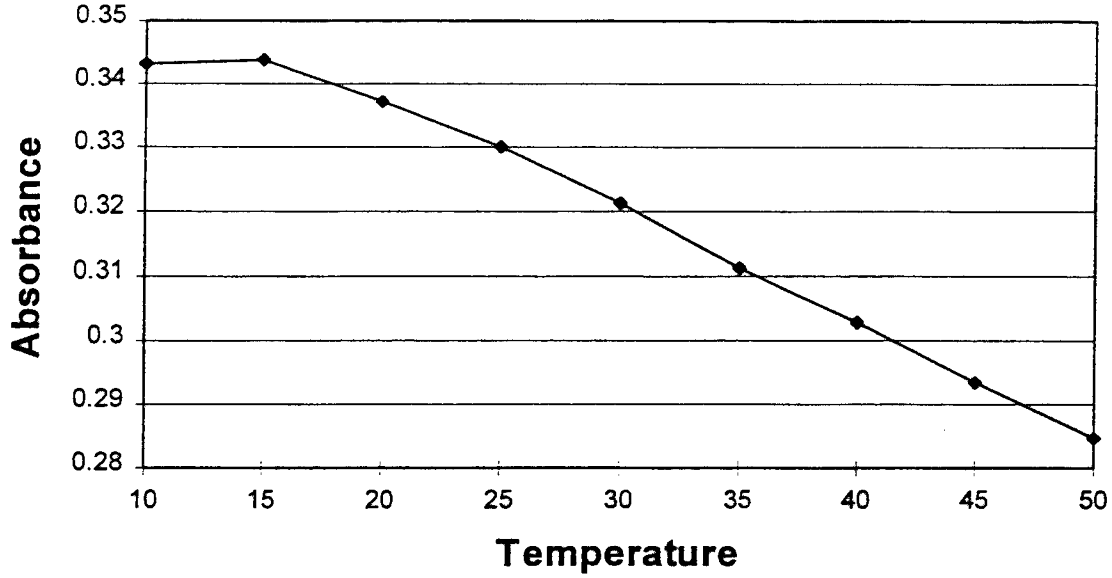
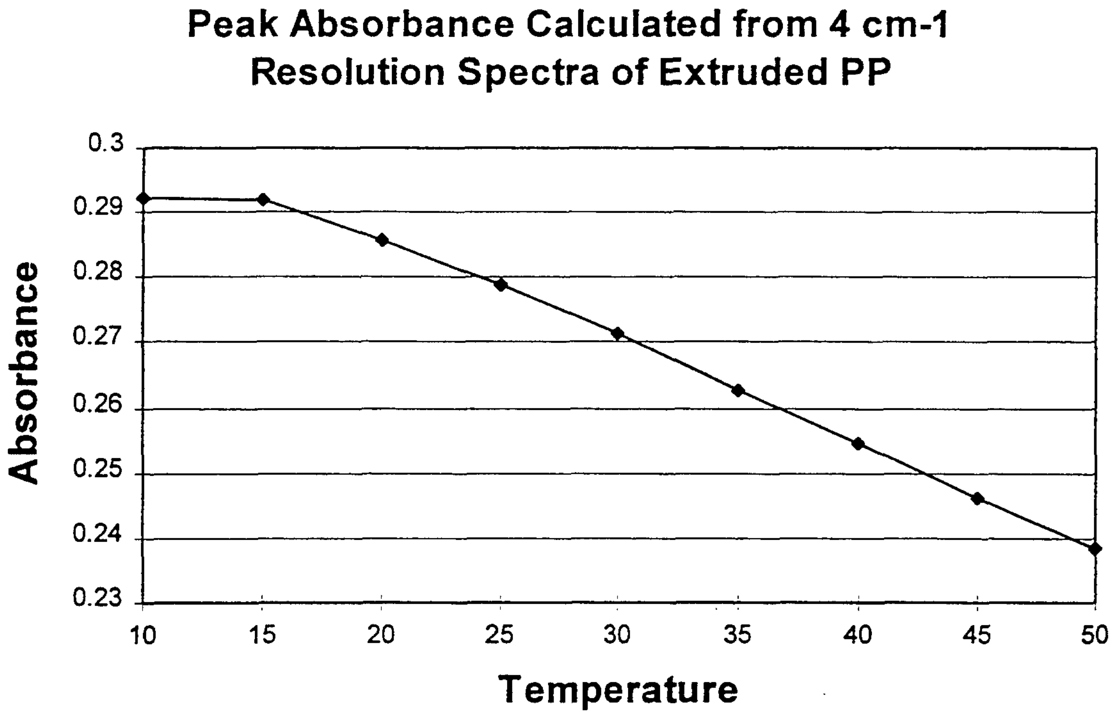
