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IN SITU ANALYSIS OF A HIGH TEMPERATURE CURE REACTION IN REAL TIME USING MODULATED FIBER-OPTIC FT-RAMAN SPECTROSCOPY

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In Situ Analysis of a High Temperature Cure Reaction in Real Time Using Modulated Fiber-Optic FT-Raman Spectroscopy

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ABSTRACT

The vibrational spectrum of a high temperature (330^0C) polymerization reaction was successfully monitored in real time using a modulated fiber-optic FT-Raman spectrometer. A phenylethynyl terminated monomer was cured, and spectral evidence for two different reaction products was acquired. The products are a conjugated polyene chain and a cyclized trimer. This is the first report describing the use of FT-Raman spectroscopy to monitor a high temperature (>250^0C) reaction in real time.

Index Headings: Fiber-optics, FT-Raman, polymer curing, high temperature

INTRODUCTION

Much emphasis has been given to the development of high performance polymers for use as composite matrix resins and adhesives. Scientists at NASA Langley Research Center have developed a class of polyenes with a phenylethynyl-termination, which possess high thermal stability and excellent mechanical properties, making them suitable candidates for aerospace applications.[1,2] These polymers display high glass transition temperatures, excellent solvent resistance, and outstanding mechanical properties.

Most polymers of this type are highly fluorescent, which makes even near-IR (~800 nm) dispersive Raman unsuccessful. The longer wavelength excitation of the FT-Raman instrument allows for the spectral acquisition of these polymers at room temperature with a reduced fluorescence background. Fiber-optic FT-Raman has been used previously[3-10] and allows for real time in situ monitoring. High temperature (>250^{0}C) monitoring has been problematic using FT-Raman because of the thermal background signal (blackbody emission) that arises at the same frequency as the Raman signal. The blackbody emission has a much greater intensity than the Raman signal and completely overwhelms it. Herein we utilize a previously described modified FT-Raman instrument, which allows collection of high temperature FT-Raman spectra without thermal background interference.[11]

This study focuses on one of the phenylethynyl terminated monomer precursors, 4-phenoxy-4'-phenylethynylbenzophenone. We propose two different reaction pathways (cyclization and chain extension) for the thermal polymerization of phenylethynyl terminated resins and spectral evidence shows that both pathways occur. Both products

seem to be major products, but actual percentages of each product formed is difficult to quantify due to signal to noise constraints.

EXPERIMENTAL

A three gram sample of 4-phenoxy-4'-phenylethynylbenzophenone was placed into a one dram glass vial and cured in a forced air oven at 330^{0}C. Raman spectra were acquired using a modified Nicolet Raman 950 spectrometer equipped with a liquid nitrogen cooled Ge detector, a Nd:YAG laser operating at 1064 nm and a co-linear 18 around 1 (single centered excitation, 18 surrounding collection fibers) probe. The laser power at the distal end of the probe was 350 mW. All fibers were 200 μm core silica/silica fibers (Polymicro Technologies Inc.). Spectra were acquired with one scan (2s) at 8 cm^{-1} resolution using Happ-Genzel apodization. Spectra were created by averaging 100 of the single scans, thus making the spectral acquisition time 200s. All spectra were acquired and processed in this manner unless otherwise noted. The modifications to the commercial FT-Raman instrument have been described in detail previously.[11] Briefly, the CW laser is modulated at a set frequency. A dual phase digital signal processor lock-in amplifier is placed between the detector and the spectrometer's collection electronics to demodulate and filter the optical signals. The resulting spectra from this dual modulation technique are free from thermal background (blackbody emission) interference.

Hexaphenylbenzene (98%), diphenylacetylene (98%) and benzophenone (97%) were supplied by Aldrich, and used as model compounds to aid in spectral assignments. The 4-phenoxy-4'-phenylethynylbenzophenone (98%) was obtained from NASA Langley.

