

Applications of Ultraviolet Resonance Raman Spectroscopy: Residual Olefins in Polypropylene

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Ultraviolet resonance Raman spectroscopy is used to probe residual olefin in polypropylene. Ratios of the olefin band to nonresonantly enhanced polymer modes increase with increasing olefin content. No UV photodamage is evident for samples which are moved through the laser beam. In contrast, an increase in intensity of the olefin band as a function of irradiation time is seen in stationary samples of polymer, which probably indicates photo-oxidative degradation.

Index Headings: Ultraviolet resonance Raman; Polypropylene; Olefins.

INTRODUCTION

The determination of low levels of olefin content in polymers is a difficult problem whether it is done by chemical or by spectroscopic methods. Chemical methods, such as Iodine Number, can suffer from interferences such as side reactions or from the need to use solvent systems incompatible with the polymer. All previously employed spectroscopic methods also have difficulties. For example, proton NMR does not directly detect the olefin bond and is blind to completely substituted olefins. ^{13}C NMR directly detects the olefinic carbons but can be obscured by aromatic resonances if they are present. Vibrational spectroscopies such as infrared and Raman, on the other hand, are directly sensitive to the olefin group without being obscured by aromatics. The C=C bond stretch, however, is inherently weak in the IR. Thus IR techniques cannot easily be used to measure residual amounts of olefin. The C=C bond is a strong Raman scatterer, but the normal Raman effect is weak, and it is usually difficult to detect concentrations below 10,000 to 5,000 ppm. In addition, quantitation in Raman spectroscopy is difficult and usually requires a suitable internal standard since laser power and focusing conditions are difficult to reproduce accurately from sample to sample.¹

However, one spectroscopic method, resonance Raman, offers a unique way to enhance the detection limit of specific chromophores. The Raman signal from a sample can be enhanced by six to eight orders of magnitude by exciting the Raman spectrum using

laser excitation which falls within an electronic absorption of the sample. Since the resonance is with a particular chromophore, the only vibrations which are enhanced are those associated with this chromophore. Thus, resonance excitation of chromophores is a possible way of overcoming the concentration problems associated with normal Raman spectroscopy while maintaining vibrational specificity. In the specific example under discussion here, we excite in the ultraviolet near 220 nm in resonance with olefin groups. We demonstrate that UV resonance Raman spectra of polypropylene excited at 220 nm monitors the olefin content.

EXPERIMENTAL

The experimental apparatus has been previously described in detail.² The tunable UV excitation source was a frequency-doubled Nd:YAG pumped dye laser operated at a 20 Hz repetition rate. The visible dye laser output was frequency doubled and mixed with the Nd:YAG fundamental to generate laser light between 217 and 260 nm. The Raman-scattered light was dispersed with a SPEX Triplemate monochromator and detected with the use of a PARC optical multichannel analyzer (OMA). The usual time required to obtain a spectrum was 5 minutes. Sampling was done with the use of a 135 degree front-surface scattering geometry to minimize interference from direct reflection from the exciting laser and to minimize self-absorption of the Raman-scattered light by the sample. The samples themselves were standard 250- μm -thick plaques which were held to a sample holder on the shaft of a motor with double-sided tape. The samples were spun at approximately 1800 rpm to minimize the amount of time any one portion of the annular area was in the beam in order to minimize degradation of the sample (*vide infra*). Band positions reported are accurate to $\pm 5\text{ cm}^{-1}$ and were calibrated according to the known positions of the Raman lines from acetonitrile.

