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Raman Spectroscopy of Polymeric Materials

Part 1 - Selected Commercial Polymers

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ABSTRACT

The He-Ne laser has greatly reduced the problem of fluorescence, which has in the past almost completely obscured conventionally excited (mercury arc) Raman spectra of all except the simplest and purest polymers. In many instances it is now possible to record Raman spectra of polymers without any prior purification whatsoever. A comparison of the Raman and infrared spectra of twelve selected commercial polymers shows the complementary nature of these two spectroscopic techniques for identification purposes. Vibrations such as C=C stretching (in polybutadiene) and S–S and C–S stretching (in polysulfide rubber) give rise to strong Raman Lines but produce weak infrared absorption bands; conversely, the C=O group of polycarbonates and polyesters is a strong infrared absorber which produces a weak Raman line.

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

AUTHORIZATION

NRL Problem C07-01
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RAMAN SPECTROSCOPY OF POLYMERIC MATERIALS

PART 1 - SELECTED COMMERCIAL POLYMERS

INTRODUCTION

The wide variety of polymeric materials in use today makes identification a more complex problem than in the past, and any new techniques which can aid in this area are worthy of investigation. Infrared spectroscopy has been applied to the problem at NRL, and compilations of reference spectra of polymers have been prepared (1-3). Recent developments in Raman spectroscopy, a complementary counterpart to infrared spectroscopy, have made this technique available for such an application (4). In an attempt to investigate its capability, a study of commercial polymeric materials was undertaken.

THEORY

In both Raman and infrared spectroscopy, the frequencies of molecular vibrations are recorded. The techniques differ, however, in the method of interaction of input energy with the vibrations and in the selectivity of the phenomena. In the case of infrared spectroscopy, incident radiation is absorbed by molecules when the frequency coincides with that of a dipole transition of a molecular vibration, and the spectrum represents the percent of energy that is transmitted by a sample over the range of infrared frequencies. The phenomenon observed in Raman spectroscopy, on the other hand, is light scattering. Illumination of a sample with a monochromatic source can produce two kinds of interaction, classed as elastic and inelastic collisions, between photons and molecules. Most of the scattered light is unshifted in frequency, resulting from elastic collisions, and is called Rayleigh scattering. Inelastic collisions can cause a molecule to undergo a transition from its ground state to a higher energy level or from an excited state to the ground state, resulting in the photon's loss or gain of energy. These scattered photons then produce the Stokes (lower frequency) and anti-Stokes (higher frequency) lines of Raman scatter, and the energy change corresponds to a molecular vibration frequency. Two entirely different conditions determine spectral activity of molecular vibrations. Only those vibrations which change the dipole moment with respect to the normal coordinate are infrared active, while the criterion for Raman activity is a change in some component of the polarizability.

These differences make the combination of Raman and infrared spectroscopy a very potent tool for elucidation of molecular structure. More often than not, vibrations which appear strongly in one spectrum are weak or absent in the other. The ultimate case is seen for molecules which possess a center of symmetry; for these molecules the modes which are Raman active are infrared inactive and vice versa (mutual exclusion). Thus, Raman spectra complement rather than duplicate infrared spectra in the vibrational analyses of molecules.

Unfortunately, however, Raman spectra have not been as easily obtained as infrared spectra. This is largely the result of less satisfactory instrumentation for recording Raman spectra. Advances in infrared spectroscopy have made it possible to obtain spectra from almost any sample, but weakness of the Raman effect and limitations of equipment, particularly the Toronto mercury arc exciting source, have greatly hampered the application of this technique. The physical parameters of the arc have necessitated

large sample size (on the order of grams), and the proximity of the exciting frequency (4358 Å) to the ultraviolet leads to fluorescence of samples, or of small amounts of impurities therein, and poses problems of photodecomposition.

These difficulties have prevented the widespread application of Raman spectroscopy, but a recent improvement in technology is changing this situation –that is, the advent of the laser exciting source. Because the illuminating flux is concentrated in a smaller volume, sample size has been greatly reduced. Wavelengths in the red and near-infrared are more readily available, which reduce problems of fluorescence and photodecomposition.

Despite the improvements effected by the laser, problems are still encountered in attempting to record Raman spectra. "Fluorescence" has been and continues to be the major problem; this is the name that has been applied to the phenomenon, but it is not fully understood. It is seen in spectra as a continuous background emission, which generally decreases in intensity toward higher Raman shifts. The purity of the sample seems to be a determining factor in the appearance of the fluorescence. This factor has made polymers particularly difficult samples for Raman spectroscopy because of the impurities inherent in them. Even when tedious purification has been performed, Raman spectra obtained using the conventional (mercury arc) excitation have been poor. The types of polymers which have given the best spectra seem to be those for which less contamination is likely to be introduced in the polymerization reaction, such as polyethylene (5-7), polypropylene (5,8), and polystyrene (9). Figure 1 shows the spectrum of polyethylene obtained by Brown (6), using a Cary 81 with a mercury arc exciting source. The sample was in the form of a cylindrical rod several inches long. The spectrum definitely leaves room for improvement.

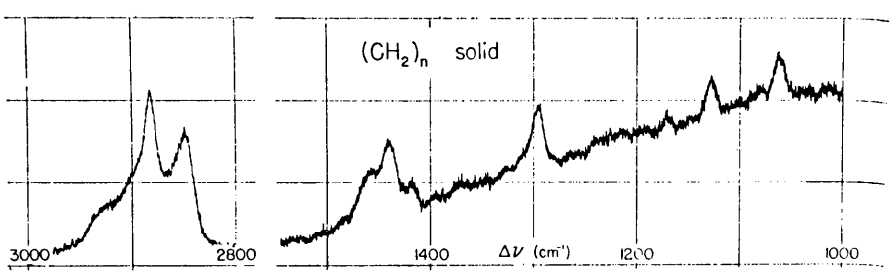

Fig. 1 - Raman spectrum of polyethylene obtained by Brown (6), using mercury arc excitation

It should be mentioned that although the red (6328 Å) laser reduces fluorescence and sample size from that of the Toronto arc (4358 Å), the longer wavelength excitation also reduces the Raman intensity, since it is proportional to the fourth power of the exciting frequency. In addition, the detector sensitivity diminishes rapidly toward longer wavelengths, so that molecular vibrations with large Raman shifts appear to be weaker.

EXPERIMENTAL TECHNIQUE

The samples used in this study were commercial preparations for which no sample pretreatment or purification was attempted. Spectra were recorded on a Cary 81 Raman spectrophotometer equipped with a He-Ne laser source (6328 Å). Solid samples were simply placed in the beam for coaxial viewing as powders, chunks, or pellets. The sample optics are illustrated in Fig. 2. For the case of liquid samples, a small amount of sample was introduced into a capillary tube, also for coaxial viewing. In contrast to infrared spectroscopy, there is no upper limit for Raman sample size, so that sampling is greatly

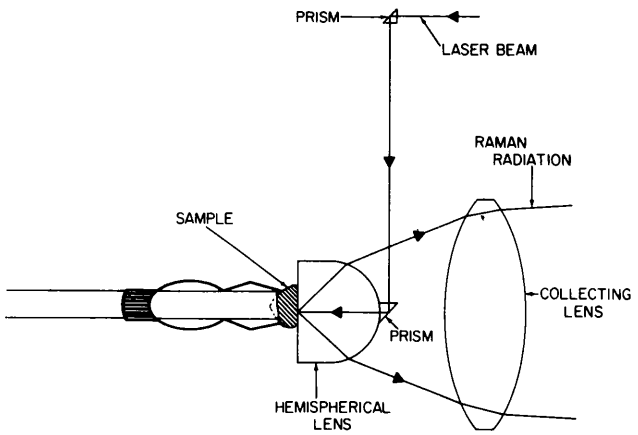

Fig. 2 - Sample optics for the case of coaxial viewing of a polymer chunk

simplified. Infrared spectra, obtained previously (2,3), are presented with the Raman spectra for comparison. In nearly every case, the infrared spectrum was obtained from a thin film, which was made by dissolving the polymer (often difficult and sometimes impossible with polymers) and evaporating the proper amount of solution.

DISCUSSION

We have been able to obtain some useful spectra using laser excitation, in spite of the fluorescence encountered in varying degrees in most of the samples. Some polymers give very satisfactory spectra; these include polymers whose Raman spectra have been previously reported by mercury arc excitation of highly purified samples. A second group of materials falls into a marginal category. They produce too much fluorescence to be examined by mercury arc excitation, except in a few favorable cases after extensive purification. However, at least fair results can now be obtained from these materials using laser excitation of untreated samples. Unfortunately, we found still another group of polymers which have too much background emission to be studied, even with laser excitation.

Figures 3 through 14 present spectra which have been selected from about forty polymers examined. The top curve in each figure is the infrared spectrum, which is given for comparison. In all Raman spectra, bands at approximately 2865, 2905, and 2938 cm^{-1} are to be disregarded, as they are instrument artifacts (grating ghosts). The wavenumber scales of both spectra correspond up to 2000 cm^{-1}, at which point the infrared scale changes. The frequencies in the Raman spectra are shifts from the exciting line, and a strong line is seen in all spectra at $\Delta\nu = 0$ (Rayleigh scatter).