RESULTS AND DISCUSSION

The chemical structure of 4-phenoxy-4'-phenylethynylbenzophenone (I), the chain extension product (II), and the cyclized trimer product (III) are shown in Figure 1. Waterfall plots of Raman spectra taken during a 300 minute, 330^{0}C curing cycle of 4-phenoxy-4'-phenylethynylbenzophenone are shown in Figure 2. Frequency assignments for the peaks are given in Table I. The primary reactive sight of this monomer is the ethynyl stretch at 2216 cm^{-1}. The intensity of this mode decreases as the cure progresses and eventually disappears upon full cure. A plot of percent cure vs. time is shown in Figure 3. The percent cure was determined by using the baseline corrected peak heights and peak areas in Eq. 1, where I_T is the height (area) of the ethynyl peak for a particular cure time and I_0 is the height (area) of the ethynyl peak before curing.

$$\%C = [1-(I_T/I_0)]*100 \qquad (1)$$

As shown in Figure 2, the first four spectra show a rapid decrease in intensity for all observed modes. This results in an apparent initial fast rate of cure in the cure plot shown in Figure 3. Following this initial jump, the curve assumes a sigmoidal shape consistent with that of a typical thermoset cure. Also shown in Figure 3 is a plot of blackbody emission vs. time. For blackbody emission, the intensity is related to temperature by

$$T = kI^{1/4} \qquad (2)$$

where k is a constant. Figure 4 shows the modulated FT-Raman spectra of the first four spectra and reveals a rapid increase in blackbody emission. This increase in blackbody emission intensity (temperature) coincides with the initial decrease in Raman intensity for the first four spectra (apparent rapid cure rate). This is likely due to the melt of the sample. Ideally, a reference peak from the spectrum would be chosen for normalization

purposes. Normalization would reduce the spectral effects of physical changes in the sample. A peak that corresponds to a moiety unaffected by the polymerization reaction would be ideal. The carbonyl peak at 1645 cm^{-1} or the phenyl C-H peak at 3064 cm^{-1} would be logical choices, but signal to noise constraints do not allow the use of these peaks for normalization.

The peak centered at 1591 cm^{-1} in the unreacted monomer is assigned to the phenyl CC stretch. This peak shifts to higher frequency and experiences a large degree of broadening on each side during the cure sequence (Figure 5). This suggests the formation of conjugated polyene chains[15,16] with multiple isomeric arrangements and varying polyene lengths. Formation of a cyclization product would be expected to yield a single product whose isomeric forms would not appreciably affect the frequency of the new phenyl ring stretching modes.

Spectral evidence of the formation of the cyclization product is shown in Figure 6. The model compound, hexaphenylbenzene, has a peak at 1345 cm^{-1}. This peak in hexaphenylbenzene is one of the strongest in the spectrum and the frequency matches one of the new peaks (1345 cm^{-1}) that appear during the polymer cure. In hexachlorobenzene, the vibration involving semicircle stretching of the carbon ring absorbs in the infrared at 1350 cm^{-1}.[17] The infrared intensity is strong for electron donor groups and weak or absent when these are not present.[18] The Raman intensity is usually weak.[19] Also, CH_2 and CH_3 deformation vibrations frequently obscure this peak.[12] In this particular case, the Raman intensity should be strong because of the increased polarizability arising from hexasubstitution with benzene rather than chlorine. A slight shift to lower frequency would also be expected.

The distinct band, which is found at 1132 cm^{-1} is assigned as the accidentally degenerate Ph-C stretch between the phenyl-ethynyl and phenyl-carbonyl moieties. The frequency of the Ph-C mode occurs at 1150 cm^{-1} and 1141 cm^{-1} in benzophenone[13] and biphenylacetylene,[14] respectively. The vibrational frequency of the Ph-C modes in the unreacted monomer is shifted to a lower frequency than either benzophenone or biphenylacetylene due to the combined influence of the strongly deactivating ethynyl and carbonyl moieties. Examination of the spectral cure sequence of the band reveals several vibrational changes in the Ph-C modes during polymerization. Figure 7 shows this peak gradually decreases in intensity while a new peak grows in at higher frequency (1144 cm^{-1}) as the polymerization reaction proceeds. The intensity decrease is due to the loss of the ethynyl mode during the cure sequence. The new peak is the result of a new Ph-C moiety resulting from the creation of polyene chains. This new mode shifts to higher frequency as a function of conjugated chain length.[16]

