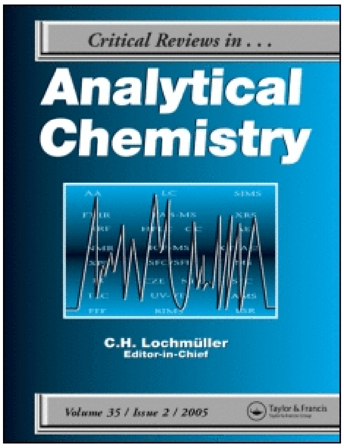


Critical Reviews in Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

Recent Developments in Polymer Analysis and Characterization. I. Spectral Methods

Harry V. Drushel; J. J. Elliott

To cite this Article Drushel, Harry V. and Elliott, J. J.(1970) 'Recent Developments in Polymer Analysis and Characterization. I. Spectral Methods', Critical Reviews in Analytical Chemistry, 1: 2, 161 — 192

To link to this Article: DOI: 10.1080/10408347008542733

URL: http://dx.doi.org/10.1080/10408347008542733

RECENT DEVELOPMENTS IN POLYMER ANALYSIS AND CHARACTERIZATION. I. SPECTRAL METHODS

Author: **Harry V. Drushel**
Esso Research Laboratories
Humble Oil & Refining Co.
Baton Rouge, La.

Referee: J.J. Elliott
Analytical and Information Div.
Esso Research and Engineering Co.
Linden, N.J.

TABLE OF CONTENTS

I. INTRODUCTION

This review will be presented in two parts. Part I deals with spectral techniques, while part II will cover the remaining non-spectral techniques such as pyrolysis gas-liquid chromatography, gel-permeation chromatography, thermal analysis, etc. It is not the purpose of this review to be comprehensive. Rather, only a few techniques representative of recent trends or advances will be discussed in a critical manner. Therefore, only a few papers within a given field (spectral technique) will be discussed in depth. Reference may be made more frequently to other papers in support of discussion, however.

Organization of the review is according to technique. In this way, techniques rather than specific polymer systems can be treated more critically and discussed in depth. This tends to favor the specialist, e.g., the infrared spectroscopist. Admittedly, this possibly overlooks the interests of the polymer chemist interested in only several specific polymer systems. Since this is part of a series of *CRC Critical Reviews in Analytical Chemistry,* such an organization is justified.

It is somewhat difficult to subclassify the various methods and studies within a given technique. Some techniques may elucidate microstructure or determine stereoregularity and crystallinity, while others provide analytical information about copolymer composition, blend ratios, antioxidant content, etc. In general, the former might be considered as polymer characterization, the latter as polymer analysis. The following discussion will deal primarily with the determination of the microstructure and the composition of ethylene-propylene copolymers (EPM) by infrared spectrophotometry. In addition, some newer techniques for the characterization and analysis of polymers such as laser Raman, C^{13} nuclear magnetic resonance, and electron spectrometry will be discussed briefly.

II. DISCUSSION OF METHODS

A. Infrared and Raman Spectrometry

1. *General Discussion*

Infrared (IR) spectrophotometry is probably the most extensively applied spectral technique. Therefore, in this review, more space will be devoted to this technique than to any of the others. From the sample preparation point of view, IR lends itself extremely well to polymer characterization and analysis. Infrared spectrophotometry has been practiced, and infrared spectrophotometers have been commercially available for a much longer period of time than nuclear magnetic resonance (NMR), for example. Raman spectrometry had not experienced the same degree of acceptance until the more recent application of laser sources.

Some idea of the extent to which IR and Raman methods have been applied may be inferred from Table 1 which lists the reviews and books, devoted wholly or in part to IR or Raman, which have appeared in the past five to ten years. Only a few older than five years have been listed. Obviously, with this much literature already available, this review can only touch on a few techniques. It will also be assumed that the reader is versed in the theory and practice of spectroscopy. Background discussion will be minimal, therefore.

Table 1 should serve as a source of references in the event that the reader wishes to refer to the almost inexhaustible literature on IR and Raman spectroscopy. Most of these references deal with the more practical aspects of polymer analysis (identification of industrial polymers, determination of antioxidants, etc.) while a smaller number deal with elucidation of polymer structure, vibrational analysis, etc. (see books by S. Krimm and by R. Zbinden).

TABLE 1

Recent Reviews and Books on Infrared and Raman Methods

Author(s)	Subject	Publisher
Anon.	Complete issue dealing with structure determinations in organic systems including homo- and copolymers	*Z. Anal. Chem.*, 235, 1 (1968).
Brame, E.G., Jr.	Applied spectroscopy reviews Vol. 1 and 2	Dekker, New York, 1968, 1969.
Chan, M.G., Hawkins, W.L.	Internal reflectance spectrometry in prediction of outdoor weatherability	*Amer. Chem. Soc., Div. Polymer Chem. Preprints,* 9 (2), 1638 (1968).
David, D.J., Staley, H.B.	Analytical chemistry of the polyurethanes, Pt. 3, high polymers, Vol. 16	Interscience, New York, 1969.
Duckett, K.E., Deeds, W.E.	Lasers in single fiber infrared microspectrometry	*Microtech,* 21 (4), 39 (1967).
Fox, R.H., Schuetzman, H.I.	Infrared identification of microscopic samples of manmade fibers	*J. Forensic Sci.*, 13, 397 (1968).
Gesner, B.D.	Review of advances in analysis of polymers	*Amer. Chem. Soc. Div. Polymer Chem. Reprints,* 8 (2), 1482 (1967).
Gottlieb, K.	Measuring infrared dichroism of crystals and oriented polymers	*Z. Instrumentenk.*, 75, 125 (1967).
Grime, D.	Identification of surface coating resins	*Brit. Ink. Maker,* 10, 36 (1967).
Harwood, H.J.	Sequence distribution in copolymers	*Angew. Chem. Int. Edit.*, 4, No. 12, 1051 (1965).
Haslam, J., Willis, H.A.	Identification and analysis of plastics	Van Nostrand, Princeton, N.J., 1965.
Hathaway, C.E., Nielsen, J.R.	Raman irradiation system for powders and polymers	*Spectrochim. Acta, A,* 23, 881 (1967).
Henniker, J.C.	Infrared spectrometry of industrial polymers	Academic Press, New York, 1967.
Hummel, D.O.	Infrared spectra of polymers	Interscience, New York, 1966.
Hummel, D.O., Scholl	Infrared analysis of polymers, resins and additives: an atlas, Vol. I, Part 2	Interscience, New York, 1969.
Kagarise, R.E.	Infrared spectra of plastics and resins. II. Materials developed since 1954	U.S. Clearinghouse Fed. Sci. Tech. Inform. *AD634427* (1966).
Kline, G.M.	Analytical chemistry of polymers. II. Molecular structure and chemical groups	Interscience, New York, 1962.
Kocskina, A.	Infrared investigations of polymers	*Kem. Kozlem.*, 29, 107 (1968).
Koessler, I.	Infrared absorption spectrometry of polymers	*Encyl. Polym. Sci. Technol.*, 7, 620 (1967).

Author(s)	Subject	Publisher
Kozlowski, W.	Preparation of fiber and polymer samples for infrared	*Polimery*, 12, 498 (1967).
Krimm, S.	Infrared spectroscopy and polymer structure	*Pure Appl. Chem.*, 16, 369 (1968).
Lever, A.E., Rhys, J.A.	Properties and testing of plastics materials	The Chemical Rubber Co., Cleveland, 1968.
Low, M.J.D., Mark, H.	Examination of organic coatings by infrared interference spectrometry	ACS National Meeting, Div. Org. Coatings Plastics Chem., Sept., 1968.
Luongo, J.P.	Infrared characterization of structural changes in polymers	*Amer. Chem. Soc. Div. Org. Coatings Plastics Chem. Preprint*, 28 (2), 58 (1968).
Mitchell, J., Jr., Chiu, J.	Review of analytical methods for high polymers	*Anal. Chem.*, 41, 249 R (1969).
Okuzumi, K.	Analysis of paints	*Benseki Kagaku*, 16, 758 (1967).
Saunders, K.J.	Identification of plastics and rubbers	Chapman & Hall, Ltd., London, 1966.
Schaufele, R.F.	Advances in vibrational Raman scattering spectrometry of polymers	*Trans. N.Y. Acad. Sci.*, 30, 69 (1967).
Schroeder, E., Hagen, E.	A review of separation and analysis procedures for plasticizers, stabilizers, antioxidants, UV absorbers, optical brighteners, etc.	*Plaste Kautschuk*, 15, 625 (1968).
Stein, R.S., Read, B.E.,	Optical characterization of orientation of amorphous polymers and amorphous parts of crystalline polymers	U.S. Clearinghouse Fed. Sci. Tech. Inform., *AD 664963* (1967).
Sukhov, F.F., Il'icheva, Z.F., Slovokhotova, N.A., Stimler, S.S.	Infrared spectra of polymers at low temperatures	*Vysokomol. Soedin., B*, 9, 851 (1967).
Swann, M.H., Adams, M.L., Esposito, G.G.	Review of analytical methods for coatings	*Anal. Chem.*, 41, 35 R (1969); 39, 42R (1967).
Tyler, W.P.	Critical review on recent developments in analysis of rubber	*Rubber Chem. Technol.*, 40, 238 (1967).
Wadelin, C.W., Trick, G.S.	Review of analytical methods for rubber	*Anal. Chem.*, 41, 299 R (1969); 39, 239 R (1967).
Zbinden, R.	Infrared spectrometry of high polymers	Academic Press, New York, 1964.
Zhbankov, R.G.	Infrared spectra of cellulose and its derivatives	Plenum Press, New York, 1966.

2. *Elucidation of Microstructure by Infrared Spectrophotometry*

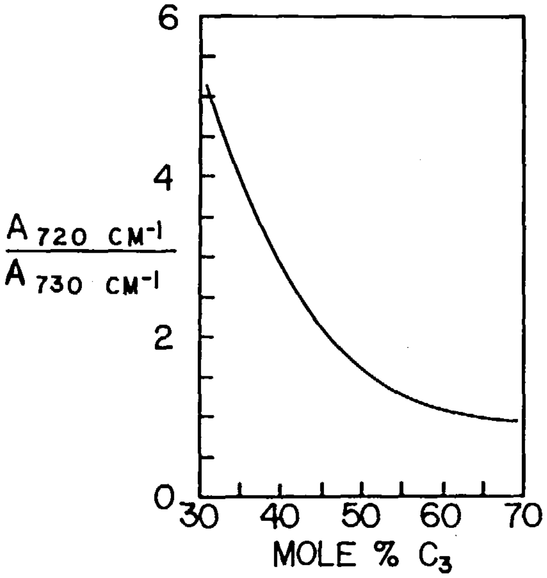
In keeping with the intent of this publication, the subject of the analytical determination of ethylene-propylene copolymer (EPM) microstructure by IR spectrophotometry was chosen for the following discussion. Information of this type when combined with other data such as molecular weight distribution, copolymer composition, etc. should make it possible, at least in principle, to predict physical properties or end use characteristics. Although this has not been achieved to date it would be of obvious industrial value.

Drushel et al.[1] evaluated the differences in EPM microstructure as a function of EPM composition by computer analysis of digitized IR spectra. Digitizing techniques and the application of digital computers have increased significantly in the last several years. In this application the computer is used, in effect, to resolve the badly overlapped bands of interest.

Two regions of the IR spectrum of EPM are sensitive to changes in microstructure or monomer sequence distribution. The methylene group rocking frequencies between 720 and 820 cm^{-1} reflect differences in the number of contiguous methylene groups. Similarly, the methyl group rocking frequencies between 930 and 980 cm^{-1} reflect differences in the number of contiguous propylene units.