Among the factors which make group frequency correlations practical is the requirement that the vibration of interest appear with reasonable intensity in a spectrum. Since frequencies of vibrations will remain the same in both infrared and Raman spectra, it is this intensity difference which becomes important. In polymers, as in any other molecules, certain vibrations are expected to produce strong infrared bands and others intense Raman lines. Table 1 gives a very general summary of the kinds of differences to be expected between Raman and infrared activity, and the figures to follow will illustrate some of these generalizations for polymer molecules.

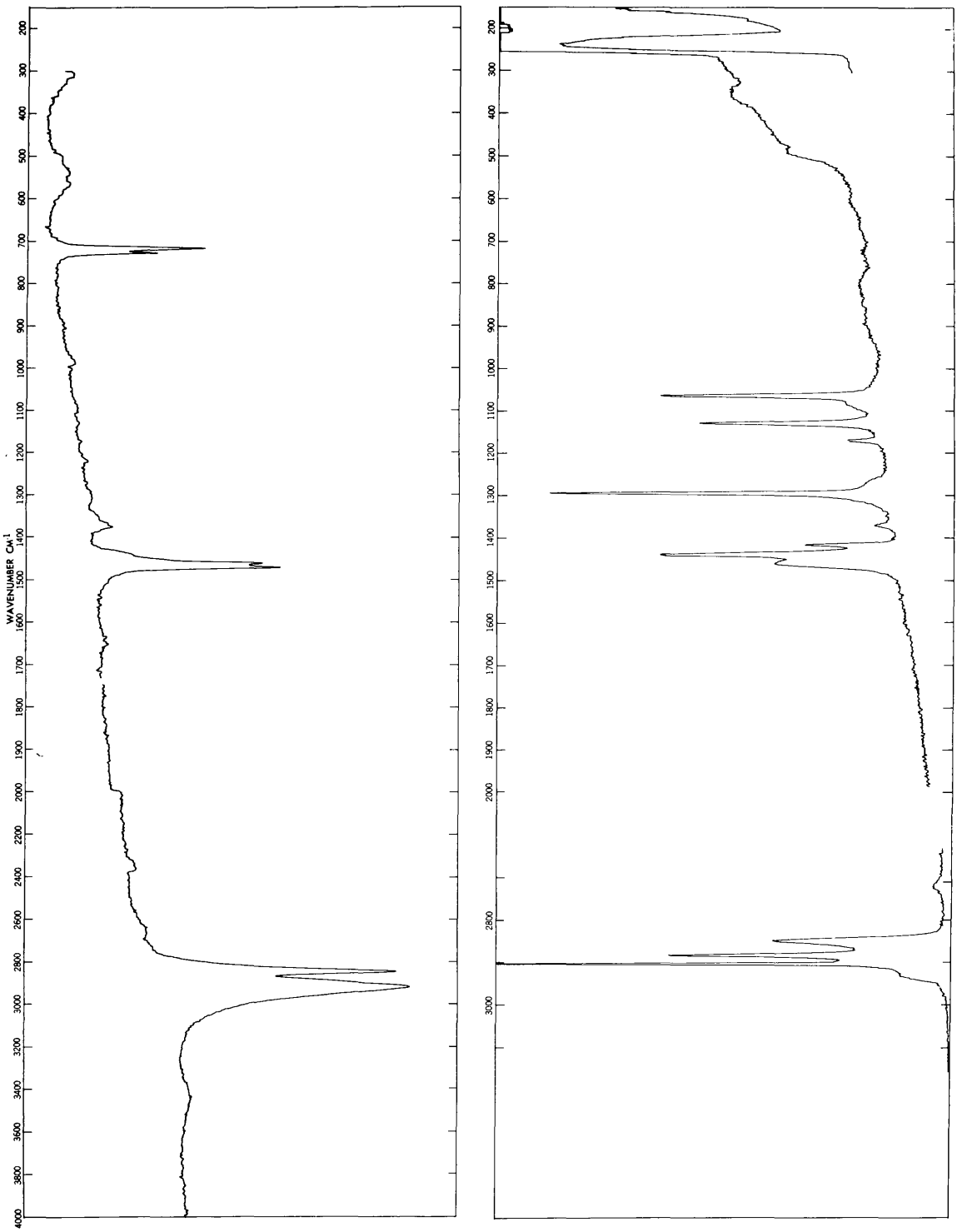

Fig. 3 - Infrared (top) and Raman (bottom) spectra of microthene polyethylene powder. The Raman instrument settings were a sensitivity of 100×2.5(50×2.0 for inset from 150 to 300 cm^{-1}), a period of 3.5 sec, slit dimensions of 10 cm × 6 cm^{-1}, single, and a scan speed of 1 cm^{-1}/sec.

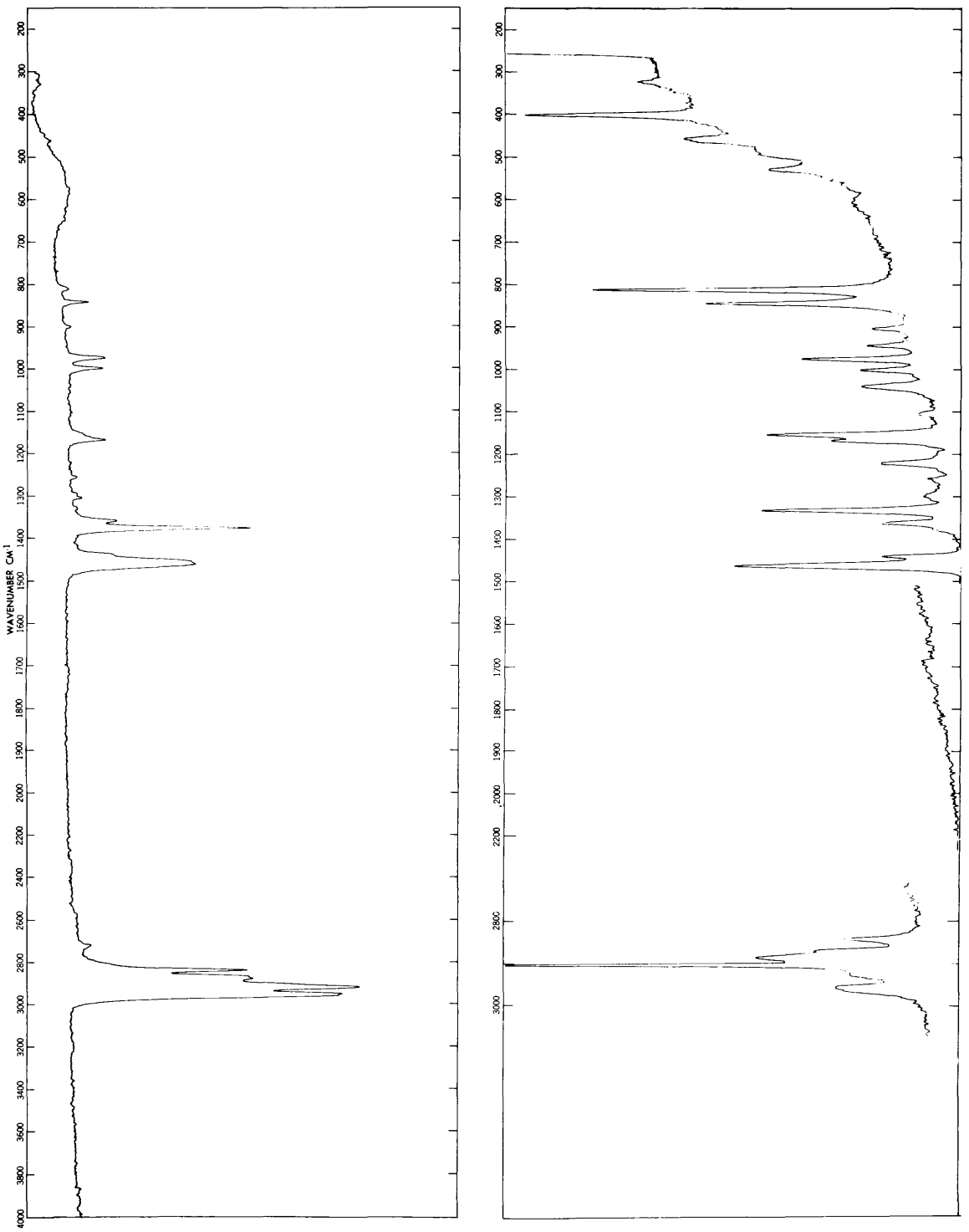

Fig. 4 - Infrared (top) and Raman (bottom) spectra of Hercules polypropylene powder. The Raman instrument settings were a sensitivity of 100 × 3.0, a period of 2 sec, slit dimensions of 10 cm × 6.5 cm^{-1}, single, and a scan speed of 2.5 cm^{-1}/sec.