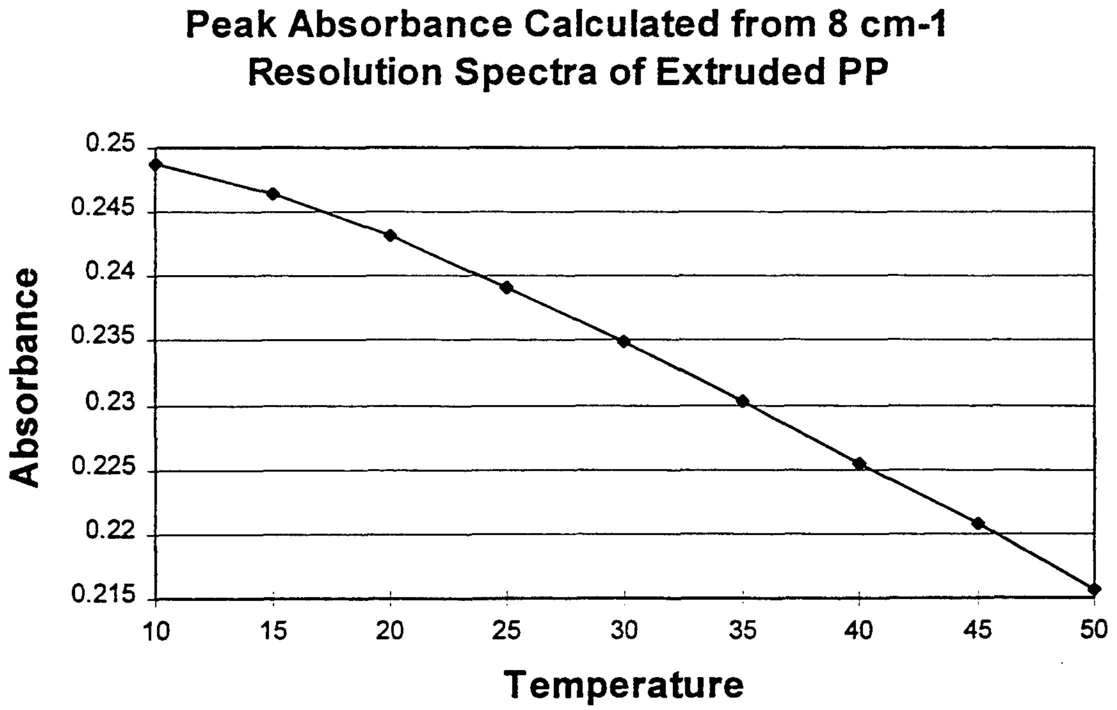