Veerkamp and Veermans[2] described a method for evaluating the relative number of methylenes in various sequences by a differential IR measurement. They ascribed methylene sequences of 5 or more to the band at 720 cm^{-1} while sequences of 3 contiguous methylenes were assumed to give rise to the band at 730 cm^{-1}. Although they recognized that the band at 752 cm^{-1} was attributed to 2 contiguous methylene groups, presumably derived from propylene monomer units (C_3) in head-to-head configuration, they refrained from measuring it by graphic methods because it was broad compared to the other bands. The intensities of the other 2 bands were measured differentially as follows. The copolymer film was placed in the sample beam while a wedge-shaped liquid cell containing *n*-hexadecane was placed in the reference beam. The variable-path-length cells currently available might achieve this more elegantly because of the fine micrometer adjustment. They adjusted the wedge so that absorption at 720 cm^{-1} was fully compensated. The base-line intensity at 730 cm^{-1} was then measured from the differential spectrum. Intensity of the 720 cm^{-1} band was measured by removing the copolymer film and, without moving the wedge, recording the spectrum of the *n*-hexadecane around 720 cm^{-1}. They assumed that the absorptivities for 3 and 5 or more contiguous groups were the same. This was based on the fact that several model compounds yielded 0.26×10^{-4} ml $mole^{-1}$ cm^{-1} for both sequences. On this basis they used the ratio of the absorbances at 720 cm^{-1} and 730 cm^{-1} to evaluate the copolymer structure as a function of overall copolymer composition. Although this approach provided moderately good results, it is unlikely that the peak absorptivities at 720 cm^{-1} and 730 cm^{-1} are identical. Furthermore, it is unlikely that the band shape (i.e., band width) is the same for *n*-hexadecane as for the 720 cm^{-1} band in the polymer. However, this would not significantly alter their general conclusions, shown in Figure 1, that Natta's theoretical calculations[3] were realistic in light of their measurements.

FIGURE 1



Absorbance ratios at 720 cm^{-1} and 730 cm^{-1} vs. copolymer composition.

Somewhat later, Bucci and Simonazzi[4] devised a method for evaluating distribution of monomeric units by means of a three point measurement and a set of three simultaneous equations. By obtaining absorptivities from n-nonadecane [5 or more contiguous methylenes, i.e., $n \geq 5$ for $(\text{—CH}_2\text{—})_n$], hydrogenated natural rubber ($n = 3$), and atactic polypropylene which contains some head-to-head propylene units ($n = 2$), they arrived at the following set of simultaneous equations:

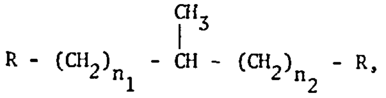
$$\frac{A_{752\text{cm}^{-1}}}{t} = A_2 + 0.20\ A_3 + 0.12\ A_5 \qquad (1)$$

$$\frac{A_{733\text{cm}^{-1}}}{t} = 0.1\ A_2 + A_3 + 0.35\ A_5 \qquad (2)$$

$$\frac{A_{722\text{cm}^{-1}}}{t} = 0.50\ A_3 + A_5\ . \qquad (3)$$

The thickness, t, was determined from the intensity of the 4310 cm^{-1} combination band. Thus, solution of the above equations gave the absorbances per unit thickness for the three unknowns A_2, A_3, and A_5. In addition, $\frac{A_{815\text{cm}^{-1}}}{t} = A_1$. They converted these values to the concentration of methylene groups by applying $\text{—CH}_2\text{—}$ absorptivities determined with "model" compounds. Absorptivities of 0.10, 0.15, 0.20, and 0.25×10^4 ml mole^{-1} cm^{-1} were obtained for CH_2 sequences of 1,2,3, and 5 or more from the following "model compounds," respectively: atactic polypropylene with head-to-tail linking, atactic polypropylene with a definite amount of head-to-head linking, hydrogenated natural rubber or squalane (2,6,10,14-tetramethylpentadecane), and linear C_{10}–C_{19} hydrocarbons. The results, plotted from their tabulated data as shown in Figure 2, agreed generally with Natta's[3] theoretical calculations. These results provided some of the best information about the methylene sequences but provided information about the propylene groups only by inference.

Natta et al.[5] added to the knowledge of the addition of propylene units in EPM. They interpreted differences in the methyl group absorption in atactic polypropylenes and propylene copolymers on the basis of the behavior of "model" compounds. They found that although the band at 1155 cm^{-1} remains fixed in position in 3- and 4-methylalkanes and other compounds of the general structure

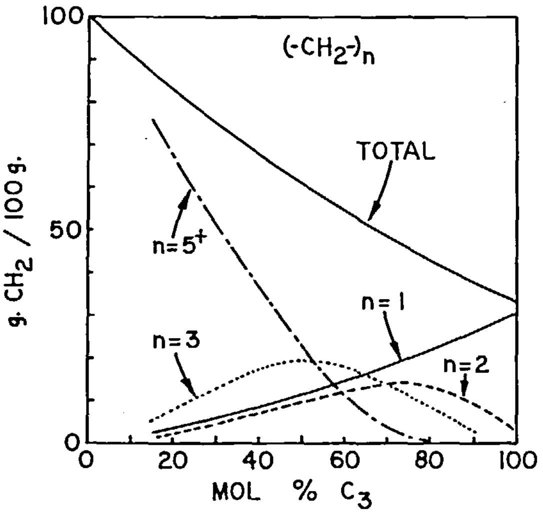


$$R - (CH_2)_{n_1} - \underset{}{\overset{CH_3}{\overset{|}{CH}}} - (CH_2)_{n_2} - R,$$

the methyl group band near 970 cm^{-1} varied measurably with differences in structure. The band occurs at 965 cm^{-1} in such compounds as 3-methylalkanes as well as in 2,2,4-trimethylhexane and 3,3,5-trimethylpentane. The frequency decreases to 955 cm^{-1} in 4-methylalkanes. This would be equivalent to the structures expected from head-to-head polymerization of propylene units. Finally, the band shifts to 930 cm^{-1} in squalane and in hydrogenated polyisoprene. Structurally, this corresponds to alternating monomer units of ethylene and propylene, viz., EPEPEP, etc.

Ciampelli and Valvasorri[6] studied the distribution of propylene units in EPM by measuring the ratio of absorbances at 972 cm^{-1} (attributed to two or more contiguous head-to-tail propylene units) and 937 cm^{-1} (attributed to isolated propylene units). They plotted these ratios vs. the propylene content and found some deviation from predicted theoretical behavior. Formation of head-to-head

FIGURE 2



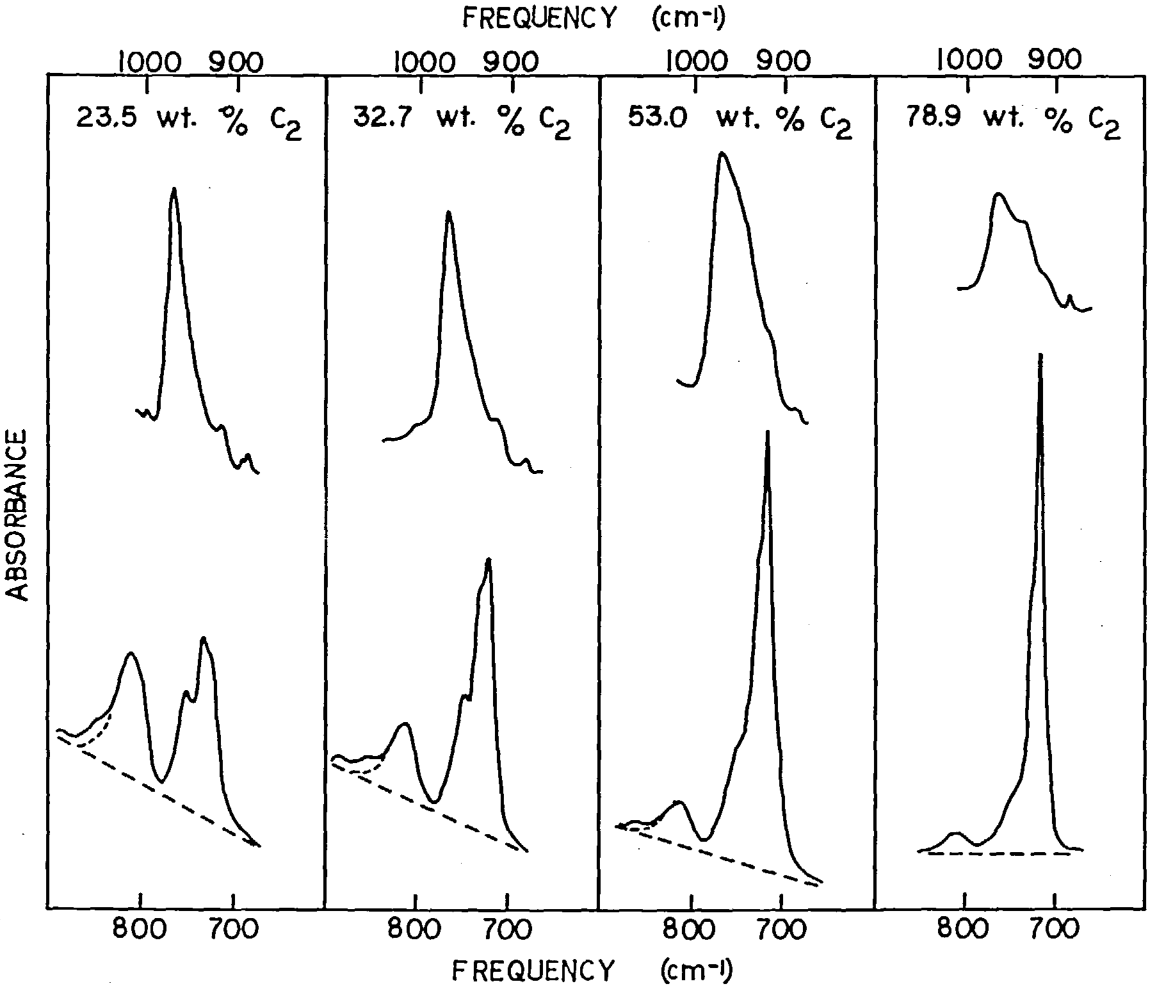
Methylene group sequence data determined by Bucci and Simonazzi.[4]

structures through propylene inversion as well as the tacticity of the propylene sequences could account for this.

Drushel et al.[1] attempted to resolve the seriously overlapped bands for the —CH_2— and —CH_3 groups at the above-mentioned frequencies by digitizing the infrared spectra and applying curve-fitting techniques on the computer. It was hoped that a complete evaluation of the behavior of both ethylene and propylene in the copolymer could be obtained. Figure 3 shows the changes which are observed in the —CH_2— and —CH_3 rocking regions of the infrared spectra of EPM as the copolymer composition is changed. The difficulty in resolving bands at the frequencies mentioned above is obvious.

Spectra were digitized by means of a general-purpose data-acquisition system constructed from standard components. Analog-to-digital conversion was accomplished by means of a pair of voltage-to-frequency converters. Electrical pulses from the converters were counted by means of electronically gated totalizers. Gate intervals were determined by the timer and preset controller. Raw digital data (counts) from each channel were converted to the proper binary code by the tape perforator adapter and then punched on paper tape by a Tally punch. Up-to-date computers are available with peripheral equipment for digitization which will accomplish this on a time-shared basis. Prior to applying the curve-fitting technique the raw digitized data were

FIGURE 3



Changes in methyl and methylene group absorption as a function of EPM copolymer composition.

converted to proper units, treated by a smoothing routine, interpolated, and prepared for plotting by means of an IBM 1620 computer. An auxiliary program was also used to calculate first and second derivatives for use in locating peaks, shoulders, or inflection points.

The digitized, smoothed, and interpolated spectra were used on an IBM 7074 computer to mathematically "resolve" the overlapped bands in the methyl and methylene rocking region of the spectrum. The computer program which was used was a modification of the iterative least-squares method described by Stone[7] altered in such a way as to be somewhat similar to the method of Meiron. A spectrum was assumed to be of the general form

$$I(\nu) = \alpha+\beta\nu+\gamma\nu^2+\sum_{j=1}^{N} a_j g_j\ (\nu,\nu_j{}^{o},\Delta\nu_j) \qquad (4)$$

where the first three terms represent background absorption, a_j is the peak intensity of band j, ν_j^0 is the band position, and $\Delta\nu_j$ is the band width parameter (half of the band width at half height). Although the Gaussian form was available in the program as an option, for these studies the function g_j was of the Cauchy (Lorentzian) form.

$$g_j = \frac{1}{1+\left(\frac{\nu-\nu_j}{\Delta\nu_j}\right)^2} \qquad (5)$$

Although this form (or distribution function) was used, it does not perfectly describe typical absorption bands from infrared spectrophotometers. Pitha and Jones[8] made a thorough study of this subject and made a comparison of optimization methods for fitting curves to infrared band envelopes. They pointed out, as have others, that isolated bands take a Lorentzian form on which is imposed a Gaussian perturbation of both physical and instrumental origin. Seshadri and Jones[9] and Abramowitz and Baumann[10] have described functions taking this perturbation into account.