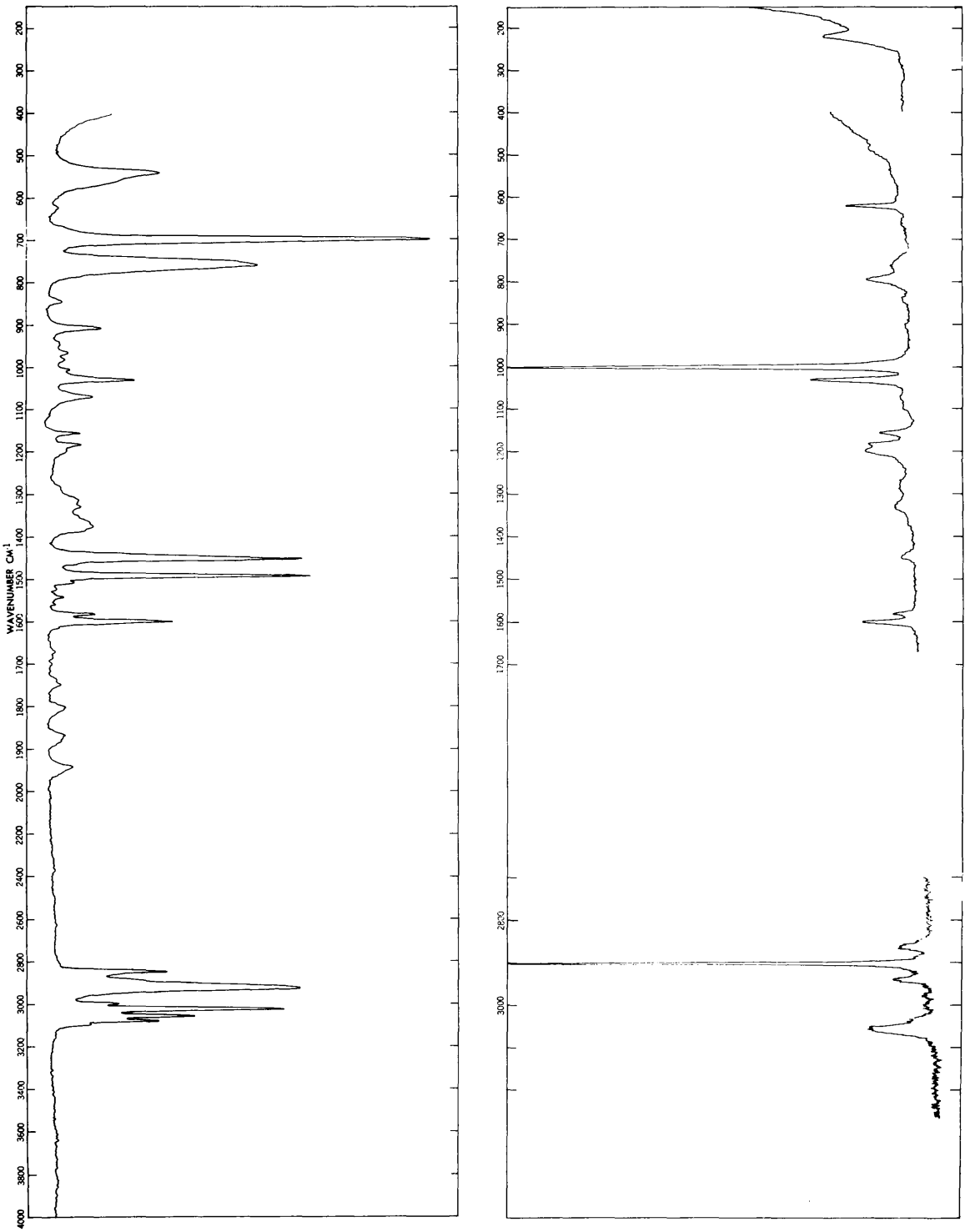

Fig. 5 - Infrared (top) and Raman (bottom) spectra of styron 690 27, polystyrene. The Raman instrument settings from 150 to 1700 cm-1 were a sensitivity of 50 × 2.3, a period of 2 sec, slit dimension of 10 cm × 5 cm-1, double (single to 400 cm-1), and a scan speed of 1 cm-1/sec, the settings from 2700 to 3200 cm-1 were a sensitivity of 100 × 3.0 and slit dimensions of 10 cm × 5 cm-1.

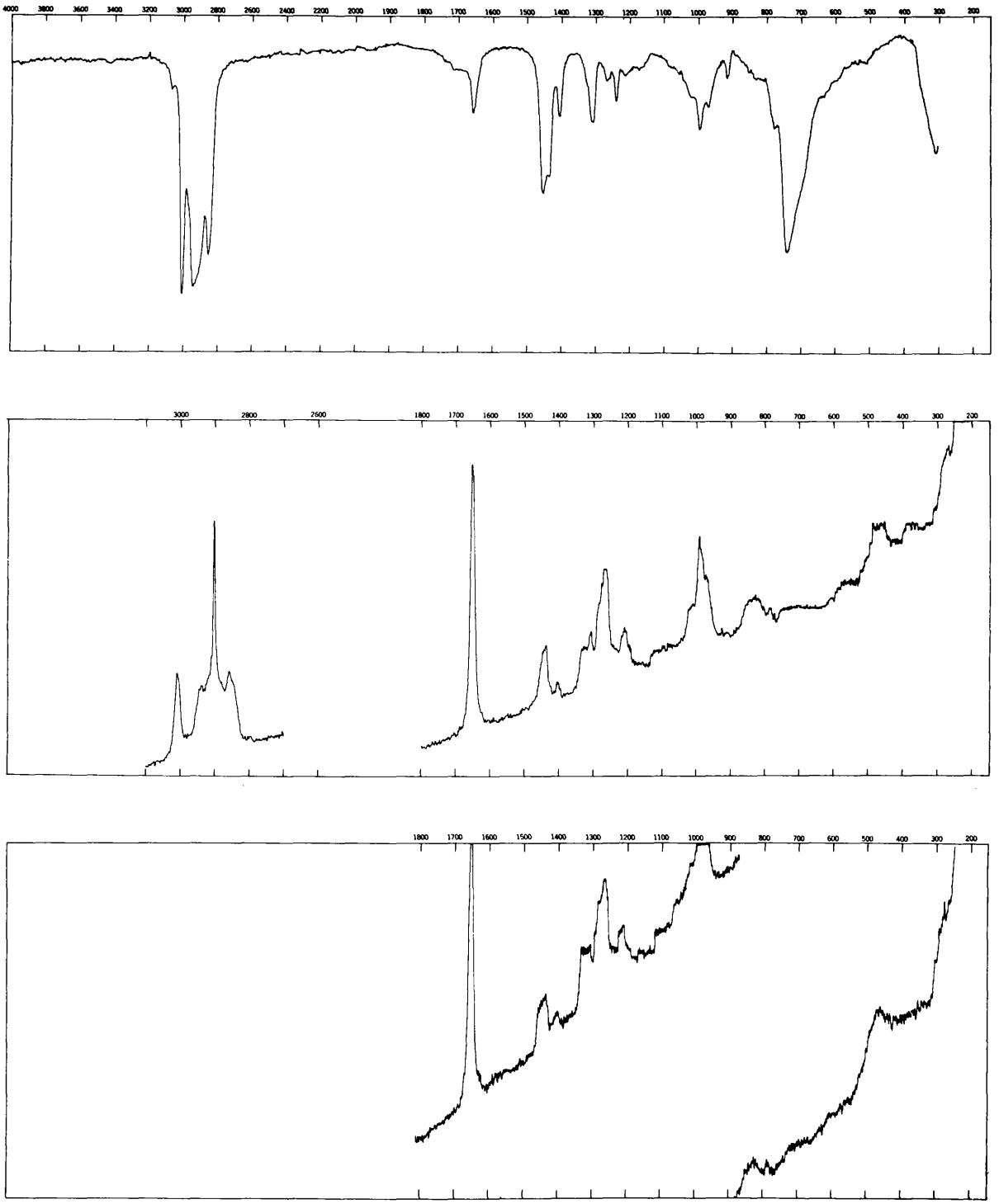

Fig. 6 - Infrared (top) and Raman (bottom) spectra of Ameripol CB 220, cis-polybutadiene. The middle curve was obtained from a warmed-up sample, while the bottom curve was given by the same sample immediately after it was placed in the beam. The Raman instrument settings were a sensitivity of 100 × 3.0, a period of 3.5 sec, slit dimensions of 10 cm × 5 cm^{-1}, double (10 cm × 4.5 cm^{-1} for middle curve), and scan speed of 1 cm^{-1}/sec.