Peak Absorbance Calculated from 2 cm-1 Resolution Spectra of Extruded PP

Figure 25



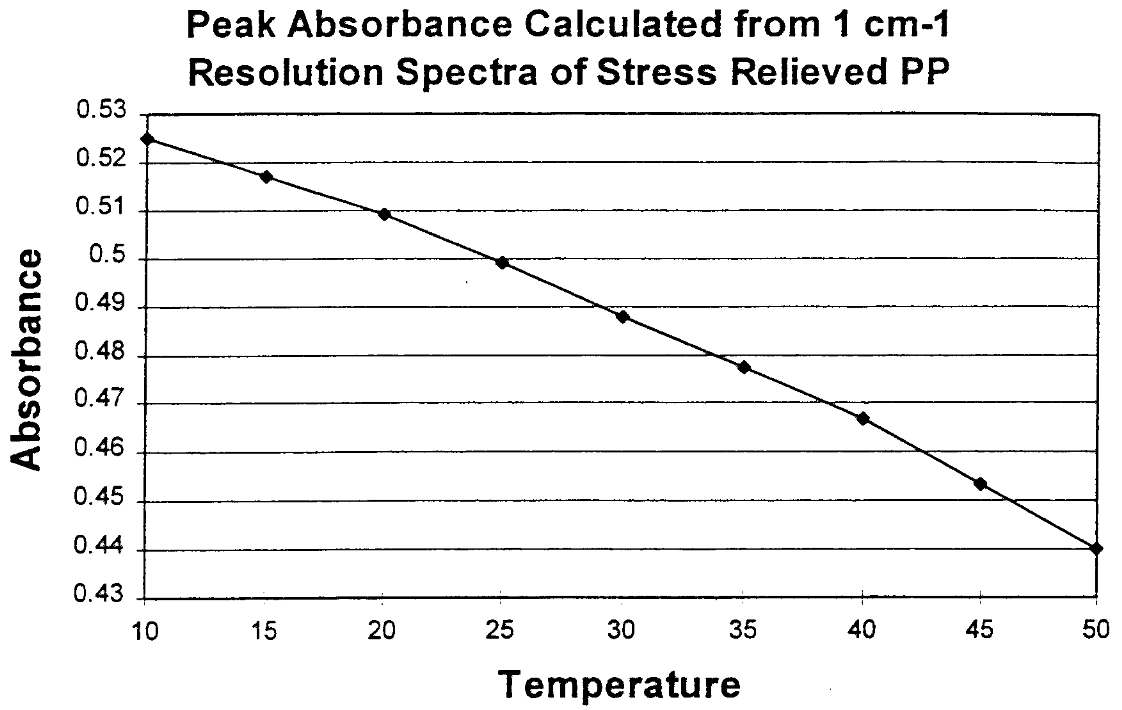
Peak Absorbance Calculated from 4 cm-1 Resolution Spectra of Extruded PP

Figure 26



Peak Absorbance Calculated from 8 cm-1 Resolution Spectra of Extruded PP

Figure 27



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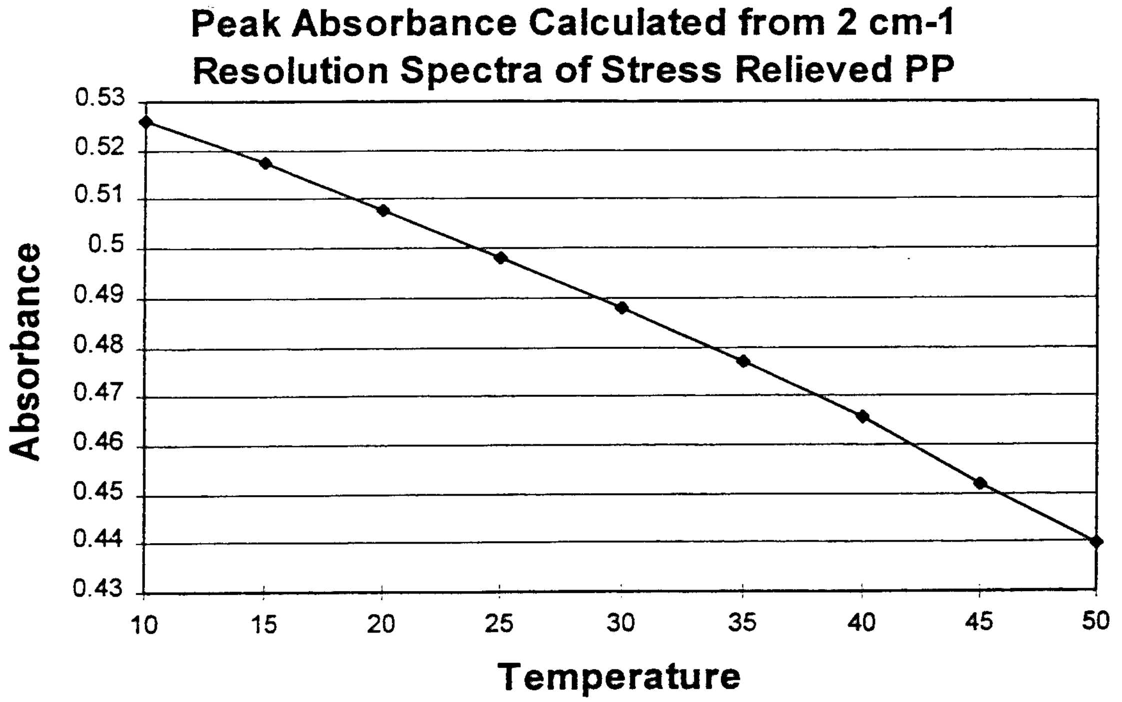