The method of least squares is used to find the values of the parameters in Equation 4 which give a minimum value of the least squares function.

$$F = \sum_{\substack{\text{data}\\ \text{points}}} (I_{\text{input}}-I_{\text{calcd}})^2 = \sum_{k=1}^{m} [I(\nu_k)-\alpha-\beta\nu_k-\gamma\nu_k{}^2$$

$$\sum_{j=1}^{N} a_j g_j\ (\nu_j,\nu_j^{o},\Delta\nu_j)]^2 \qquad (6)$$

The minimum value of the function is found by setting the derivative, with respect to the parameters, equal to zero and solving for the values of the parameters. This becomes complex and is solved by a series of successive approximations. If the resulting set of partial differential equations is expanded in a Taylor series about a set of initial values for the unknown parameters, $p_1^0, p_2^0, \ldots\ldots\ldots\ p_{3n+3}^0$, the following equation is obtained, written in matrix form

$$\vec{0} \simeq \vec{g} + (\vec{p} - \vec{p}^{o})\ H \qquad (7)$$

where $\vec{g}$ is the vector with components $\partial F/\partial p_1^0$, $\vec{p}$ and $\vec{p}^{o}$ are the vectors of the parameters (i.e., band width, band position, etc.) and their current values, and H is the matrix whose i,j*th* element is

$$\left.\frac{\partial^2 F}{\partial_{p_i}\partial_{p_j}}\right|_{I_{in}=I_{calcd}} = 2\sum_{k=1}^{m}\frac{\partial I_{k\ \text{calcd}}}{\partial_{p_i}}\ \frac{\partial I_{k\ \text{calcd}}}{\partial_{p_j}} \qquad (8)$$

This linear system of equations may be solved $\vec{p}$ if the matrix, H, is nonsingular

$$\vec{p} = \vec{p}_o - \vec{g}\ \tau\ H^{-1} \qquad (9)$$

Stone[7] simplified the matrix H, which is often difficult to invert, by using only the diagonal elements (he let the i,j*th* element be zero unless i = j). Drushel et al.[1] obtained more rapid convergence by using the entire matrix and its diagonal form similar to that described by Meiron[11] and discussed by Pitha and Jones[8]

$$\vec{p} = \vec{p}_o - \vec{g}\ \tau\ (H+0.01\ B)^{-1} \qquad (10)$$

where H is the entire matrix and B is the diagonal form of the matrix. As pointed out by Pitha and Jones,[8] Meiron's method yields rapid convergence because the scalar is selected which gives the lowest value of F at each step. Instead, Drushel et al.[1] used a fixed value of 0.01 which, nevertheless, provides reasonably rapid convergence. As seen in Equation 10, a decrease in the value of F can be achieved by internal adjustment of the step length factor τ (a multiplying factor of the matrix). For spectra which cannot be fitted well, considerable computer time is often used in going through the τ routine on each iteration in order to reduce F.

A parameter may be held constant by setting the value of $\partial F/\partial p_k$ equal to zero just before p_k^i is computed. It was found to be necessary to modify the program to prevent peaks from becoming negative (an unrealistic situation) in an attempt to find the minimum value of F. Another feature which prevents the matrix from becoming unwieldy is that the program scales the frequency (cm^{-1}) data to average zero (by subtracting the average value) in order to avoid large numbers in the matrix, particularly for the background terms.

The computer output lists information of value in analyzing the spectrum. It lists the values of the parameters after each iteration, the gradient vector ($\vec{g}$) and its norm (GQT), the value of F, and the step length factor τ. The final results (when $|\vec{g}|$ is less than a preset value or when a preset number of iterations have been completed) include the standard error of estimate

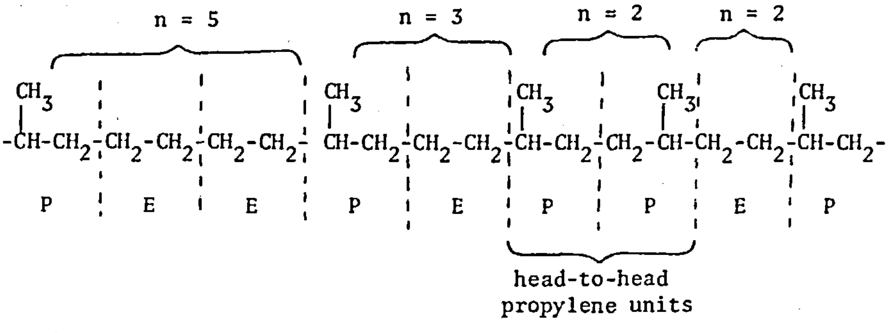
$$\sigma = [F/(M-N)]^{\frac{1}{2}} \qquad (11)$$

and an error analysis (difference between actual and calculated values at all digitized points along the spectrum).

The program was shown to yield good results for the integrated absorptivities of the overlapped bands in the C-H stretching region of the *n*-alkanes. The following equation for the area of a Lorentzian band was used:

$$\text{Area} = (\pi/2)\ (\text{band width})\ (\text{band intensity}) \qquad (12)$$

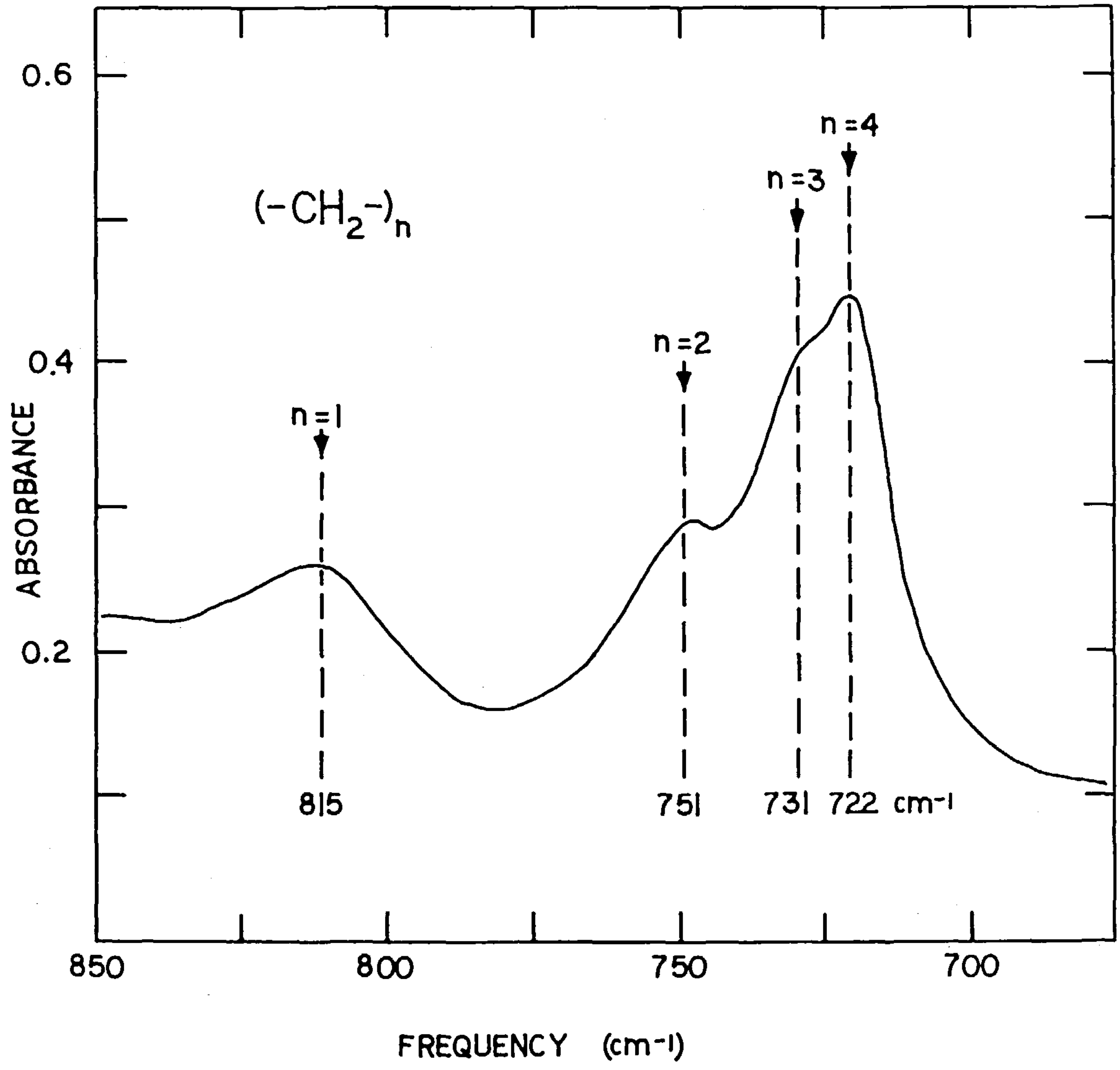
A typical spectrum of EPM in the methylene rocking region is presented in Figure 4. Four bands are clearly discernible but poorly resolved. The natural band width is such that they cannot be resolved even with very narrow spectral slit widths. The number of contiguous methylene groups which each band represents and the average frequency of the bands as obtained from the above computer program are shown in the figure. Origin of the $(CH_2)_n$ bands can be visualized from the hypothetical polymer structure shown below (the structure as drawn is not intended to convey the nature of the actual insertion mechanism):



Three or five contiguous methylenes arise from one or two ethylene units, respectively, inserted into the growing chain between two propylene units. The occurrence of two contiguous methylene groups clearly must involve polymerization of two propylene units in head-to-head configuration or from an ethylene unit between normal and inverted propylene units.

Although inspection of the spectrum in Figure 4 does not reveal it, the error curves from the computer output show evidence of bands at 770 cm^{-1} and 858 cm^{-1} (in addition to the major bands of interest at 722, 732, 750, and 815 cm^{-1}). In order to obtain the best fit and achieve the smallest standard error these must be included in the program. In practice, the position (cm^{-1}) of the band at 770 cm^{-1} and its half-width parameter should be fixed (once these parameters are established) so that they do not assume the parameters of the bands of interest. The band at 770 cm^{-1} is near the frequencies normally quoted for pendant ethyl groups. Such a structure might arise from insertion of butene-1, which is believed to be present in the diluent as a result of ethylene dimerization. In fact, the writer has identified a number of trimers and tetramers in recycle diluent from EP polymerization by liquid-solid chromatography and combined GLC-mass spectrometry and GLC-infrared spectrophotometry. Relative mole percentages for each of the eight possible trimers (for the usual termination mechanism) identified are listed in Table 2. Butene-1 was identified in recycle gas. Such a mechanism is, therefore, conceivable. It is interesting from the trimers identified that neither ethylene nor propylene appears to selectively initiate a polymer chain whereas propylene termination is favored over ethylene termination by about 7 to 1. The same pattern

FIGURE 4



Infrared spectrum of EPM in the methylene rocking region.

TABLE 2

Trimers Identified in EP Diluent by Combined GLC-MS and GLC-IR

Compound	Probable monomer sequence	Relative mol %
Hexene-1	EEE	5
4-Methylhexene-1	EPE	2
2-Methylhexene-1	EEP	12
Heptene-1	PEE	2
2,4-Dimethylhexene-1	EPP	30
4-Methylheptene-1	PPE	3
2-Methylheptene-1	PEP	33
2,4-Dimethylheptene-1	PPP	13

seems to exist within the tetramers, most of which were also identified.