The vibration at 997 cm^{-1} corresponds to a phenyl ring breathing mode. In each monomer, there are 4 phenyl rings. The cyclization reaction forms one phenyl ring for every three monomer units. Therefore, a percent increase of ~8 percent in the spectral intensity of this band would correspond to the cyclization consisting of 100 percent of the product assuming a relatively constant Raman cross-section. This intensity increase is difficult to determine accurately due to signal to noise constraints.

CONCLUSION

Modulated fiber-optic FT-Raman allows the high temperature (330^0C) polymerization reactions of compounds such as 4-phenoxy-4'-phenylethynylbenzophenone to be monitored in situ and in real time. Information obtained from Raman spectra indicate

that products result from reactions forming a conjugated double bond system of varying chain lengths and cyclization.

ACKNOWLEDGMENT

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LIST OF FIGURES

Figure 1: Structure of 4-phenoxy-4'-phenylethynylbenzophenone (I) and two probable products: polymer chain extension (II) and cyclized trimer (III). Multiple isomeric forms are also possible.

Figure 2: Modulated fiber-optic FT-Raman spectra of 4-phenoxy-4'-phenylethynylbenzophenone taken at 330^{0}C for 300 minutes. Each spectrum consists of 100 scans (200s).

Figure 3: Plot of percent cure vs. time of the ethynyl peak height (circles) and area (triangles). Plot of blackbody emission vs. time (line). First four points of cure curve correspond to sample heating and melt.

Figure 4: First four modulated fiber-optic FT-Raman spectra of 4-phenoxy-4'-phenylethynylbenzophenone in the cure series. Spectra are numbered in order of acquisition. Rapid increase in blackbody emission intensity (numbered peaks) corresponds to the initial rapid cure rate in Figure 2.

Figure 5: Modulated fiber-optic FT-Raman spectra of the phenyl CC peak. The spectral cure times are shown in minutes. As cure progresses, the peak broadens and shifts to higher frequency, suggesting formation of a conjugated polyene chain.

Figure 6: Modulated fiber-optic FT-Raman spectra of cured and uncured 4-phenoxy-4'-phenylethynylbenzophenone and hexaphenylbenzene. Cured polymer has a new peak formation at 1345 cm^{-1} suggesting formation of a cyclization product. All spectra are full scaled.

Figure 7: Modulated fiber-optic FT-Raman spectra of the peak at 1132 cm^{-1}. This peak (Ph-C stretch) disappears over time and a new peak appears (1144cm-1). This is due to the loss of the ethynyl mode during the cure sequence. The shift to higher frequency is a function the formation of a new Ph-C moiety, and the length of the conjugated polyene chain. The spectra shown are at 30 min cure intervals from 0-300 min.

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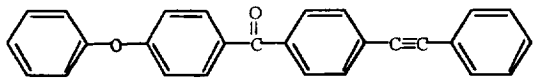
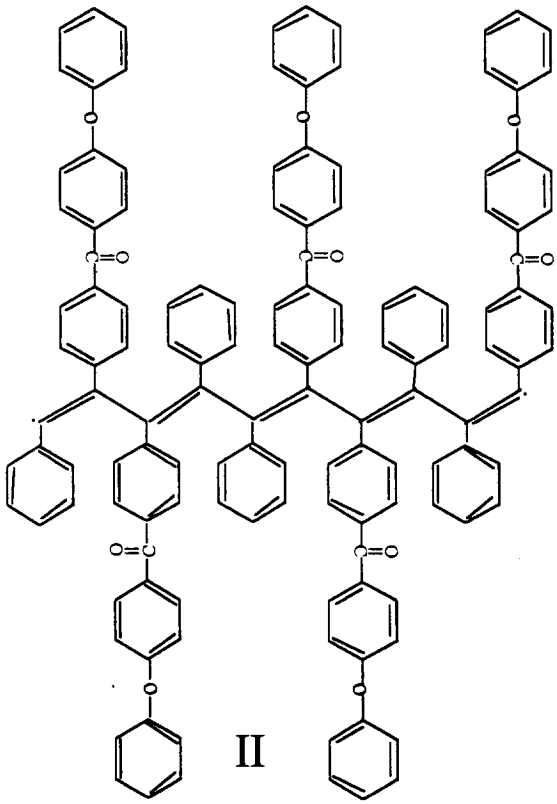
Table I: Spectral Assignments for Peaks Observed in 4-phenoxy-4'-phenylethynylbenzophenone Cure