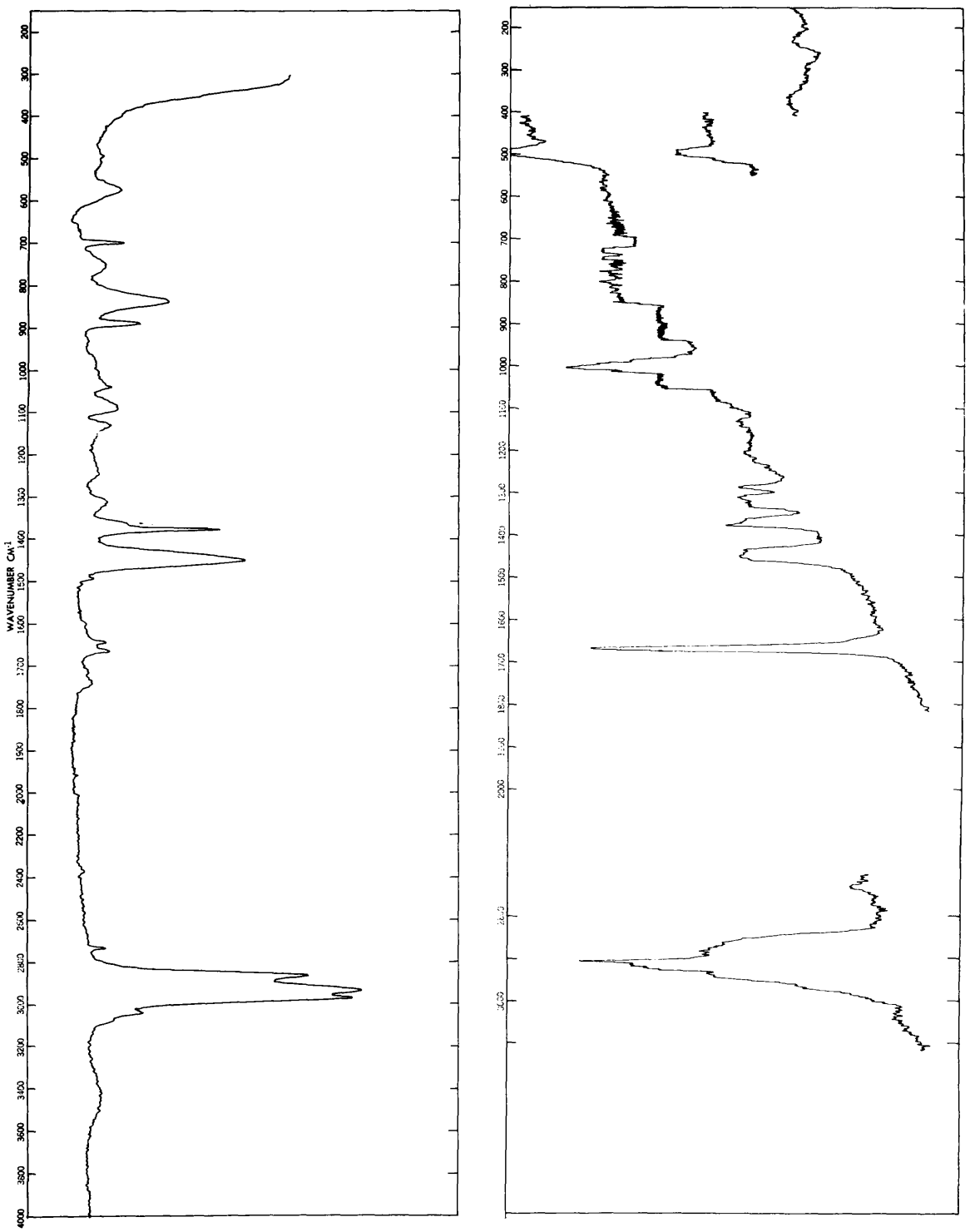

Fig. 7 - Infrared (top) and Raman (bottom) spectra of Isoprene 350, synthetic polyisoprene. The Raman instrument settings from 150 to 1800 cm^{-1} were a sensitivity of 100 × 3.0, a period of 3.5 sec, slit dimensions of 10 cm × 6 cm^{-1}, double (single to 400 cm^{-1}), and a scan speed of 1 cm^{-1}/sec; the settings from 2700 to 3100 cm^{-1} were a sensitivity of 200 × 3.0 and slit dimensions of 10 cm × 7.5 cm^{-1}, double.

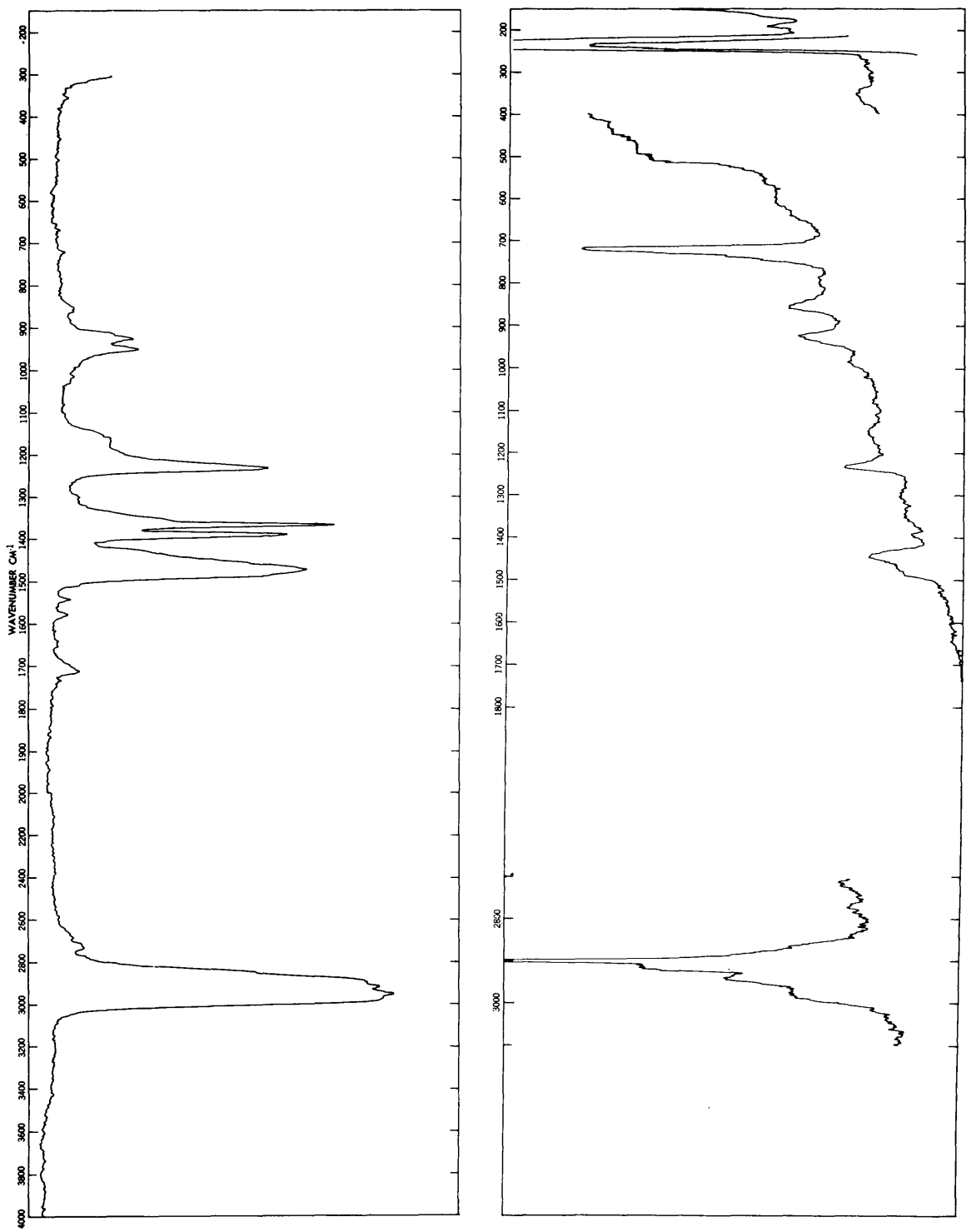

Fig. 8 - Infrared (top) and Raman (bottom) spectra of butyl HT 10-66, isobutylene-isoprene copolymer. The Raman instrument settings from 150 to 1700 cm^{-1} were a sensitivity of 200 × 1.7, a period of 3.5 sec, slit dimensions of 10 cm × 6 cm^{-1}, double (single to 400 cm^{-1}), and a scan speed of 1 cm^{-1}/sec; the setting from 2700 to 3100 cm^{-1} were a sensitivity of 200 × 3.0 and slit dimensions of 10 cm × 8 cm^{-1}, double.