Some typical values of parameters obtained from the computer program for the methylene region of the spectrum are presented in Table 3. Relative concentrations of methylene groups in each sequence category were calculated from relative band areas (actually, since the results were normalized, the term $\pi/2$ was dropped and only the product $\Delta\nu \cdot A$ was used). Absorptivities from "model" compounds were not used because they showed wide variations. Unfortunately, sample thicknesses were not recorded so that it would not be possible to apply absorptivity data if this problem could be resolved at a later date. It was assumed for convenience that absorptivities were the same for all bands. Actually, it is quite unlikely that the

TABLE 3

Typical Computer-Resolved Band Parameters for the Methylene Region

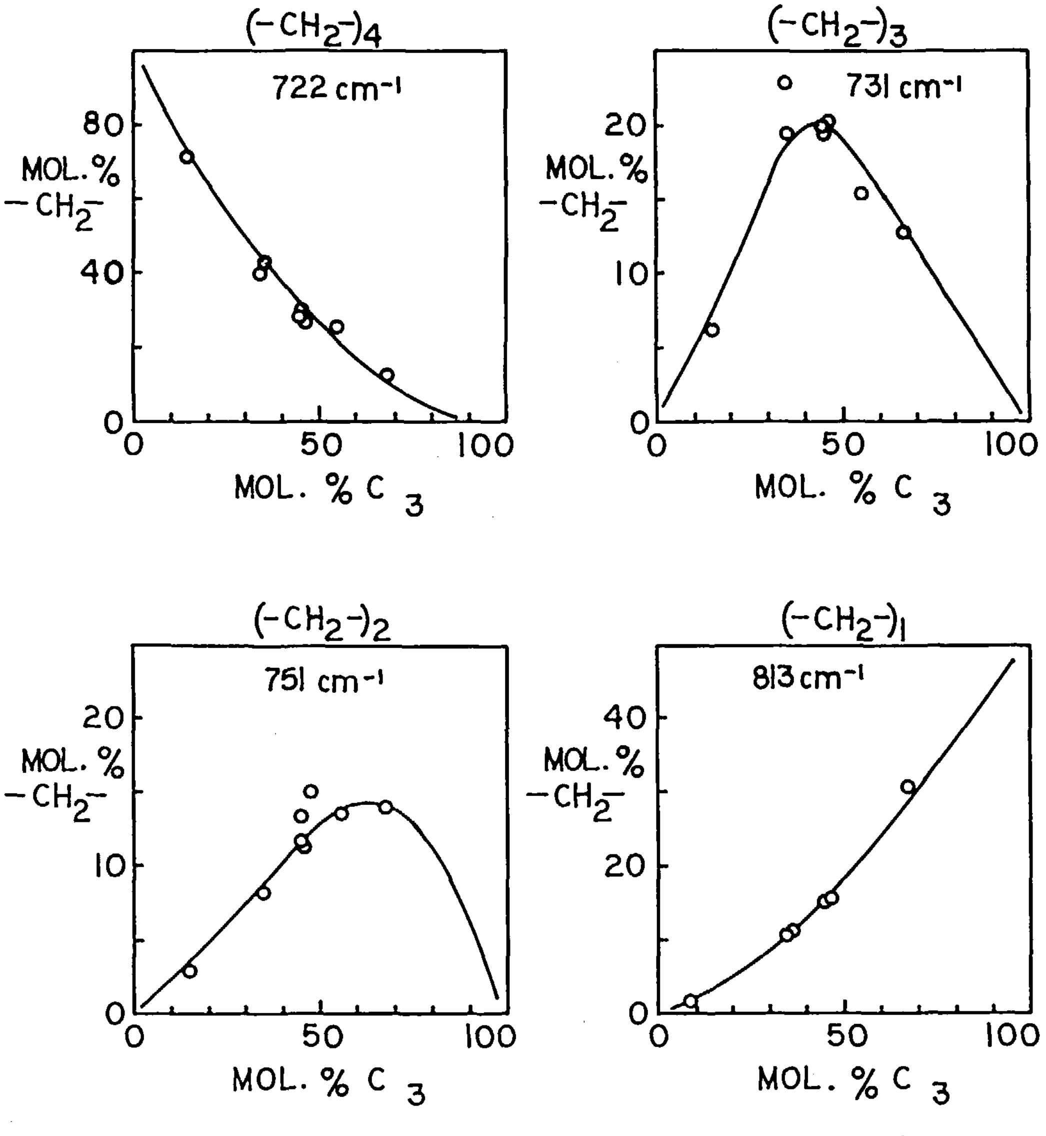
Sample	Mol % C_3	νmax (cm^{-1})	$\Delta\nu$ (cm^{-1})	Intensity A	$\Delta\nu \cdot A$	Normalized[b] mol % $-CH_2-$
2	34.5	721.3[a]	6.56	0.359	2.253	40.1
		731.9[a]	9.77	0.139	1.358	23.1
		751.4	9.25	0.055	0.511	8.7
		767.0[a]	10.00[a]	0.013	0.125	—
		815.0[a]	17.00[a]	0.038	0.638	10.9
						82.8[b]
3	46.8	721.3[a]	6.81	0.546	3.718	27.8
		731.4[a]	9.65	0.289	2.791	20.9
		750.7	11.33	0.138	1.567	11.7
		767.0[a]	10.00[a]	0.003	0.033	—
		814.4[a]	17.00[a]	0.127	2.166	16.2
						76.6[b]
3,stripped[c]	46.8	730.8	9.31	0.273	2.542	19.5
		750.8	7.58	0.120	0.910	7.0
		812.5[a]	17.00[a]	0.167	2.836	21.7
		721.3[d]	6.81[d]	0.546[d]	3.718[d]	28.5
						76.6[b]

a. fixed parameters
b. normalized to mol % C_2 + mol % $C_3/2$
c. by computer subtraction of the n-hexadecane spectrum
d. copied from sample 3, line 1

absorptivities are the same. Note in Table 3 that the band width increases as the frequency (cm^{-1}) of the band increases. The absorptivities may vary similarly. Normalizing to mole % C_2 + mole % $C_3/2$, consequently, represents a compromise. In using a curve-fitting program it is often necessary to fix certain parameters in order to obtain internally consistent data suitable for correlation purposes. If this is not done, band parameters may assume unrealistic values in order to reduce the value of the least squares function. Spectral stripping was tried on sample 3 in Table 3. This is the computer equivalent of the differential approach of Veerkamp and Veermans.[2] After subtraction of the *n*-hexadecane spectrum, the band positions for 3 and 2 contiguous methylene groups were found to be 730.8 cm^{-1} and 750.8 cm^{-1}, respectively.

Methylene group sequence distributions as calculated from the computer-resolved band parameters are shown in Figure 5. The results conform to the data of Bucci and Simonazzi[4] presented graphically in Figure 2.

FIGURE 5



Methylene group sequence distribution as calculated from computer-resolved band parameters.

Methyl group sequences were treated in a similar way. Typical spectra showing assignment of the bands are reproduced in Figure 6. The appearance of bands at about 937 cm^{-1}, 960 cm^{-1}, and 972 cm^{-1} conforms to the interpretation of Natta et al.[5] previously mentioned. As indicated in Figure 6, isolated propylene groups are most probably responsible for the band at 937 cm^{-1} seen to predominate in the polymer with the lowest C_3 content. At somewhat higher C_3 levels (22.2 wt % C_3) alternating structures (i.e., EPEP) should be evident, and these would also probably absorb at 937 cm^{-1}. Structures with two contiguous propylene units (i.e., EPPE) should also be present, giving rise to a band at 960 cm^{-1}. Three or more contiguous propylene units or blocks of propylene units should absorb at 972 cm^{-1} as is the case for propylene homopolymer. Table 4 shows some typical data from the computer study of this region of the spectrum. Notice in the case of isotactic polypropylene that the 972 cm^{-1} band is narrow (half-width of 7.5 cm^{-1}) and the contribution from the 962 cm^{-1} band (fixed in program) was negligible. However, in atactic polypropylene (ether extract) the 972 cm^{-1} band is somewhat broader (10.2 cm^{-1}) and the contribution from the 962 cm^{-1} band is appreciable. This parameter was not fixed and was found to occur at 964.2 cm^{-1}. Koenig et al.[12] observed that the 972 cm^{-1} band in polypropylene becomes asymmetric toward lower frequencies as atactic content increases. Distortion in the chain caused by syndiotactic placements in the isotactic chain could reduce the helical content of the polymer resulting in shifts in band position of a few wave numbers. A logical explanation is that propylene occasionally enters the growing chain in such a way (via hydride transfer) that no pendant methyl

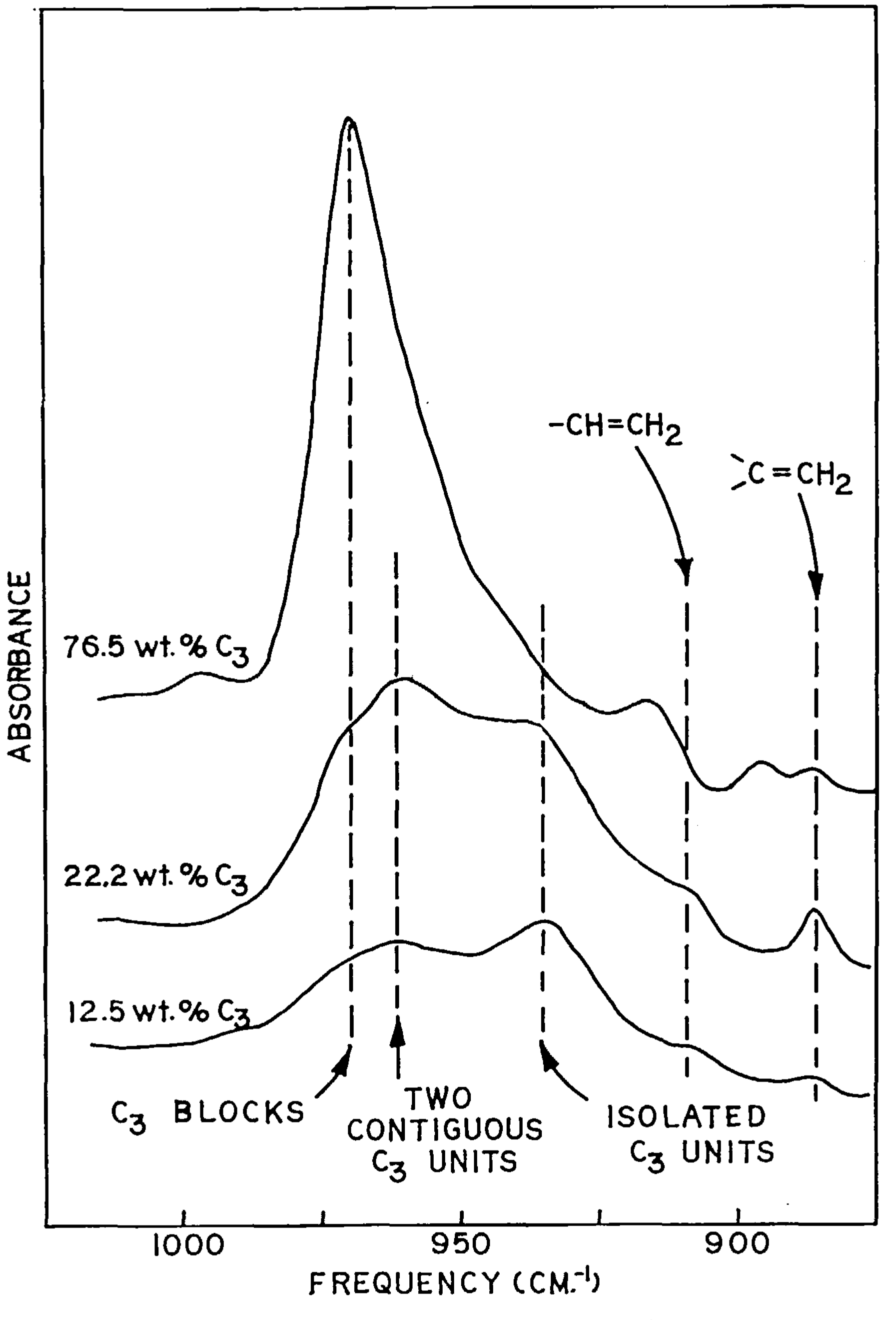
TABLE 4

Typical Computer-Resolved Band Parameters for the Methyl Region

Sample	Mol % C_3	νmax (cm^{-1})	$\Delta\nu$ (cm^{-1})	Intensity A	$\Delta\nu \cdot A$	Normalized[b] mol % —CH_3
Isotactic polypropylene	100	962.0[a]	1.15	0.005	0.006	0.1
		972.0	3.75	0.796	2.985	49.9
						50.0[b]
Amorphous polypropylene	100	939.0[a]	3.72	0.009	0.032	0.3
		964.2	9.52	0.254	2.417	23.5
		973.0	5.10	0.530	2.702	26.2
						50.0[b]
4	44.5	937.5[a]	17.53	0.224	3.919	8.0
		960.5[a]	12.43	0.356	4.425	9.0
		971.1[a]	6.64	0.394	2.615	5.3
						22.3[b]
5	15.0	937.5[a]	17.62	0.153	2.702	4.2
		961.5[a]	12.87	0.148	1.900	2.9
		972.0[a]	5.25	0.051	0.270	0.4
						7.5[b]

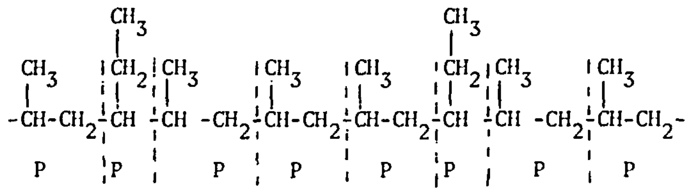
a. fixed parameters
b. normalized to mol % $C_3/2$

FIGURE 6



Typical IR spectra of EPM in the methyl rocking region.

groups are formed (instead, ethyl groups are formed) as exemplified below.