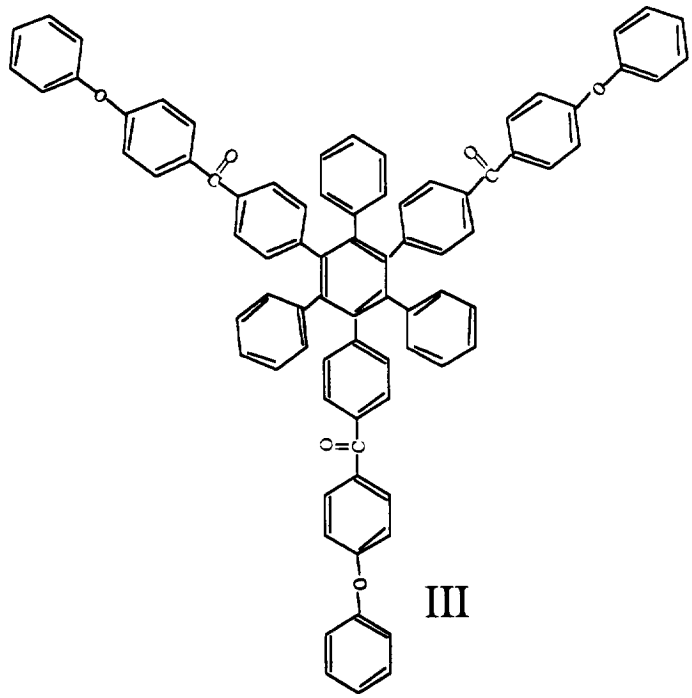
Vibration Frequency (cm^{-1})	Assignment (Ref.)
3064	Phenyl C-H[12]
2216	Disubstituted Acetylene[12]
1645	C=O[12]
1591	Phenyl CC[12]
1131	Ph-C[13,14]
997	Ring breathing mode[12]