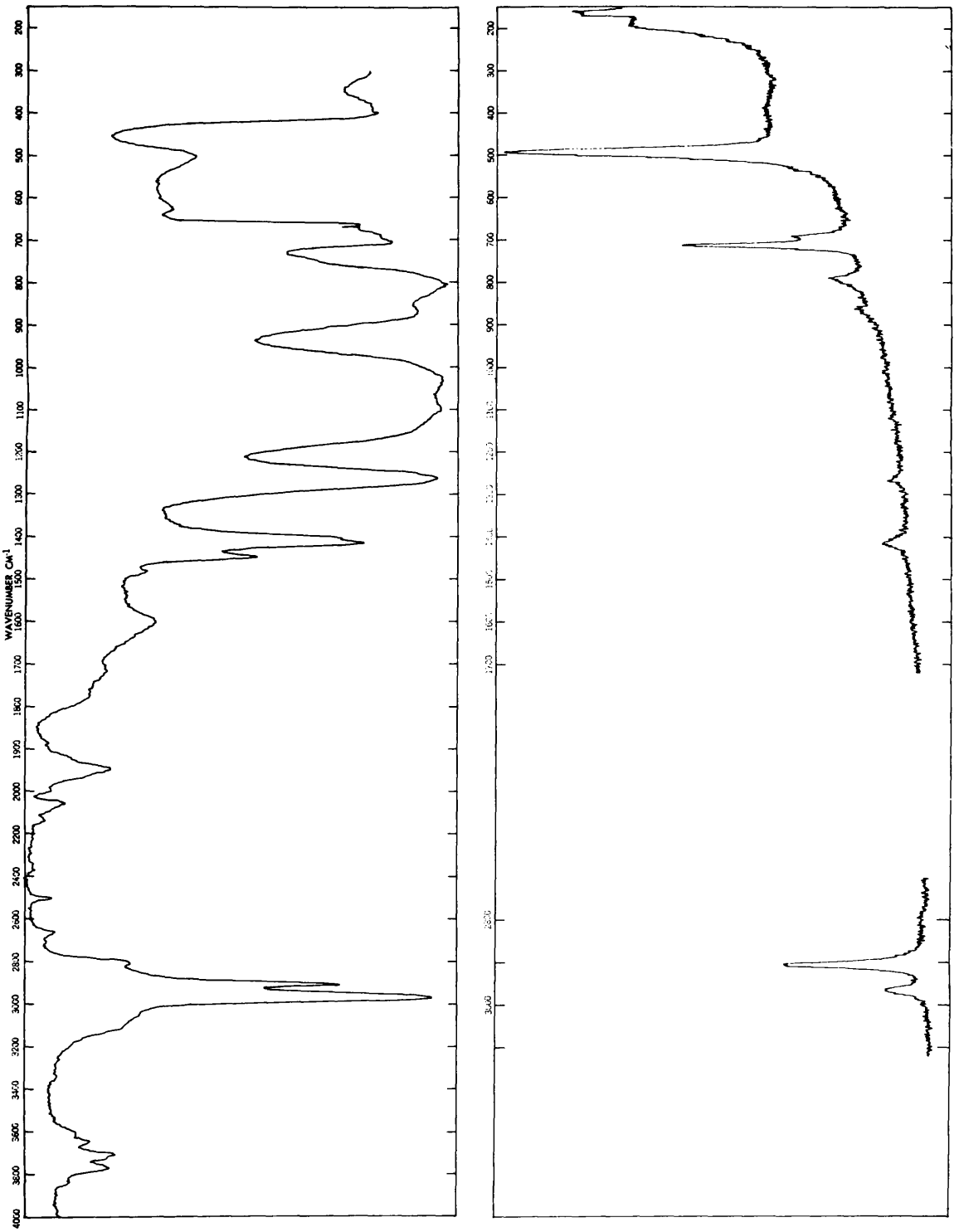

Fig. 9 - Infrared (top) and Raman (bottom) spectra of Silastic 400, poly(dimethylsiloxane). The Raman instrument settings were a sensitivity of 100 × 3.0, period of 2 sec, slit dimensions of 10 cm × 5.5 cm^{-1}, double (10 cm × 7 cm^{-1} from 2700 to 3100 cm^{-1}), and a scan speed of 1 cm^{-1}/sec.

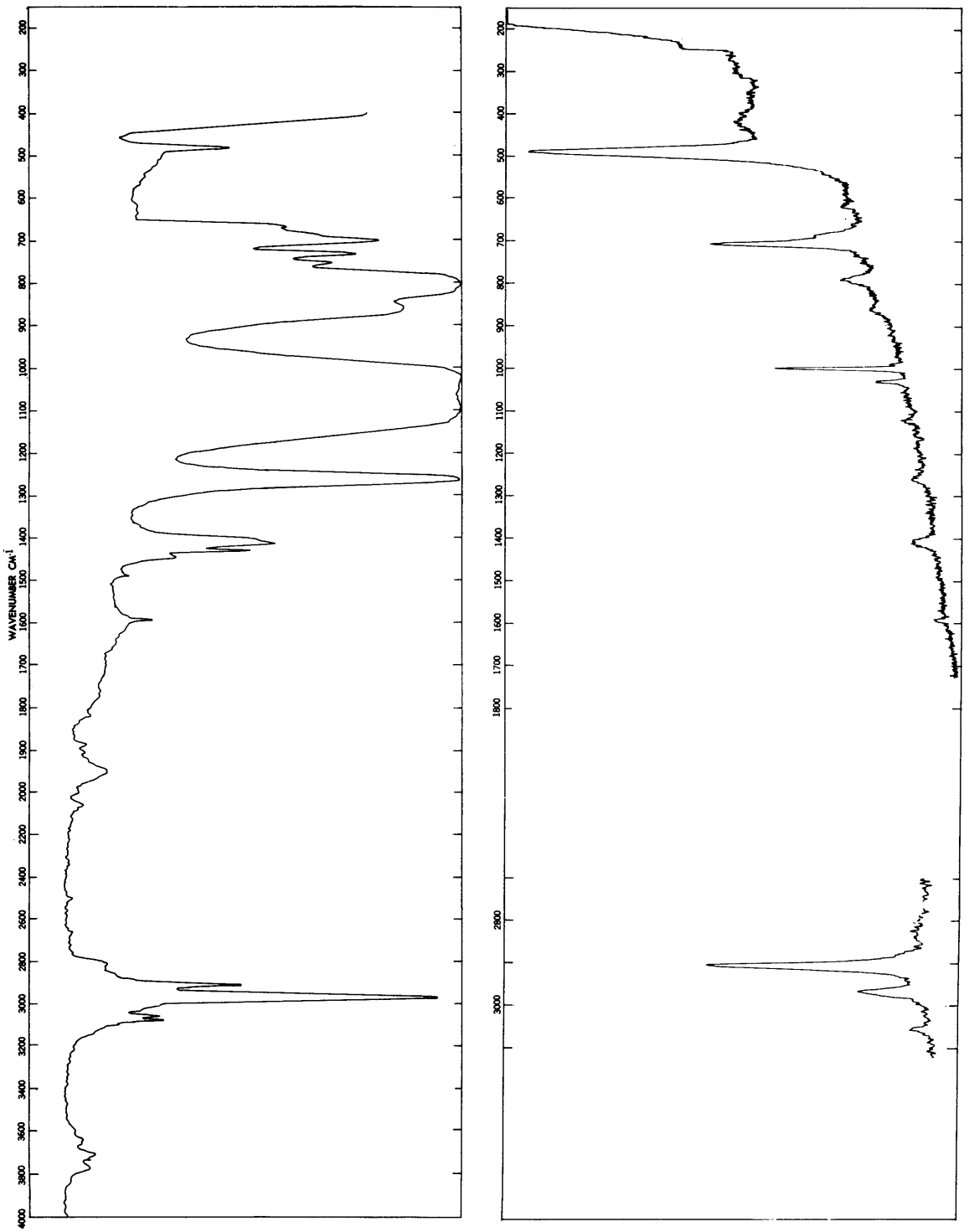

Fig. 10 - Infrared (top) and Raman (bottom) spectra of Silastic 440, a mixed methyl phenyl vinyl silicone. The Raman instrument settings were a sensitivity of 100 × 3.0, a period of 2 sec, slit dimensions of 10 cm × 7 cm^{-1}, double, and a scan speed 1 cm^{-1}/sec.