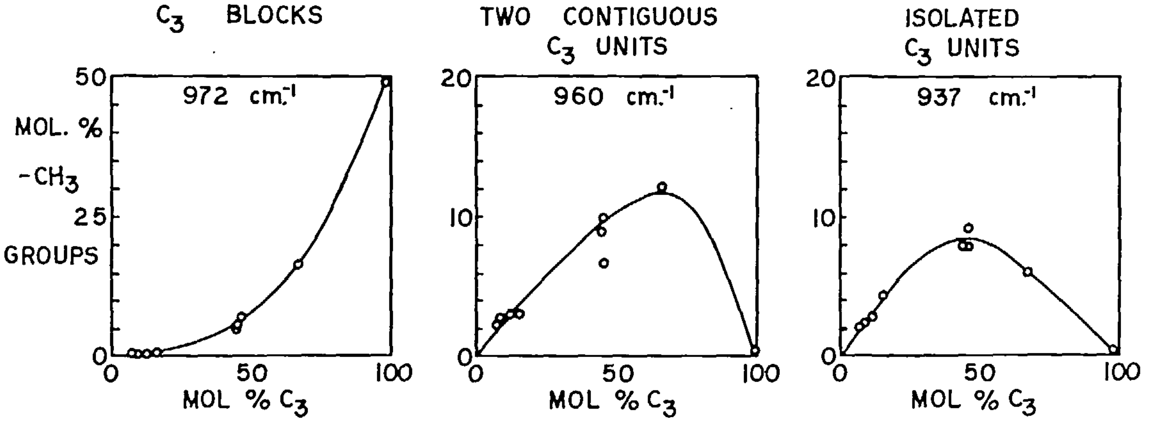


Plots of the methyl group sequence distribution as derived from the computer-resolved band parameters are shown in Figure 7. Notice that the curves show a striking parallelism to those for the methylene sequences in Figure 5. If the propylene entered the polymer only in large blocks, the curve for the 972 cm^{-1} band would be a straight line rather than concave upward.

Tosi et al.[13] recently discussed the infrared determination of sequence distribution and randomness in copolymers and presented results of a study on EPM. They point out, as has been discussed above, that the infrared spectrum contains bands useful for determination of both composition and distribution of monomer units. In order to define the distribution of propylene units they used the "distribution index," ϕ, which is the ratio of absorbances at 937 cm^{-1} and 972 cm^{-1} as discussed by Ciampelli and Valvasorri.[6] This index is defined as the ratio of the amount of isolated propylene units to the amount of propylene in sequences of 2 or more contiguous units for an ideal mechanical mixture of atactic polypropylene ($\phi = 0$) and EPM of alternating structure such as obtained by hydrogenating natural rubber ($\phi = \infty$). Experimentally, this index was found to agree closely with the ratio between the number of propylene-ethylene bonds and the number of propylene-propylene bonds, so that it serves as a measure of the sequence distribution in EPM. Unfortunately, ϕ varies with composition and a comparison of sequence distributions becomes difficult when copolymer compositions are different. Tosi et al.[13] developed an equation (from fundamental copolymerization laws) describing the relationship between ϕ and the product of reactivity ratios.

$$r_1 r_2 = (1/f)[1/\phi^2 - (f-1)/\phi] \qquad (13)$$

FIGURE 7



Propylene sequence distribution as calculated from computer-resolved band parameters.

where

$$r_1 = \frac{k_{EE}}{k_{EP}}$$

$$r_2 = \frac{k_{PP}}{k_{PE}}$$

f = molar ratio of propylene to ethylene

$$\phi = A_{937\,cm^{-1}}/A_{972\,cm^{-1}}$$

Therefore, the product of reactivity ratios can be evaluated without a knowledge of feed composition. They introduced an additional concept which is useful in defining the amount of "regularity" (formation of long sequences when r_1r_2 departs from unity) for a given r_1r_2. They termed this "informational entropy" which they derived from application of information theory. Their calculations led to the following expression for the informational entropy per monomeric unit:

$$S/N = [1/(f+1)]\{[K/(2\,r_1r_2+K)]\ \ln r_1r_2 + f\ \ln (K+2)/K + \ln[(2\,r_1r_2 + K)/2\,r_1r_2]\} \tag{14}$$

where $K = (f-1) + [(f-1)^2 + 4\ r_1r_2\ f]^{1/2}$

Their plot of S/N against r_1r_2 showed that S/N varied slowly with the product of reactivity ratios. In conclusion, from the viewpoint of randomness, copolymers wherein $r_1r_2 = 0.1$ to $r_1r_2 = 5$ are almost equivalent.

Much more study is needed. The problem of absorptivities has not been satisfactorily resolved. If "model" compounds are selected for evaluating these absorptivities, they must be selected judiciously. Integrated absorptivities may show trends different from simple peak absorptivities. Temperature effects may be important, particularly in the methylene wagging region where the distribution of *trans* and *gauche* conformations may influence the coupled motions of the hydrogen atoms and their corresponding absorptivities.

Spectrometers based on interferometry usually employ a small dedicated computer to perform a necessary Fourier analysis for spectral presentation. Because the data must be obtained in digital form and output spectra are digitized, curve-fitting techniques could be applied conveniently.

Finally, analog computers might also be useful for evaluating the contribution from each of the overlapped bands discussed above. The commercially available Du Pont 310 Curve Resolver is an instrument based on the development of F. W. Noble.[14] [15] In contrast to the use of digital computers, the operator becomes, more or less, an integral part of the system. In this sense, his knowledge of the system can be brought to bear upon the analysis. Unfortunately, a great deal of personal objectivity is involved. The use of this system would give consistent results only if certain parameters were essentially fixed as in the digital computer method described above. It might be best to fix both band position and width, once these were reasonably well established, and allow only intensity (band height) to vary. It should also be pointed out that, in using this type of instrument, the spectrum should be in the linear absorbance vs. frequency (cm^{-1}) format. The digital computer has the advantage that it can easily convert from % transmission to absorbance or from wavelength to frequency. If an older spectrophotometer must be used, the latter capability may be a restrictive requirement.

3. *Copolymer Composition by Infrared Spectrophotometry*

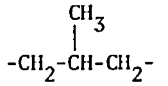
Infrared spectrophotometry has also proven to be one of the most desirable methods for the determination of copolymer composition. Drushel and Iddings[16] studied IR and near infrared (NIR) spectra of EPM and discussed the relative merits and disadvantages of each region. Shortly after this, Corish and Tunnicliffe[17] made a critical evaluation of infrared methods for the determination of EPM composition.

Natta[18] first used the methyl symmetrical C—H bending band at 1378 cm^{-1} to determine the propylene content of EPM dissolved in CCl_4. Gössl[19] found this band to have the same absorptivity for determination of methyl group content in polypropylene as well as in EPM. Corish and Tunnicliffe[17] reassessed this approach and found that polypropylene and hydrogenated natural rubber showed absorption proportional to their respective methyl contents. They further checked it against a number of C^{14}-labeled standards and found the accuracy and reproducibility to be very good (within 3%, absolute, at the 30 to 80 mole % propylene level). Ciampelli et al.[20] also used the 1378 cm^{-1} band but used a baseline from the region around 1700–2000 cm^{-1} drawn parallel to the abscissa while Corish and Tunnicliffe[17] used a baseline drawn from the minimum near 1420 cm^{-1} to about 1310 cm^{-1} (i.e., drawn under the $—CH_3$ band only). Although the 1378 cm^{-1} band has a rather constant absorptivity from one structure to another, this method suffers from the fact that not all of the polymers are completely soluble in CCl_4. In the writer's experience, even EPM recovered from reactor cement by evaporation of the solvent cannot be completely redissolved in CCl_4. This is particularly true if any homopolymer or block copolymer has formed in the reaction. Although this approach is impractical for analytical control purposes, it can be, and has been, used for preparation of secondary standards for calibration of other IR methods for EPM composition.

Gössl[19] and Wei[21] overcame the problem of solubility by using a pressed film technique and a ratio of the absorption intensities at 1150 cm^{-1} (methyl wagging) and 720 cm^{-1} (methylene chain rocking). For calibration, Wei[21] prepared secondary standards by means of the solution method in which the 1378 cm^{-1} band is used. As might be implied from the discussion in the previous section, objections have been raised as to the use of these two bands for composition because of the effects of sequence distribution on these bands. It would be particularly objectionable if the compositions of copolymers from several different catalysts were being determined. Therefore, the ratio of the band intensities at 1150 cm^{-1} and 720 cm^{-1} should be used only on copolymers prepared from the same catalyst as was used in preparing the standards.

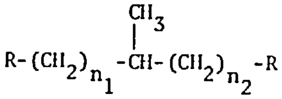
Drushel and Iddings[16] also proposed using the absorbance ratio of bands at 1150 cm^{-1} and 720 cm^{-1} calibrated with C^{14}-labeled standards prepared with the same catalyst used in producing the samples. Composition of the labeled standards was determined by a modification of the method of Stoffer and Smith[22] who described a procedure for carrying out the liquid scintillation counting measurements. C^{14}-labeled polyethylene was used to obtain the specific activity. Even though corrections were made for counting efficiency, differences in the solubility of polyethylene vs. the copolymer may lead to errors. For example, the polyethylene is only slightly soluble in the scintillator solution (phosphor dissolved in xylene). After heating, shaking, and cooling it tends to produce a milky gel. If more of the polymer remains near the bottom of the vial, the count rate could be different than if the polymer were completely dispersed. In contrast, the copolymer tends to dissolve rather completely, giving a semitransparent solution. Even though a C^{14}-labeled internal standard such as benzoic acid is used, and the ratio of efficiency figures for polyethylene and the copolymer is included in the calculations, some error in measured % ethylene can be encountered. A calibration curve determined by the writer is shown in Figure 8. The plot of log $(A_{1150\ cm^{-1}}/A_{720\ cm^{-1}})$ against mole % C_3 is linear between 20 and 70 mole % C_3 but becomes non-linear below 20 mole % C_3. At the lower C_3 contents, the absorbance at 1150 cm^{-1} becomes small in comparison to that at 720 cm^{-1} and the measurement becomes impractical and neither precise nor accurate. Instead, at low C_3 content another ratio such as $A_{1378\ cm^{-1}}/A_{1467\ cm^{-1}}$, which will be discussed later, should be used.