I

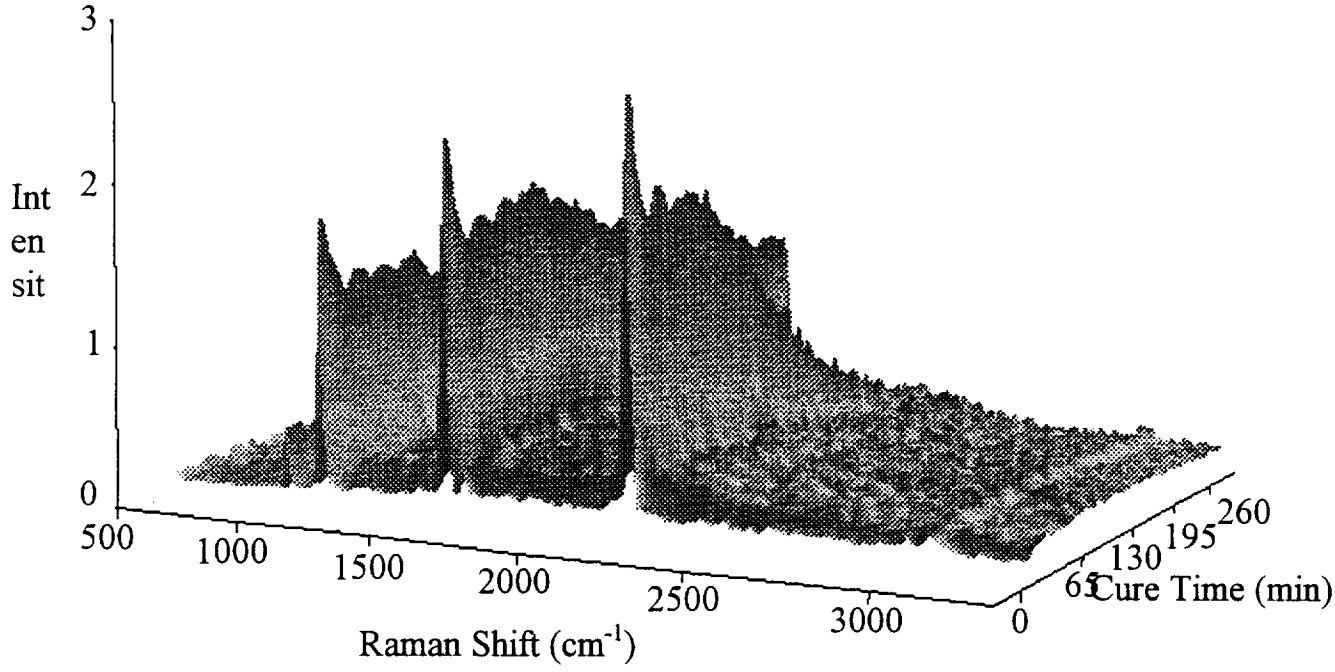


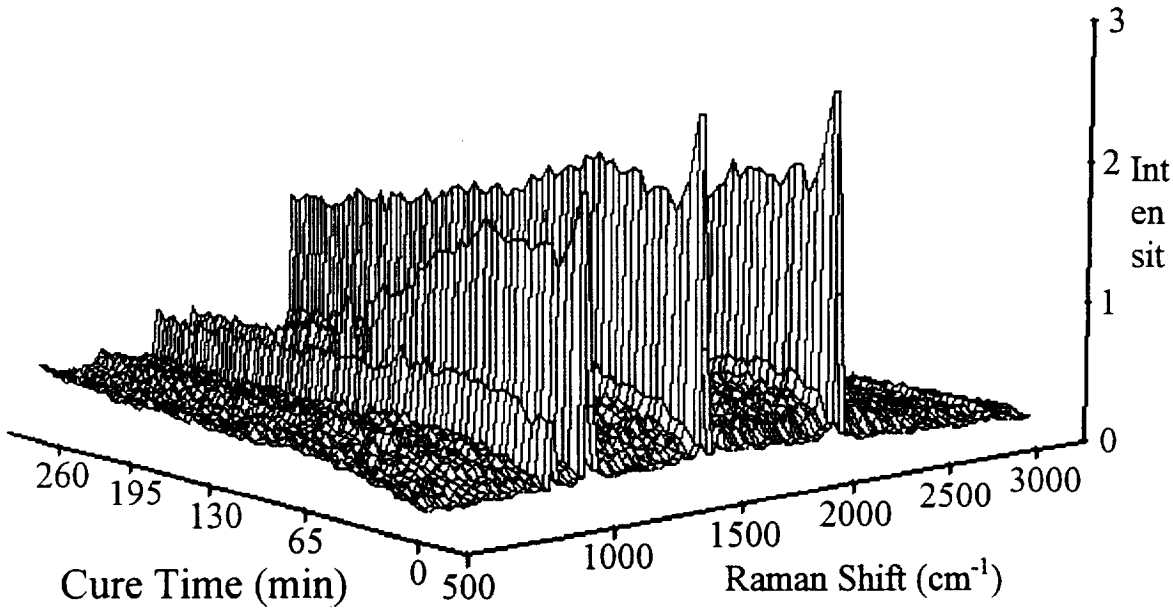
II



III

Fig. 1


Int
en
sit
3
2
1
0
500
1000
1500
2000
2500
3000
Raman Shift (cm-1)
0
65
130
195
260
Cure Time (min)