RESULTS AND DISCUSSION

The Raman spectrum of a polypropylene sample obtained with UV excitation (Fig. 1) compares well with a published Raman spectrum of isotactic polypropylene obtained with visible excitation.³ Only bands associated with UV absorbing chromophores

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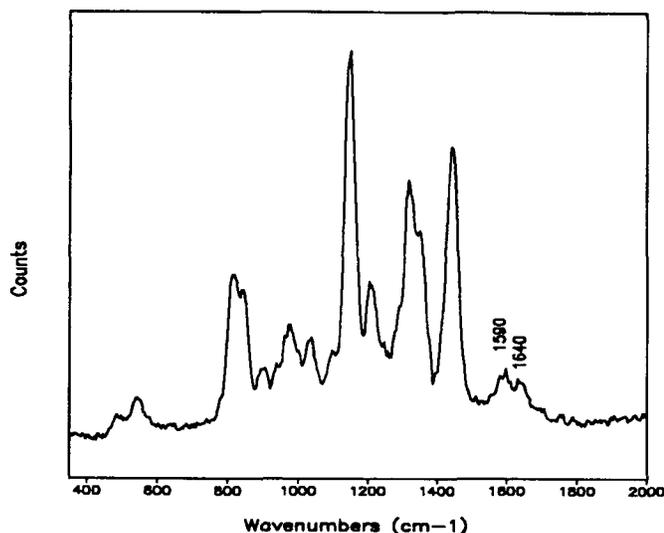


FIG. 1. Raman spectrum of isotactic polypropylene excited at 220 nm. Frequency-labeled bands are not seen in a Raman spectrum of this sample excited by visible light.

should be resonantly enhanced. Since the polypropylene skeleton consists mainly of singly bonded species (which should absorb only in the vacuum UV), resonance enhancement of the backbone is not expected. The major bands in this spectrum are consistent with the expected nonresonant excitation of the polypropylene by the UV laser. Careful comparison of the UV-excited and the visible-wavelength-excited Raman spectra shows that the UV-excited Raman spectrum contains two bands which do not appear in the visible-wavelength-excited spectrum. These bands appear at approximately 1590 and 1640 cm^{-1} . The band at 1640 cm^{-1} occurs in the expected group frequency region for carbon-carbon double bond stretching, while the band at 1590 cm^{-1} is somewhat lower in frequency than would be normally expected for assignment to this type of vibration (*vide infra*).

Because of the high energy carried per photon in the UV, care must be taken to prevent degradation of the sample. Figure 2 demonstrates that as long as the sample was spun at a reasonable rate, no changes in the spectrum occurred over approximately a thirtyfold change in excitation energy flux density. However, if the sample is not spun, the band at approximately 1640 cm^{-1} begins to increase rapidly in intensity, eventually overwhelming the rest of the spectrum (Fig. 3). This spectral change does not result from laser heating since calculations indicate temperature increases of only a few degrees. Photo-oxidative degradation of polypropylene is a likely mechanism. This degradation process has been reviewed by Carlsson and Wiles.⁴ These authors suggest that photo-instability in polypropylene derives from hydroperoxide complexes formed by thermal oxidation of the polymer melt and during the processing of polymer films. Radicals can also be produced from photo-reduction of halides and hydroxides from any catalyst residues present. Hydroperoxides decompose under UV excitation to alkoxy radicals, which can then undergo bond scission in a Norrish Type II

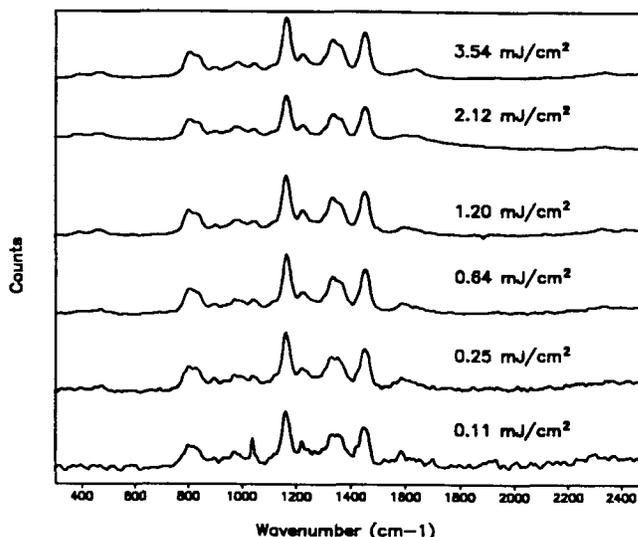


FIG. 2. Laser damage / laser power study of spun polypropylene film.

reaction to form olefins and oxygen-containing species. We suggest that UV excitation leads to the production of the olefin band seen in Fig. 3. Oxygen-containing species would not be seen here due to a lack of resonance enhancement and to their rapid destruction in the beam.