Folt, Shipman, and Krimm[23] have erroneously claimed that the 1155 cm^{-1} band most probably arises only from helical isotactic propylene sequences. They concluded (again erroneously) that this band cannot be used to measure the total propylene content in EPM. Their conclusions did not take into account the behavior of other systems (e.g., hydrogenated natural rubber) which most certainly contain isolated pendant methyl groups (propylene unit in normal head-to-tail enchainment) and which, indeed, exhibit the 1155 cm^{-1} band. Likewise, Lomonte[24] also erroneously concluded that the 1155 cm^{-1} band is related to polypropylene segments either as blocks in the copolymer or as segments of propylene homopolymer. Again, these conclusions overlook the behavior of many model compounds or polymer systems. Natta and coworkers[5] have shed some light on this problem. They point out that the 1155 cm^{-1} band as well as one appearing in the range 975–930 cm^{-1} have been cited in the literature (e.g., McMurry and Thornton[25]) as being characteristic of the pendant methyl group.



$$-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-$$

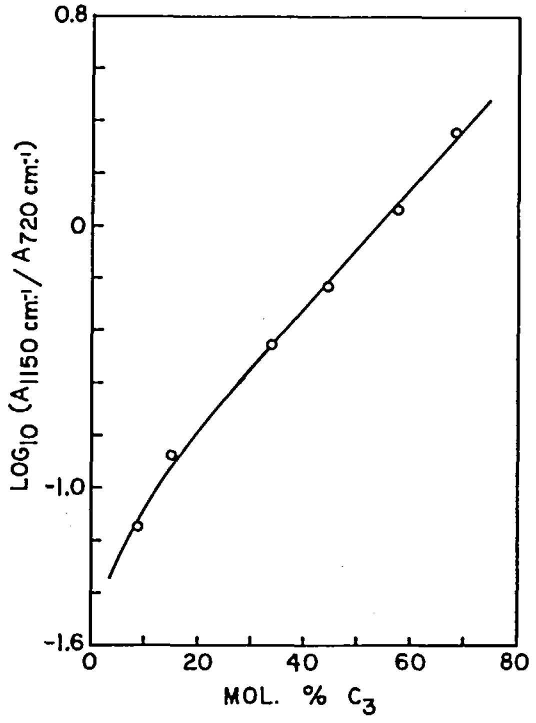
Furthermore, the 1155 cm^{-1} band is well defined and at a constant position (cm^{-1}) for 3-methyl or 4-methylalkanes as well as for other compounds having the pendant methyl grouping as in the structure



$$R-(CH_2)_{n_1}-\overset{CH_3}{\overset{|}{CH}}-(CH_2)_{n_2}-R$$

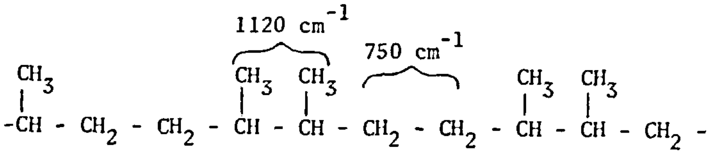
provided n_1 and n_2 are equal to or greater than unity. The band occurs at 1155 cm^{-1} in squalane (2,6,10,15,19,23-hexamethyltetracosane; see API IR spectrum no. 2290) and in hydrogenated natural rubber which corresponds to alternating monomer units in EPM (i.e., EPEPEP, etc.). Similarly, the second band falls in the range 975 to 930 cm^{-1}, the position depending upon the values of n_1 and n_2 (see discussion of this region in Section A2 above).

FIGURE 8



IR calibration curve for EPM composition using the methyl wagging and methylene rocking regions.

Whereas polymers of α-olefins obtained by anionic coordinated polymerization are usually linear, regular, head-to-tail polymers, those prepared from unbranched α-olefins via cationic polymerization are usually, although not always, amorphous polymers in which there is no chemical regularity. This statement does not necessarily apply to branched olefins where specific hydride transfer to produce tertiary carbonium ions may result in formation of highly regular crystalline polymers as reported by Kennedy, Elliott, and Groten.[26] Lomonte[24] and Folt et al.[23] failed to take these structural differences into account and their conclusions were incorrect because the polymers they examined, in fact, contained few pendant methyl groups and lacked the presupposed chemical regularity (head-to-tail propylene units). The work of Ketley and Harvey[27] on the low temperature cationic polymerization of propylene by Friedel-Crafts catalysts is pertinent here. They found appreciable percentages of pendant ethyl and propyl groups but very few pendant methyl groups. Logical mechanisms involving hydride transfer were proposed. Natta[5] made a rather complete analysis of the amorphous polymer obtained by a cationic mechanism [$Al(C_2H_5)Cl_2 + TiCl_4$ at an Al/Ti molar ratio of 1.5] such as that of Liang and Watt[28] which shows no 1155 cm^{-1} band. The observed chemical non-regularity implies excessive transfer or rearrangement reactions. He obtained the following breakdown in terms of approximate concentrations. A band was found at 735 cm^{-1} which was assigned to propylene polymerized in such a way as to give 3 contiguous methylene groups, —$(CH_2)_3$—. Using hydrogenated polyisoprene (natural rubber) as the standard, this structure accounted for 30% of the polymer. A band at 775 cm^{-1} was assumed to be due to pendant ethyl groups and the structure —$CH(CH_2$—$CH_3)$— amounted to about 20% by comparison with polybutene-1. Bands at 1120 and 750 cm^{-1} were assumed to be derived from head-to-head and tail-to-tail enchainment via inverted addition.

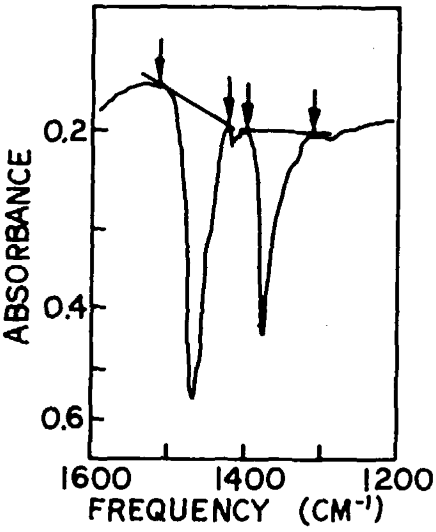


$$-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_2-\overbrace{\overset{CH_3}{\overset{|}{CH}}-\overset{CH_3}{\overset{|}{CH}}}^{1120\ cm^{-1}}-\overbrace{CH_2-CH_2}^{750\ cm^{-1}}-\overset{CH_3}{\overset{|}{CH}}-\overset{CH_3}{\overset{|}{CH}}-CH_2-$$

The above structures were estimated to amount to about 20% by comparison with ethylene-butene-2 copolymer. Geminal dimethyl structures —$C(CH_3)_2$— were estimated to be 10% from the bands at 1378 cm^{-1} and 1245 cm^{-1}. Only a few of the propylene units were incorporated in the usual manner. Natta calculated about 15% based on the weak 1155 cm^{-1} band used for analysis of EPM. In summary, incorrect conclusions concerning the 1155 cm^{-1} band were made by others by failure to consider the true chemical structure of certain amorphous polypropylenes prepared by catalysts in which cationic mechanisms are operative.

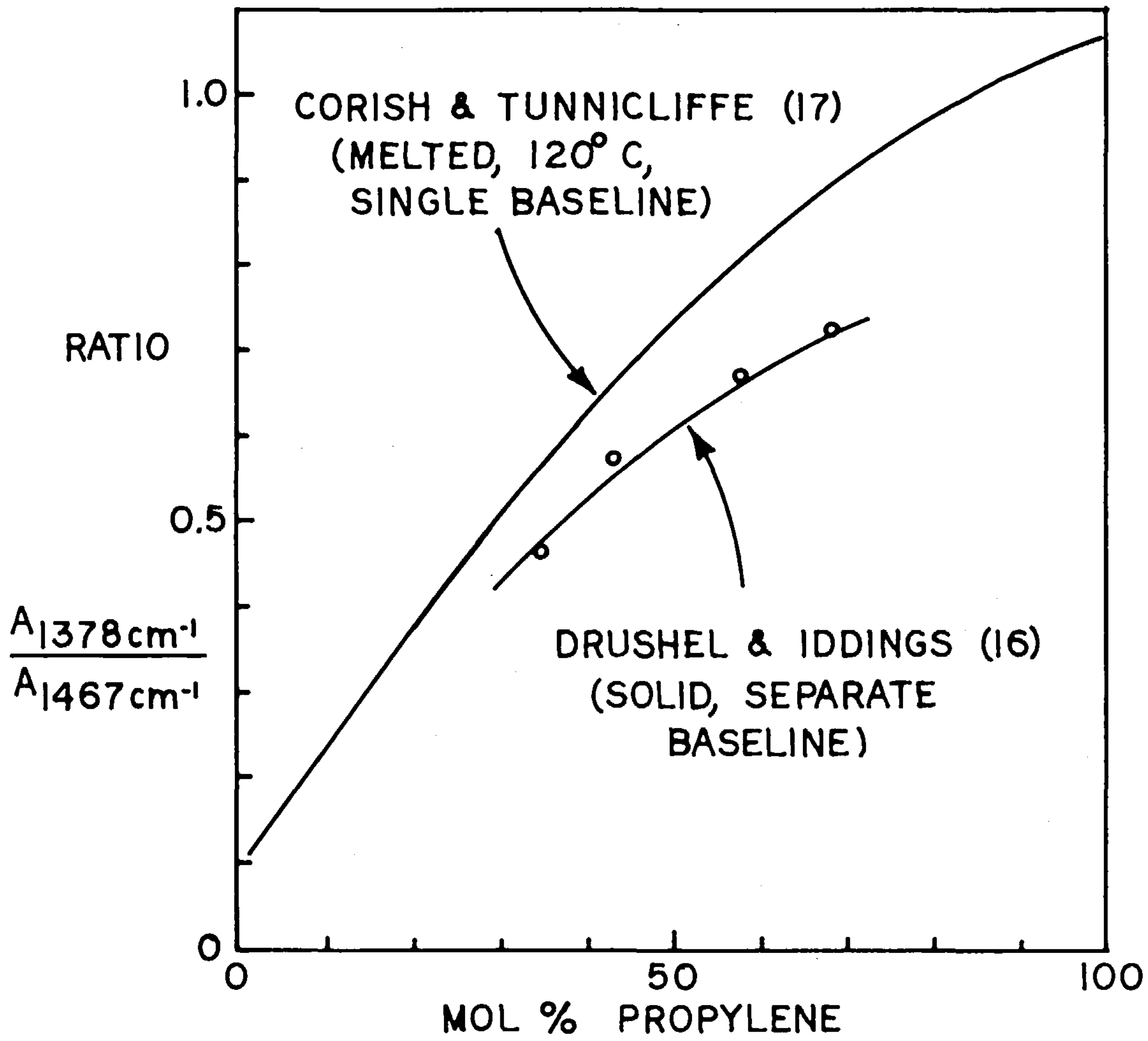
Drushel and Iddings[16] investigated the use of the bending region for composition measurements. Figure 9 shows a typical spectrum and the baseline points used in calculating the ratio $A_{1378\ cm^{-1}}/A_{1467\ cm^{-1}}$. Separate baselines were drawn under each band because the spectrophotometer interchange (from prism-grating to prism) occurred at 1420 cm^{-1} and a discontinuity often appeared. For instruments without this problem, a single baseline might be more desirable. The band at 1378 cm^{-1} is assigned to the methyl symmetrical bending mode. The band used as the base is assigned to two very close bands. One is the methylene scissoring mode (1467 cm^{-1}). The other is the asymmetric methyl bending mode (nearer to 1460 cm^{-1}). Therefore, the ratio $A_{1378\ cm^{-1}}/A_{1467\ cm^{-1}}$ should tend to increase more slowly as propylene content is increased because the methyl group contribution at 1467 cm^{-1} is increasing concurrently. Thus, this ratio should work best in analyzing copolymers of intermediate or low propylene content. Corish and Tunnicliffe[17] also recommended this ratio and prepared a similar calibration curve with C^{14}-labeled standards and recommended it as a good, general reliable method. They found that hydrogenated natural rubber as well as polyethylene and polypropylene fit the curve also. Their samples were scanned at 120°C to prevent solid-state effects which, as mentioned by Drushel and Iddings,[16] may possibly cause difficulty. A comparison of these two calibrations is presented in Figure 10. The difference between the two curves is probably a reflection of the difference between the solid and liquid

FIGURE 9



Typical IR spectrum of EPM in the bending region.