3
2 Int
en
sit
1
0
260
195
130
65
0
Cure Time (min)
500
1000
1500
2000
2500
3000
Raman Shift (cm-1)

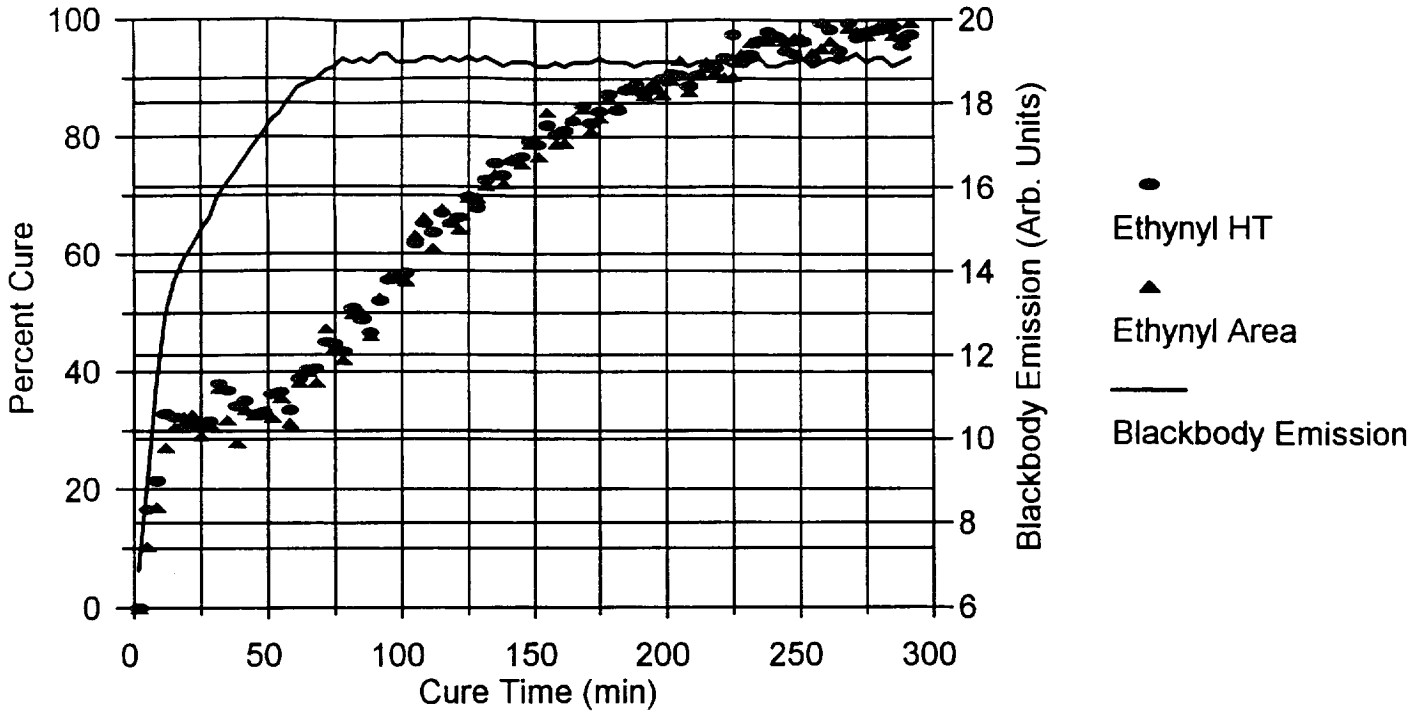

100
80
60
40
20
0
Percent Cure
0
50
100
150
200
250
300
Cure Time (min)
20
18
16
14
12
10
8
6
Blackbody Emission (Arb. Units)
Ethynyl HT
Ethynyl Area
Blackbody Emission