Figure 4 is the UVRR spectrum of a solution of the antioxidant AO 330 in acetonitrile. On the basis of this spectrum, the band at 1590 cm^{-1} in the polypropylene spectra is assigned to an antioxidant such as AO 330 or BHT. This antioxidant may have been introduced into the samples during an extraction procedure of the polypropylene with xylene which contained an antioxidant.

A suitable internal standard is required for quantitative comparisons of olefin content. One possible method of quantitation is to ratio the olefin band to a band from a suitable polypropylene backbone mode whose intensity is effectively constant since it is not resonantly enhanced (*vide supra*), and which is present at essentially identical concentrations in comparison to the residual olefin. The relative ratio of the 1640 cm^{-1} olefin band to the 1460 cm^{-1} methylene deformation band increases as a function of the olefin content for the samples studied here.

CONCLUSIONS

These UV Raman spectral data demonstrate that it is possible to detect residual olefins in polymers by resonance enhancement of the π - π^* transition.

While quantitative Raman spectroscopy is complicated due to the necessity for reproducing beam characteristics and focusing with differing samples, it is expected that by ratioing the olefin band to aliphatic hydrocarbon bands UVRR can be used as a semiquantitative rapid screening technique to probe for olefin content.

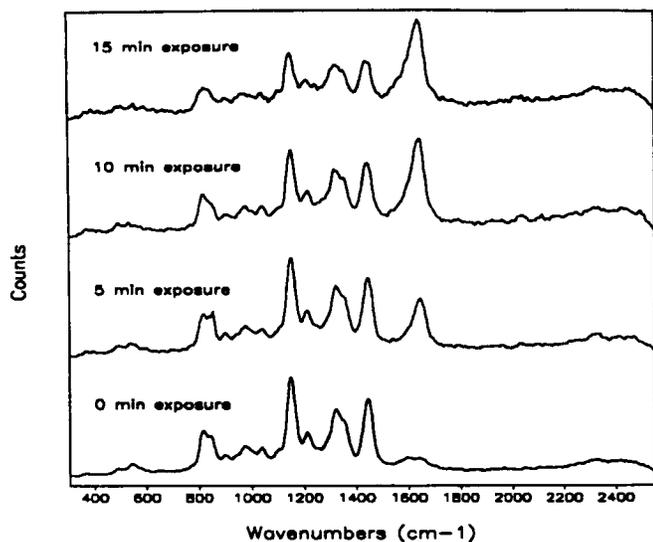


FIG. 3. Laser damage to stationary sample of polypropylene film. Zero minute exposure refers to spun sample.

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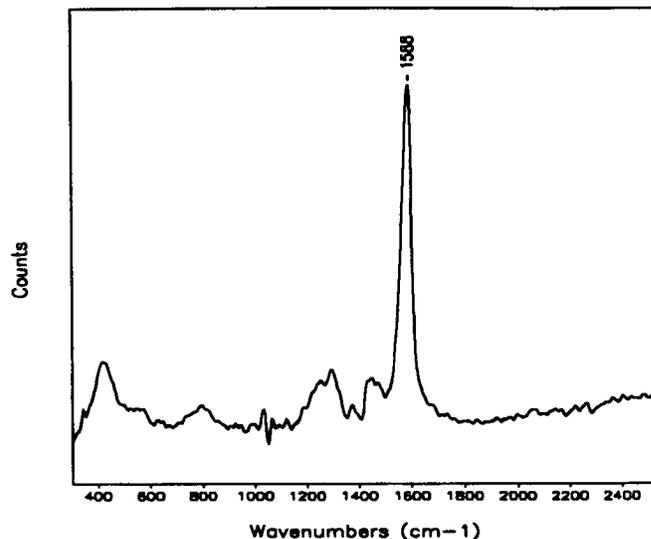


FIG. 4. Raman spectrum of a solution of AO330 in acetonitrile excited at 220 nm excitation. The solvent spectrum has been subtracted.

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