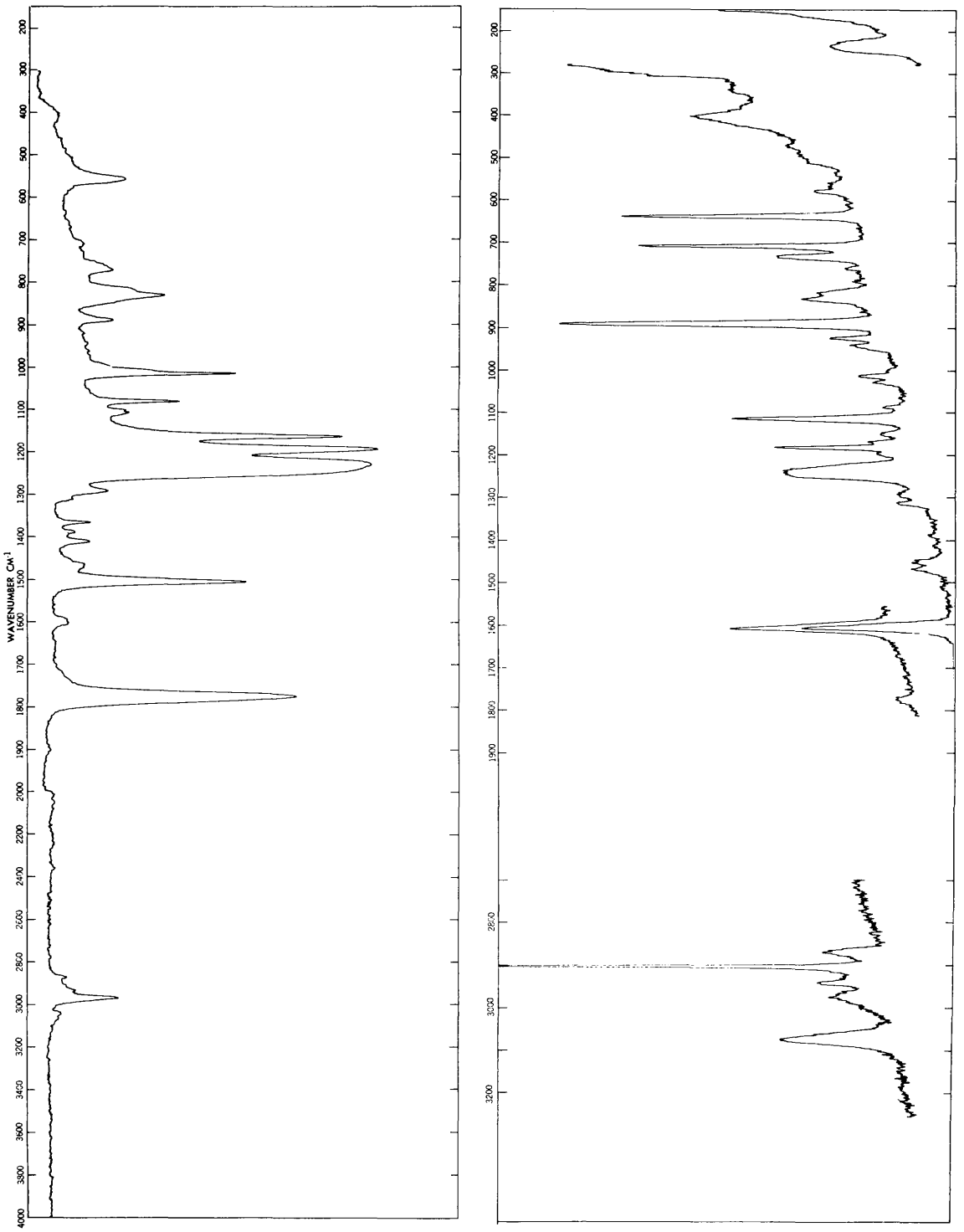

Fig. 11 - Infrared (top) and Raman (bottom) spectra of Merlon M-90, polycarbonate. The Raman instrument settings from 150 to 1800 cm^{-1} were a sensitivity of 100 × 2.4, a period of 2 sec, slit dimensions of 10 cm × 4 cm^{-1}, double (single to 300 cm^{-1}), and a scan speed of 1 cm^{-1}/sec, the settings from 2700 to 3200 cm^{-1} were a sensitivity of 200 × 2.4 and slit dimensions of 10 cm × 5 cm^{-1}, double.

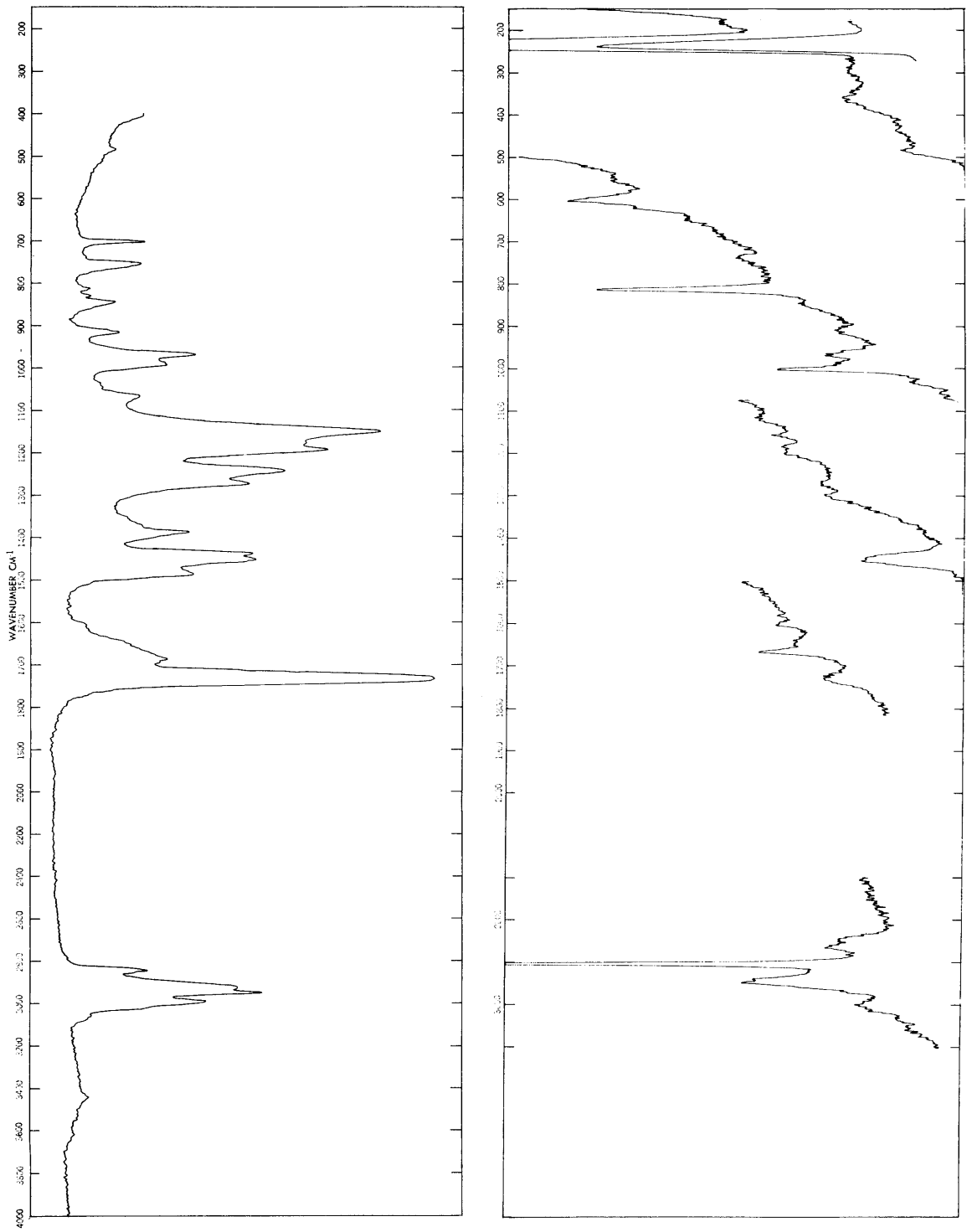

Fig. 12 - Infrared (top) and Raman (bottom) spectra of implex, modified poly(methyl methacrylate). The Raman instrument settings were a sensitivity of 100 × 3.0 (50 × 3.0 for inset from 150 to 300 cm^{-1}), period of 3.5 sec, slit dimensions of 10 cm × 7 cm^{-1}, double (single to 500 cm^{-1}), and a scan speed of 1 cm^{-1}/sec.