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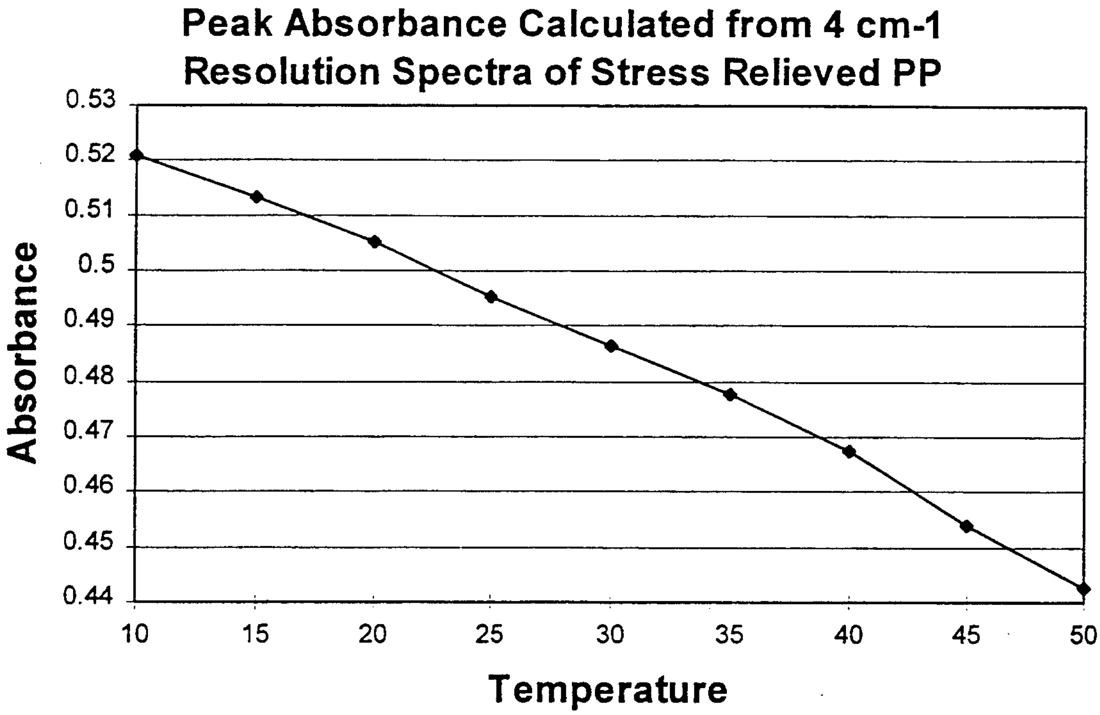

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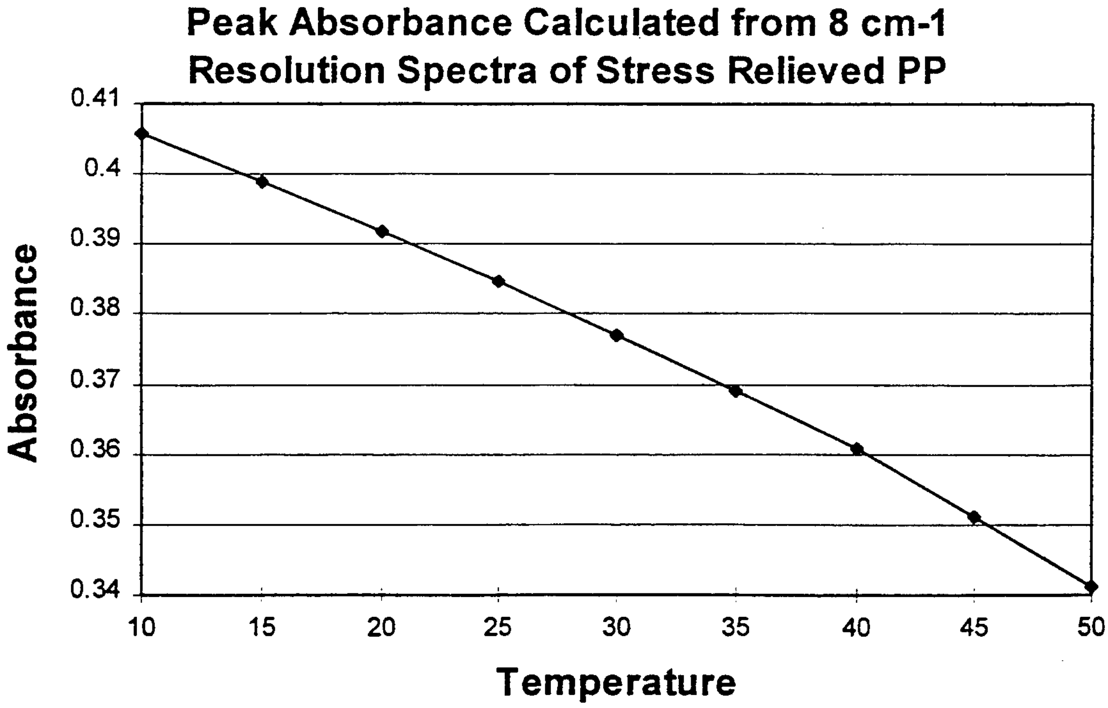