Fig. 3

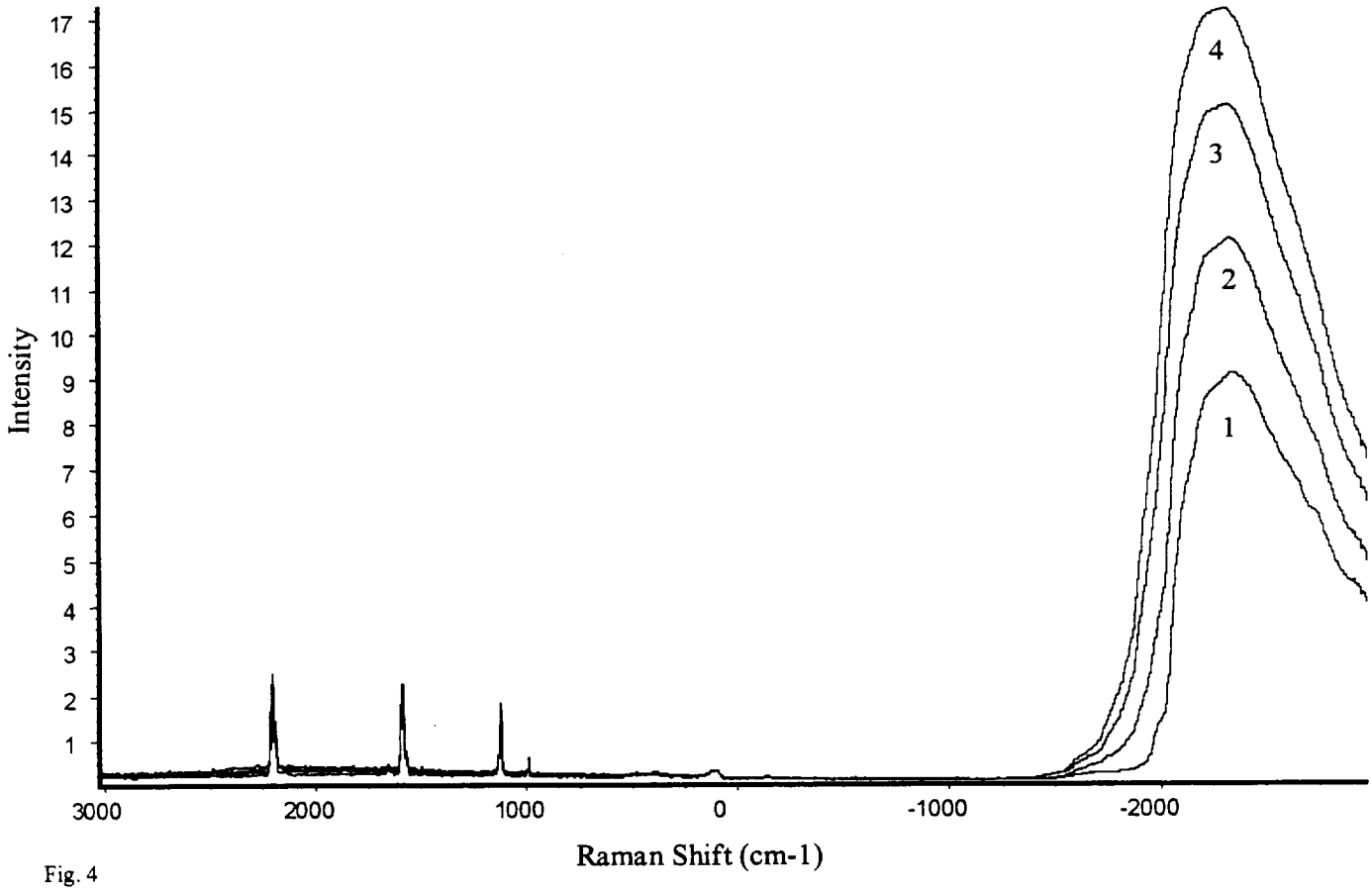

Intensity
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
3000
2000
1000
0
-1000
-2000
Raman Shift (cm-1)
4
3
2
1

Fig. 4