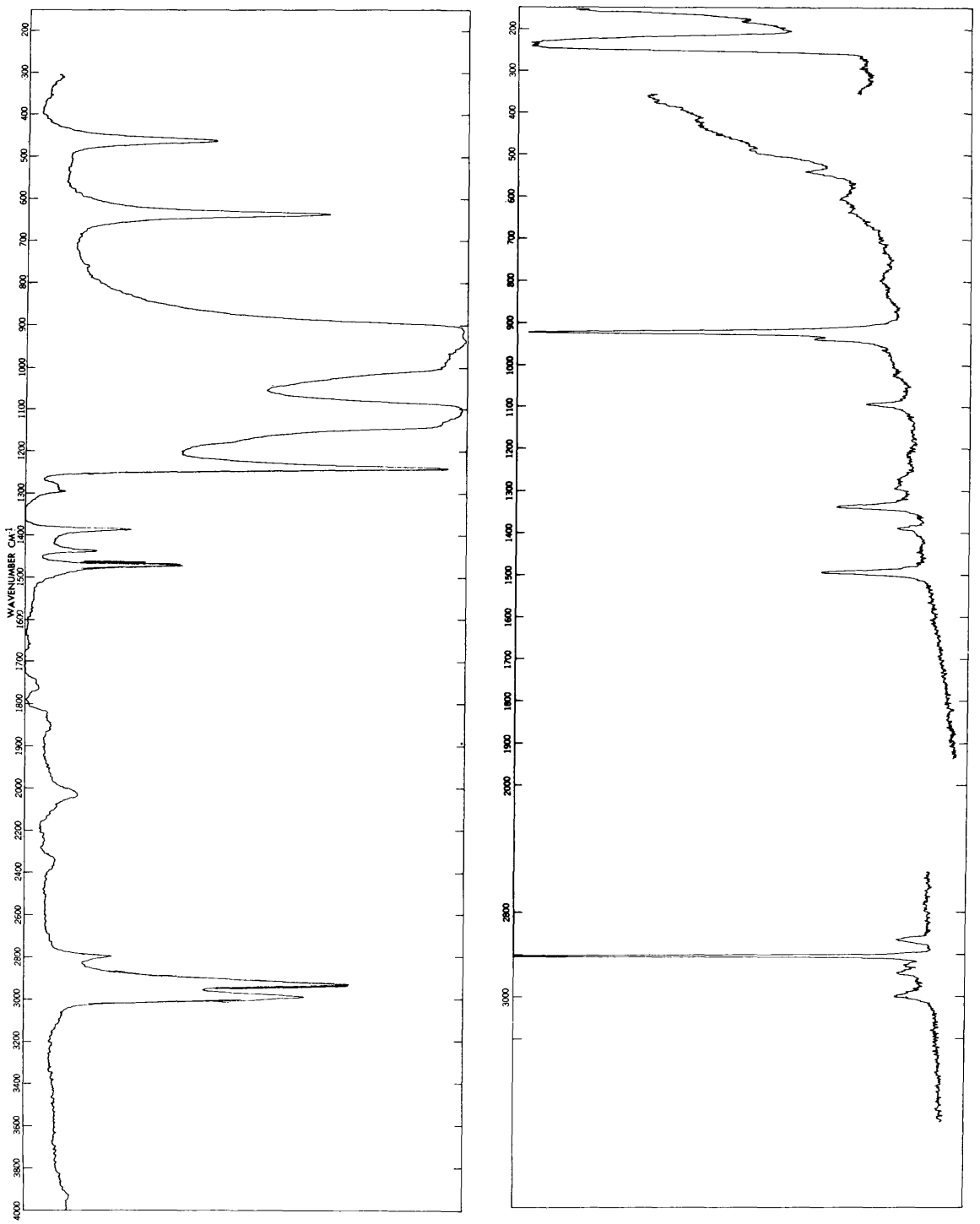

Fig. 13 - Infrared (top) and Raman (bottom) spectra of Delrin, polyoxymethylene. The Raman instrument settings were a sensitivity of 100 × 2.8, a period of 2 sec, slit dimensions of 5 cm × 6 cm^{-1}, double (single to 350 cm^{-1}), and a scan speed of 1 cm^{-1}/sec.

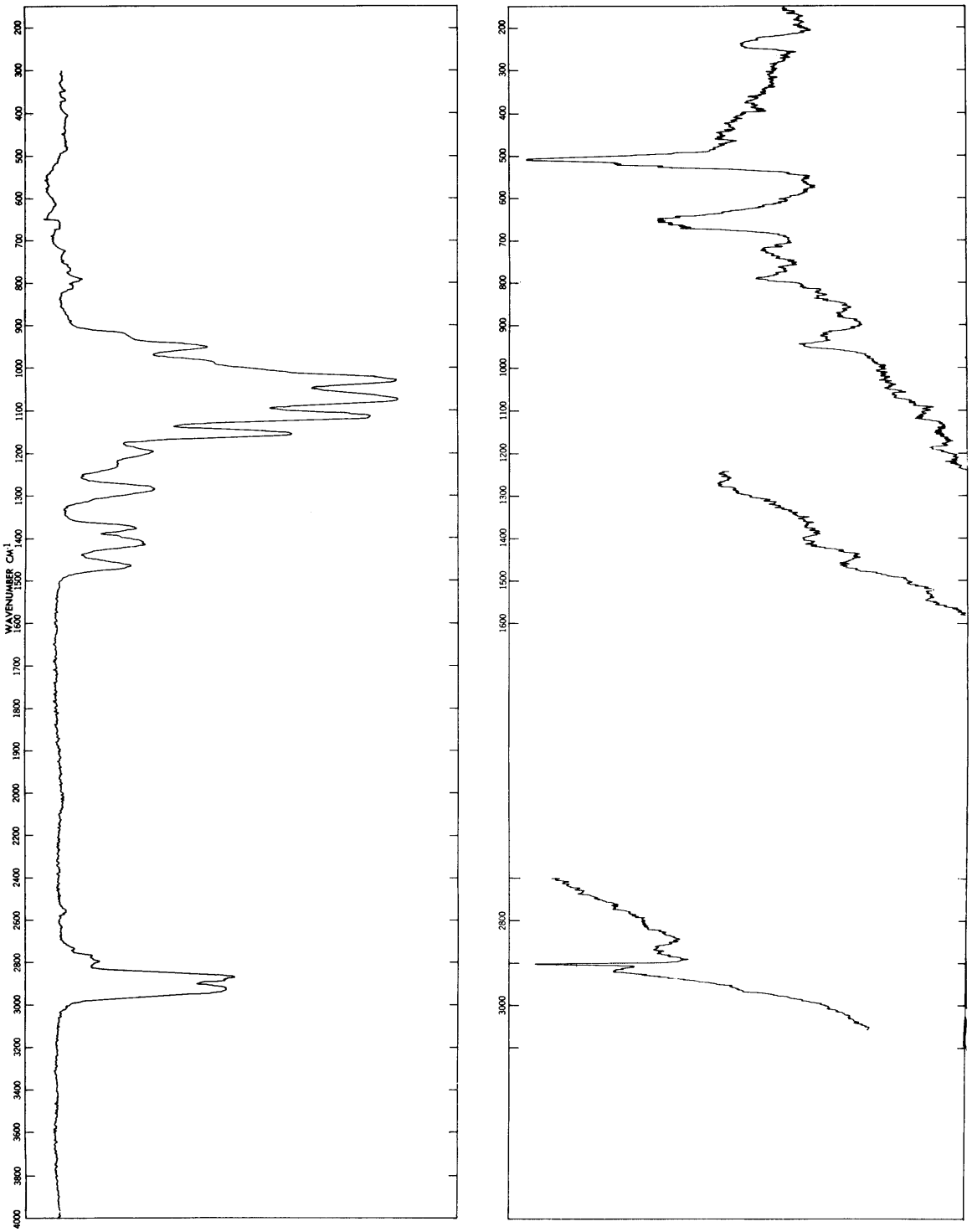

Fig. 14 - Infrared (top) and Raman (bottom) spectra of Thiokol LP-3, liquid polysulfide rubber. The Raman instrument settings from 150 to 1600 cm^{-1} were a sensitivity of 100 × 2.6, a period of 3.5 sec, slit dimensions of 10 cm × 5.5 cm^{-1}, single, and a scan speed of 1 cm^{-1}/sec, the settings from 2700 to 3100 cm^{-1} were a sensitivity of 100 × 3.0 and slit dimensions of 10 cm × 5.5 cm-1, double.

Table 1
Common Intensity Differences Between Infrared and Raman Spectra

Strongly Raman Active		Strongly Infrared Active		Strong in Both	
Vibration	Frequency Range (cm^{-1})	Vibration	Frequency Range (cm^{-1})	Vibration	Frequency Range (cm^{-1})
Aromatic C–H stretch	3000-3100	C=O stretch	1600-1800	Aliphatic C–H stretch	2800-3000
C=C stretch	1600-1700	C–O stretch	900-1300	C≡N stretch	2200-2300
C≡C stretch	2100-2250	O–H stretch (H bonded)	3000-3400	Si–H stretch	2100-2300
S–S stretch (Se–Se, etc.)	400-500	Aromatic CH out-of-plane deformation	650-850	C-halogen stretch	500-1400
C–S stretch (C–Se, etc.)	600-700	N–H stretch (H bonded)	3100-3300		
Aromatic ring breathing	950-1050	Si–O–Si antisymmetric stretch	1000-1100		
Aromatic C=C in-plane vibration	1500-1700				
N=N stretch	1575-1630				
Si–O–Si symmetrical stretch	450-550				
In general: 1. Vibrations of symmetrical groups 2. Stretching of bonds, particularly nonpolar or slightly polar bonds		In general: 1. Vibrations of asymmetric groups 2. Bending modes 3. Stretching of polar bonds			

Figures 3 through 5 illustrate the type of spectrum to be expected from laser-excited commercial samples of products which, after tedious purification, gave only poor to fair spectra using the mercury arc. It is interesting to note in these spectra some differences between Raman and infrared activity. Several fundamental vibrations appear in the Raman spectrum of polyethylene (Fig. 3) which are infrared inactive. It was not until the Raman spectrum was available that some combination bands seen in the infrared could be explained, since they are combinations of Raman and infrared active vibrations (10). The same type of situation exists for polypropylene, shown in Fig. 4. One of the interesting features of the polystyrene Raman spectrum in Fig. 5 is the ring-breathing vibration seen near 1000 cm^{-1}, characteristic of monosubstituted aromatic rings. This vibration is weak in the infrared and can be useful for detecting phenyl groups by means of Raman spectra. The aromatic C–H stretch is also a good diagnostic line in Raman spectra, although this region is not always as helpful as in the infrared because the sensitivity of our detector diminishes in the region of greater Raman shifts.