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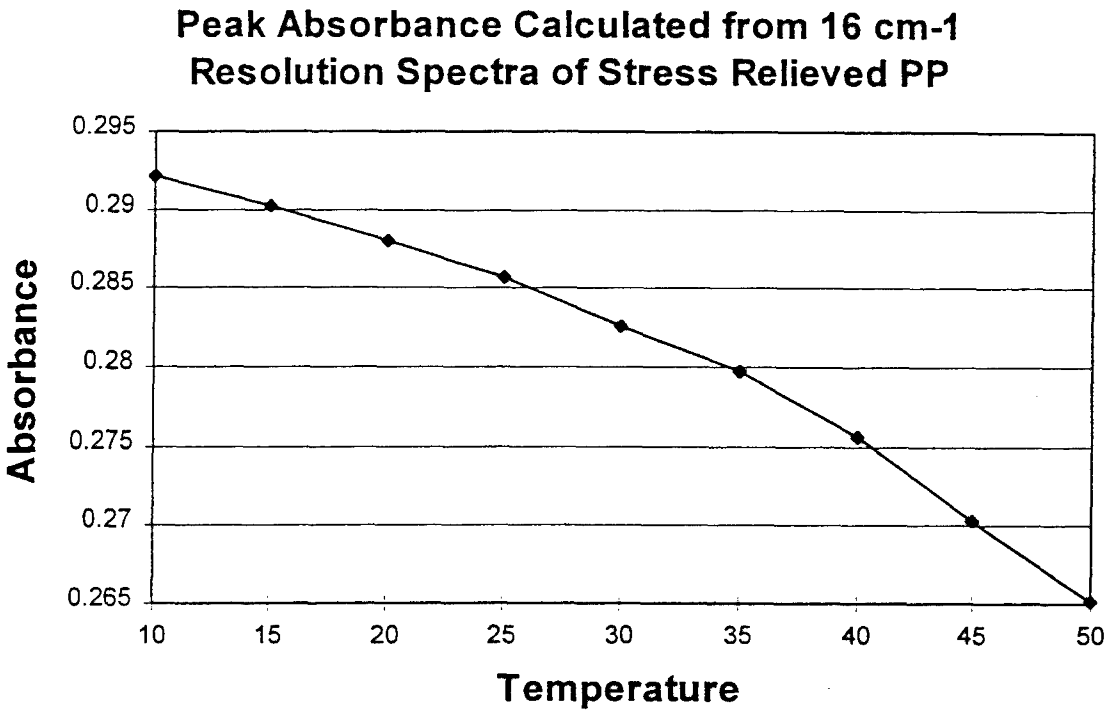