FIGURE 10



IR calibration curve for EPM composition using the bending region.

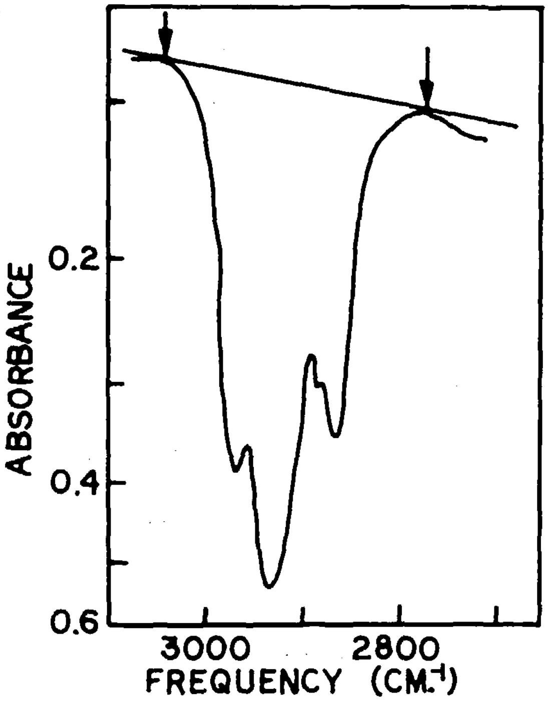
states rather than differences between spectrophotometers. This is a very useful method for composition but requires the preparation of very thin films. Hot press molding techniques usually require special attention in order to obtain films thin enough. Often, it is convenient to cast a film on a KBr or NaCl disc from solution. Because small samples are used this approach is useful for limited polymer fractions.

Drushel and Iddings[16] investigated the fundamental C—H stretching region as a means of measuring composition. A typical spectrum showing baseline points is reproduced in Figure 11. Absorptivities for these bands are higher than those in the bending region of the spectrum. Pressed films cannot be made thin enough for measurements in this region. The cast film technique is most convenient. The writer has analyzed the very small samples from gel permeation chromatography (GPC) by taking advantage of the high absorptivities for these bands. Another advantage of this region is that quartz disks can be used to support the samples and they may be reused with less difficulty than with KBr or NaCl disks. The ratio of absorbances for the asymmetrical C—H stretching modes of the $—CH_3$ (2963 cm^{-1}) and $—CH_2—$ (2935 cm^{-1}) groups did not prove to be too reproducible. Possibly, nonuniformity of the cast film may cause problems when the band intensities are too dissimilar as they are in this case. This is evidenced by a slight truncation of the peaks at high absorbance. The most desirable ratio is probably $A_{2963\ \mathrm{cm}^{-1}}/A_{2860\ \mathrm{cm}^{-1}}$ which represents the ratio of intensities for the asymmetrical methyl and the symmetrical methylene C—H stretching vibrations. These bands have more nearly equal intensities. The calibration curve was found to be a straight line between 30 and 70 mole % propylene:

$$\log_{10} (A_{2963\,\mathrm{cm}^{-1}}/A_{2869\,\mathrm{cm}^{-1}}) = 0.0125\ (\text{mole } \%\ C_3) - 0.585 \quad (15)$$

This method should be relatively free from monomer sequence distribution effects as is the method using the bending region of the spectrum. Complete freedom from structural effects should not be expected. Jones [29] has expressed concern that the absorptivity for a methylene group adjacent to a —CH—CH$_3$ group may not be identical to that of a methylene group in a methylene sequence.

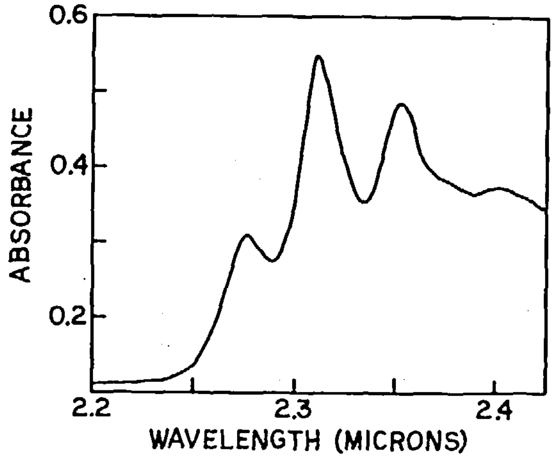
FIGURE 11



Typiral IR spectrum of EPM in the C—H stretching region.

The near infrared (NIR) region can be used for determination of copolymer composition, also. Much thicker films are required because the absorptivities of the combination and overtone bands are smaller than those for the fundamental stretching or bending modes. Sample preparation is quite simple, therefore. Bucci and Simonazzi[30] proposed the use of the overtone region (around 5900 cm^{-1}) which was not too successful because of the rather poor resolution. Ciampelli et al.[20] proposed the use of the combination band at 4320 cm^{-1} as a measure of ethylene content or as a total thickness measurement for use (as a ratio) with the methyl group band at 1155 cm^{-1}. Drushel and Iddings[16] proposed the first practical method for composition using several absorbance ratios in the combination region (4000 to 4550 cm^{-1}). Bands used in this method are shown in Figure 12, a typical NIR spectrum of EPM in the combination region. The band at 4396 cm^{-1} probably corresponds to the combination of an asymmetric methyl C—H stretching frequency (2963 cm^{-1}) and a bending frequency near 1400 cm^{-1} and is sensitive to the propylene content of the polymer. The bands at 4329 cm^{-1} and 4255 cm^{-1} are sensitive to ethylene content and are probably combinations of asymmetrical and symmetrical methylene stretching frequencies with bending frequen-

FIGURE 12



Typical NIR spectrum of EPM in the combination region.

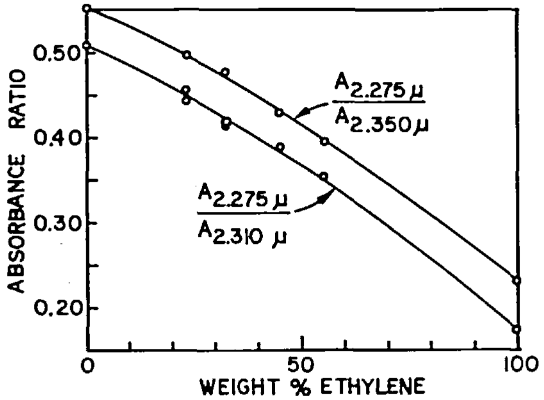
cies. Therefore, the ratio of the absorbance at 4396 cm^{-1} to the absorbances at either 4329 cm^{-1} or 4255 cm^{-1} should provide a measure of the composition of the copolymer (see Figure 13). Unfortunately, these bands are not well resolved, and at low propylene contents the precision is poor. Bly, Kiener, and Fries,[31] more recently, examined the use of the ratio of the absorbances at 4329 cm^{-1} and 4396 cm^{-1}. C^{14}-labeled standards were used for calibration. They used a combustion technique prior to scintillation counting in order to eliminate the solubility problems encountered in preparing the samples in the technique of Stoffer and Smith[22] or Drushel and Iddings.[16] They used separate baselines drawn under each band whereas Drushel and Iddings[16] used a single baseline point at 4550 cm^{-1}. Bly et al.[31] found that this method was unaffected by crystallinity effects and that it applied equally well to multisegment block copolymers and random copolymers. They found that the precision was about 4% absolute up to 55% (wt) ethylene. In comparison, the writer has determined the precision of the method using the 720 cm^{-1} and 1155 cm^{-1} bands to be about 3% (2σ, absolute) at the 50 mole % propylene level. The precision using the combination region should be as good as the precision using the fundamental bending or rocking region if several replicate analyses are run for each sample. Takeuchi et al.[32] very recently reported the use of another band at 4059 cm^{-1} which is sensitive to propylene content. They assign this band to the combination of the symmetrical C—H stretching mode at 2880 cm^{-1} and the methyl rocking frequency at 1155 cm^{-1}. They claim improved precision (0.7 to 2.0% relative) using the absorbance at 4059 cm^{-1} (as a ratio with the 4329 cm^{-1} or 4255 cm^{-1} bands) as compared to using the absorbance at 4396 cm^{-1} (again, as a ratio with the 4329 cm^{-1} or 4255 cm^{-1} bands) which resulted in a precision of 2 to 5% relative. In contrast to the statement of Bly et al.,[31] Takeuchi et al.[32] observed a difference between the calibration curve for physical blends of polypropylene and polyethylene and the curve for random copolymers. From the writer's experience, the latter observation is correct. Regarding precision, however, there should be no reason, a priori, why the use of the band at 4059 cm^{-1} is so much better than the use of the band at 4396 cm^{-1}. Takeuchi et al.[32] cited a preference for using the 4255 cm^{-1} band in the ratio rather than the 4329 cm^{-1} band because of an observed shift in the 4329 cm^{-1} band position with changes in composition. Using the ratio $A_{4059\ cm^{-1}}/A_{4255\ cm^{-1}}$ and a baseline point at 4550 cm^{-1} they obtained a straight calibration line over the 30 to 50 wt % ethylene range as given below:

$$y = 0.0028\,x + 0.535 \qquad (16)$$

where $y = A_{4059\ cm^{-1}}/A_{4255\ cm^{-1}}$

x = wt % ethylene

FIGURE 13



Calibration curve for EPM using the combination region.

Several other miscellaneous methods have been reported. The use of the ratio $A_{972\ cm^{-1}}/A_{4320\ cm^{-1}}$ as suggested by Ciampelli[20] was mentioned above. Corish and Tunnicliffe[17] investigated the ratios $A_{1150\,cm^{-1}}/A_{1467\,cm^{-1}}$ and $A_{972\,cm^{-1}}/A_{1467\,cm^{-1}}$. These ratios present a problem in that the intensities at 1150 cm^{-1} and 972 cm^{-1} are low in comparison to the intensity at 1467 cm^{-1}. Consequently, absorbances cannot be measured accurately on the same film or spectrum. Other ratios can be conceived which should provide a measure of composition. These include such ratios as $A_{1150\ cm^{-1}}/A_{4329\ cm^{-1}}$, $A_{1378\ cm^{-1}}/A_{4329\ cm^{-1}}$, and $A_{1378\,cm^{-1}}/A_{720\,cm^{-1}}$. The first of these should work best at moderate to high propylene contents whereas the latter two should work best at low propylene contents. It should be emphasized that calibration should be made with polymer standards (e.g., C^{14}-labeled) prepared with the same catalyst and conditions as used in preparing the samples being analyzed. Changes in conditions (catalyst, solvent, etc.) which might alter microstructure (monomer sequence, etc.) will negate the general applicability of many of these ratio methods. Veerkamp et al.[83] propose the use of beta-ray absorption to provide a measure of film thickness in the analysis of EPM. This approach has the advantage of providing an average thickness (effective optical thickness) which cannot be accomplished with a mechanical device (it often sticks to the film or causes deformation of the sample). In using this method, it would seem to be imperative that the β-ray emission from the Co^{60} source be made to pass (by proper masking) through only that portion of the film through which the infrared beam passes.