The remaining figures show some spectra of samples that have been more difficult to handle in the past, and most have not been reported previously. Those for which Raman spectra have been given were not examined as untreated samples.

Figure 6 illustrates a tactic that was used to improve marginal spectra. We found that some samples which had high background emission when first inserted in the beam improved after irradiation for an hour or two. This warming-up process is not peculiar to polymers, and it is reversible; that is, a warmed-up sample which is removed from the beam reverts to giving a high background if it is reinserted. The bottom curve in Fig. 6 was run immediately after placing the sample in the beam; the fluorescence is high and the entire spectrum could not be obtained without changing the baseline setting. The middle curve was recorded after the same sample had been allowed to remain in the beam about 2 hours; the improvement is obvious. Moderate heating of a sample with a heat gun was found to have a similar effect, also reversible but not as controllable. Further investigation of this effect and the fluorescence phenomenon will be necessary to cope with the problems.

The C=C stretching mode is a vibration for which Raman spectroscopy is generally more sensitive than infrared spectroscopy. Figures 6 through 8 illustrate this utility. Figure 6 shows the spectra of a cis-polybutadiene rubber, for which the characteristic C=C stretch is seen at 1660 cm^{-1}, strong in the Raman spectrum and very weak in the infrared. For this case of a stereoregular polymer, the C–H out-of-plane bending vibration is very apparent in the infrared at approximately 730 cm^{-1}.

Another and perhaps more dramatic example of this double bond vibration is seen in the spectrum of polyisoprene (Fig. 7). Here the C–H out-of-plane bending does not give the help provided in the previous case, and the unsaturation might be doubtful from the infrared spectrum alone. Although this sample was a synthetic isoprene rubber, natural rubbers were examined as well. Some Raman lines were seen for pale crepe and smoked sheet samples of natural rubber, but the fluorescence was much worse than for the synthetic sample. This again suggests that the problem lies with impurities, since the natural product would be expected to contain more fluorescing materials.

Spectra of Butyl rubber, a copolymer of isobutylene and isoprene, are shown in Fig. 8. If the isoprene content were significant, a Raman line would have been observed at 1660 cm^{-1} as was seen in Fig. 7 for polyisoprene. The absence of this line in the Raman spectrum of the Butyl rubber indicates the isoprene content is very small. This is not as easily deduced from a comparison of the infrared spectra, which are similar enough that the absence of a weak 1660-cm^{-1} band in the copolymer spectrum is not very indicative. Because the vibration is strong in the Raman effect, however, its absence clearly indicates the lack of isoprene. This illustrates nicely the utility which Raman spectroscopy can have.

Another interesting group of polymers is the silicones. Work done on the structure of disiloxane (11,12) has shown this molecule to be approximately linear, the Si–O–Si bond angle being about 155 degrees as a result of back bonding. The near linearity creates an approximate center of inversion and leads to approximate mutual exclusion between Raman and infrared spectra. A similar situation evidently exists for the silicone polymers. Figure 9 presents spectra for poly(dimethylsiloxane), a silicone rubber. As in disiloxane, the strong Si–O–Si antisymmetrical stretching vibration seen in the infrared between 1000 and 1100 cm^{-1} is absent from the Raman spectrum, but the strong Raman line at about 490 cm^{-1} is probably the symmetrical Si–O–Si stretching vibration, which is weak in the infrared. The other prominent feature of the Raman spectrum is the C–Si stretch at approximately 710 cm^{-1}, while the methyl groups are responsible for the other infrared bands.

The Raman spectrum of a mixed methyl phenyl vinyl silicone is seen in Fig. 10; this resembles that of the previous polymer, with the addition of Raman lines indicative of the phenyl substituents (ring-breathing vibration at 1000 cm^{-1}, ring mode at 1600 cm^{-1}, and C–H stretch at 3060 cm^{-1}). Unfortunately, the C=C stretch of the vinyl group did not appear in the Raman spectrum, although this might be expected to be weaker than other olefinic stretches because of the asymmetry of the group.

The 1000-cm^{-1} ring-breathing mode in Raman spectra is a good diagnostic peak for monosubstituted aromatic rings and seems to be observed in meta-disubstituted and 1,3,5-trisubstituted rings as well. Para-disubstituted systems do not show this vibration, however, and a line at 1050 cm^{-1} occurs in many ortho-disubstituted compounds. The spectra of a polymer containing para-substituted rings, a polycarbonate, are shown in Fig. 11. Here, there is no 1000-cm^{-1} Raman line, but the 1600 and 3060 cm^{-1} lines are very strong. Another interesting feature of these spectra is the carbonyl stretching vibration. Typical of infrared spectra, this curve shows the very characteristic strong band at 1780 cm^{-1} arising from the C=O stretch. Only a very weak line is seen in the Raman spectrum at this frequency, however.

Another example of this C=O intensity difference is seen in poly(methyl methacrylate), which has been examined by other workers (13) and whose spectra are shown in Fig. 12. Again, the strong infrared bands, characteristic of the C=O group and C–O stretch of the ester, have only weak Raman counterparts. This was a modified methyl methacrylate polymer, and the combination of Raman and infrared data suggests that the modification

is the introduction of phenyl groups and unsaturation. The Raman spectrum, particularly, shows the 1000- and 1600-cm^{-1} lines of the monosubstituted ring and the 1670-cm^{-1} C=C stretch.

Polyoxymethylene is another polymer whose Raman spectrum has been studied. Tadokoro, et al. (14), using mercury arc excitation, examined Carbowax samples that were purified by reprecipitation, but they were not able to obtain a spectrum from Delrin acetal resin because of background fluorescence. Figure 13 presents the spectrum obtained from this polymer using laser excitation. Band assignments have been made by Tadokoro, et al (14,15).

An interesting example of the complementary nature of infrared and Raman spectra is seen in Fig. 14 for the case of a liquid polysulfide rubber. The molecule contains two characteristic linkages, those of the ether groups and of the polysulfide units. The prominent infrared feature is the strong absorption in the 1000-cm^{-1} region, arising from C–O–C vibrations; little indication is seen of the S–S linkage in the 500-cm^{-1} region expected for S–S stretching. Quite another situation exists in the Raman spectrum, however. Here the S–S stretch is observed at 510 cm^{-1} and the C–S stretch at 650 cm^{-1}, and these are the strongest lines. Conversely, little indication is seen of the ether groups so apparent in the infrared spectrum. This is a striking example of the necessity of both spectra for complete characterization of a molecule.

APPLICATIONS

There seems to be a place for Raman spectroscopy in identification of polymers. The usefulness for detecting unsaturation, aromatic substituents, and other groups, such as polysulfide, has been demonstrated. Extension of this preliminary work will include the preparation of compilations of reference spectra similar to infrared collections, possibly with depolarization measurements on some samples, and more detailed examination of some specific polymers of interest.

Another area of interest in which Raman spectroscopy can be of value to the polymer chemist is structural analysis. In addition to the information to be obtained merely from Raman activity, depolarization measurements on specific lines can give important symmetry and structural information. Recent work of Cornell and Koenig (16) illustrates the value of the laser in this application. Hendra and Willis (17) have used the polarized nature and directionality of the laser beam to investigate orientation effects of stretched polyethylene fibers. Also, the far-infrared region is easily accessible in the Raman effect. Vibrations having frequencies in the range of 50 to 300 cm^{-1} can be observed in the ordinary Raman spectrum, while special equipment is necessary to determine infrared absorption in this range. These vibrations may be of particular interest in polymer samples, since lattice modes of crystals, conformational transitions, and low-lying skeletal vibrations fall in this range. The Raman effect has contributed to conformational studies of polypropylene (18).

Of course, problems still exist in the application of the technique – the laser has not cured everything. Fluorescence, while decreased, does occur, and spectra cannot be obtained from some samples. However, from this preliminary work on commercial samples with no pretreatment, it appears that new capabilities exist and that the way is now open for Raman spectroscopy to make valuable contributions in the field of polymer chemistry.

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13. ABSTRACT

The He-Ne laser has greatly reduced the problem of fluorescence, which has in the past almost completely obscured conventionally excited (mercury arc) Raman spectra of all except the simplest and purest polymers. In many instances it is now possible to record Raman spectra of polymers without any prior purification whatsoever. A comparison of the Raman and infrared spectra of twelve selected commercial polymers shows the complementary nature of these two spectroscopic techniques for identification purposes. Vibrations such as C=C stretching (in polybutadiene) and S-S and C-S stretching (in polysulfide rubber) give rise to strong Raman lines but produce weak infrared absorption bands; conversely, the C=O group of polycarbonates and polyesters is a strong infrared absorber which produces a weak Raman line.

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