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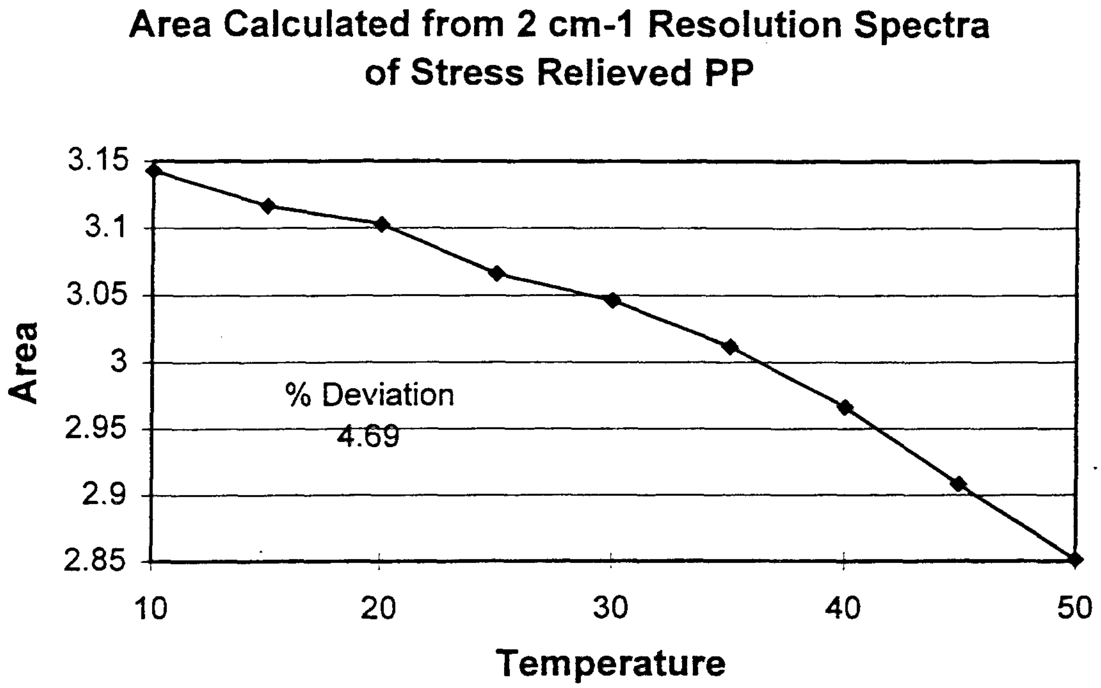

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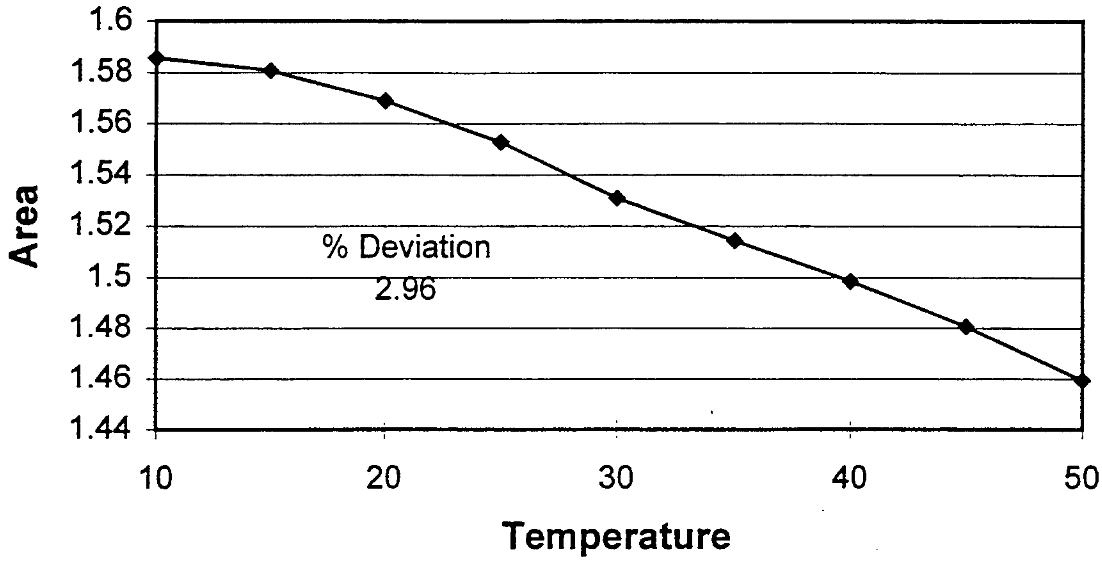

Area Calculated from 2 cm-1 Resolution Spectra of Extruded PP

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