4. *Raman Spectrometry*

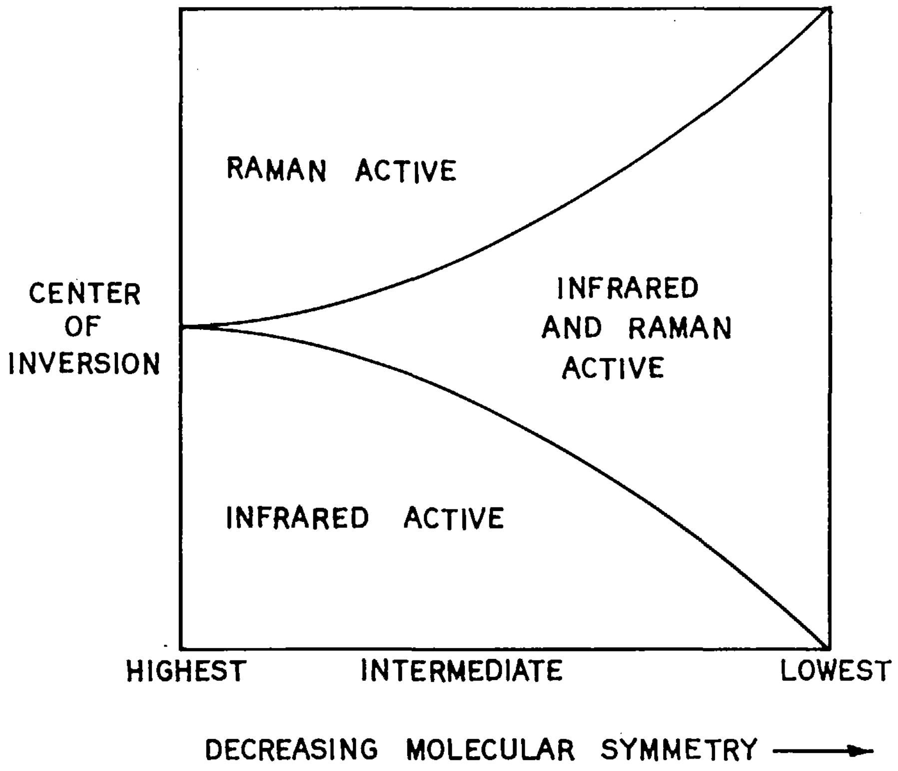
Recent developments in laser sources for Raman spectrometers have resulted in a significant advance in polymer characterization. Prior to this, Raman spectroscopy received only a moderate amount of attention, even in studies of simple molecules, because of experimental problems. For polymer characterization, the problems in using older instrumentation were particularly troublesome. Nielson[34] delineates some of these difficulties.

Schaufele[35] has discussed recent advances in vibrational Raman scattering spectroscopy of polymers. As is well known to spectroscopists, absorption of infrared energy resulting in vibrational transitions requires that a change in the molecular dipole moment occur during the transition. In contrast, occurrence of a vibrational transition via Raman scattering depends upon the formation of an induced dipole moment through interaction with the oscillating electric field vector of the incident radiation. Molecular symmetry also determines the selection rules for occurrence of IR- or Raman-active vibrations. In molecules with high symmetry, such as those with a center of inversion, selectivity is such that IR and Raman transitions are mutually exclusive. As molecular symmetry decreases, an increase in mutual activity is observed as shown schematically in Figure 14. With respect to hydrocarbon polymers, IR-active modes of significant intensity are primarily C—H motions, such as those discussed in the previous sections, whereas Raman-active modes of significant intensity are mainly the skeletal motions of the C—C "backbone" of the polymer. The value of Raman spectroscopy as a complementary technique for the characterization of polymers by vibrational analysis is obvious.

Before the advent of the laser, as was pointed out by Schaufele,[35] Raman scattering studies on polymers were hampered by factors such as low source intensity, interference from unwanted source line and continuum frequencies, and competition by various processes for the incident excitation energy. The latter competitive processes include absorption with radiationless dissipation or emission as fluorescence, photodecomposition of the molecule into other species, and Rayleigh or Tyndall scattering. The laser is a more ideal source for Raman scattering which overcomes many of these limitations because of its monochromaticity, intensity, directionality, and linear polarization. In addition, the range of laser frequencies now available permits more flexibility in selecting a frequency to eliminate the disadvantages of mercury arcs (e.g., fluorescence). Schaufele[35] listed some of the laser sources suitable for continuous Raman scattering as shown in Table 5. These were chosen by Schaufele on the basis of their intensity, reliability as practical devices, and also to span a frequency range in which the probabilities for absorption, fluorescence, and photodecomposition are reduced while remaining in the spectral region for which the photocathodes (e.g., S-20 and S-1) of available photoelectric detectors retain adequate response.

One of the first successful applications of laser Raman spectroscopy to solid polymers was reported by Schaufele[36] who assembled a He-Ne laser Raman system at Esso Research & Engineering Co. to study polymer systems. He obtained an excellent spectrum of polypropylene with a high Raman-Rayleigh intensity ratio showing little or no fluorescence or pho-

FIGURE 14



Relationship between molecular symmetry and vibration activity.

TABLE 5

Some Selected Laser Lines Suitable for Raman Excitation[a]

Type	Wavelength (Å)	Power[b] (Watts)
Ar^{+1}	4880, 5145	1
Kr^{+1}	5208, 5309, 5682, 6471, 6764	0.8
Xe^{+1}	5419, 5971, 6271	0.1
He-Ne	6328	0.1
Ga-As	8400-9000 (depends upon temperature)	5
YAG: δ Nd^{+3}	10,650	5

a. As taken from Schaufele.[32]
b. Output power refers to the strongest individual line which, for multiple lines, is underlined.

todecomposition and permitting definition of the lowest frequency Raman modes to within about 50 cm^{-1} of the laser frequency. Similar spectra on other polymer systems were also obtained with the apparatus assembled from available components.[37] The advantages of a modern double-dispersion grating monochromator in reducing stray light and in providing discrimination between the Raman and Rayleigh scattered light (even at low frequencies) was discussed. Discrimination between Raman scattered bands of low intensity and frequency as well as ghosts (from the grating) can be made by comparison with the scattering spectrum of MgO, whose first-order Raman spectrum is inactive.

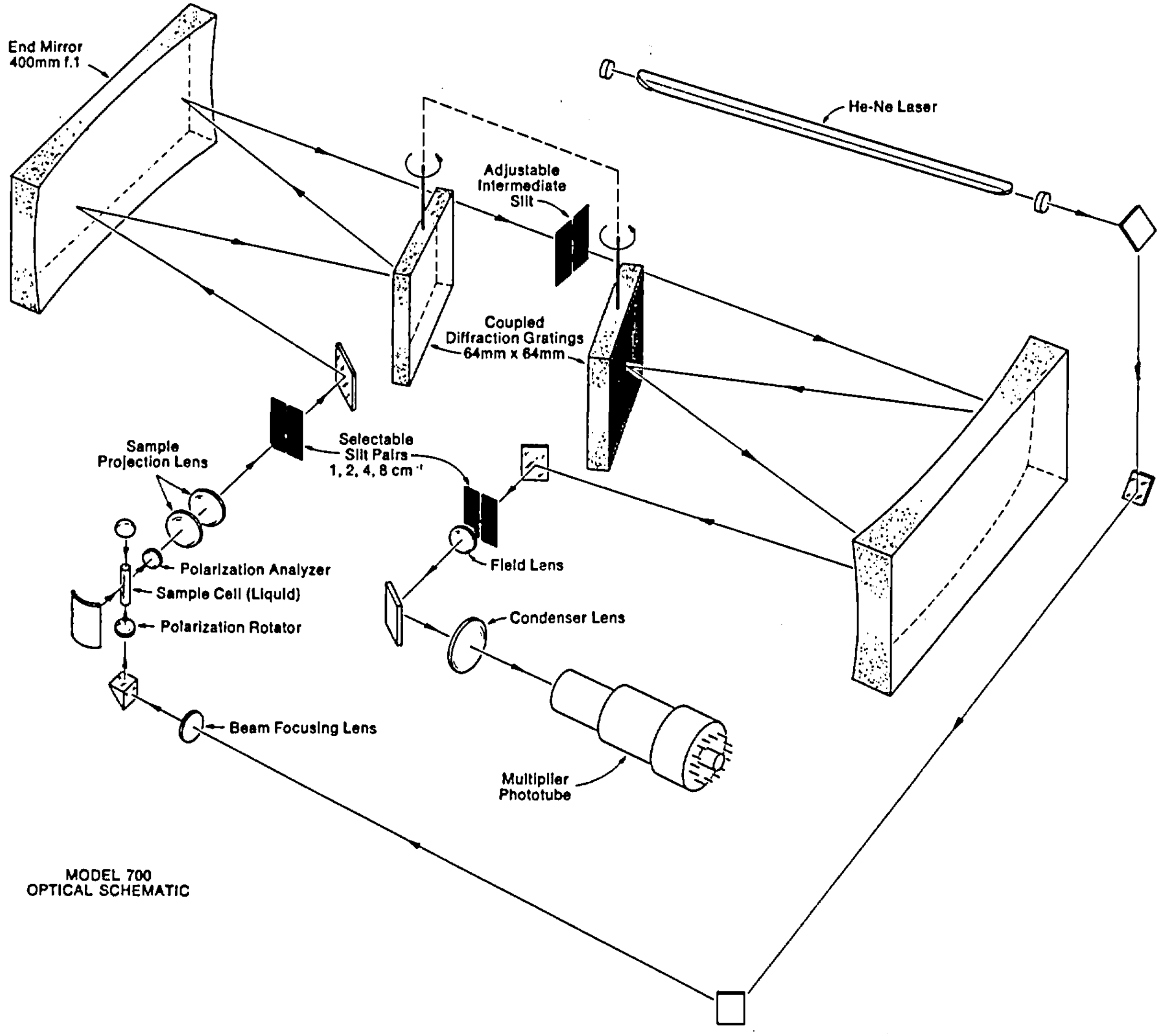
The development of laser-Raman instrumentation and its application to polymer systems has moved forward at a rapid pace in the last several years. Use of the He-Ne lasers on polymer systems has given way to the use of the higher powered Ar^+ lasers (available up to 6 watts commercially). Instead of chopping the radiation and using lock-in amplification as reported by Schaufele,[35] modern commercially-available spectrometers employ photon counting techniques and d.c. amplification. Eight companies now supply commercial instruments, most of which have just been made available. Newer instruments include those of Jarrell-Ash, Spectra-Physics, Jeolco and Huet. Older instruments which have recently been modernized include Perkin-Elmer, Coderg, Cary and Spex. A schematic diagram of a typical spectrometer is presented in Figure 15.

Schaufele[35] discussed the various experimental arrangements for laser-excitation of sample specimens in different physical forms in order to maximize the Raman/Rayleigh scattering intensity ratio. For a translucent solid (e.g., polyethylene) this is best accomplished by focusing the laser beam into a conical cavity cut either into the cast piece or a pellet formed by compression of the powder. This is shown in Figure 16a. The cavity functions as a light trap, producing multiple scattering of the incident photons via the intrinsic reflectivity and transmittance of the sample to the laser frequency. By adjusting the thickness from the cavity wall to the front surface (usually one mm or less), an optimum Raman/Rayleigh intensity ratio can be obtained which is superior to either front or back surface illumination. With the high-powered Ar^+ lasers now available, front surface illumination is now the most convenient approach. The spectrum, shown in Figure 17, of polyoxyethylene obtained using a conical cavity was superior to that obtained by Matsui et al.,[38] who used the standard mercury arc excitation source and obtained poor results below 800 cm^{-1}. Figure 17 shows good definition down to within 25 cm^{-1} of the laser frequency. Several predicted[38] torsional and bending modes of low frequency were well resolved. The directionality of the laser beam is preserved as it passes through a transparent solid polymer. This produces a scattering image which is colinear with the monochromator slit aperture when observed at 90° to incident radiation as shown in Figure 16b. Use of the lens produces a better signal to noise ratio and permits examination of small, selected spatial regions within the sample specimen. Obviously, transparent samples permit a study of the polarization characteristics of the Raman scattering because it is less likely that depolarization will occur via Rayleigh scattering. Melting to produce a liquid may overcome the latter phenomenon in the case of translucent polymers. For liquids, a capillary cell (5 μl) is used to prevent flow during measurement and the laser beam is reduced in diameter by the lens to decrease the active scattering volume as shown in Figure 16c. The intensity of Raman scattering of polymers in solution is attenuated by a factor proportional to the solute volume fraction. Enhanced Raman intensities can be obtained by exploitation of the natural collimated directionality of the laser beam through multiple reflection within the cell as shown in Figure 16d.

The vibrational analysis of polymer systems has been advanced by the above laser Raman improvements and by improved theoretical techniques yielding more accurate values for the force fields for hydrocarbon polymers. Better high speed computers and the development of techniques for regenerative interaction between experiment and theory have aided greatly.

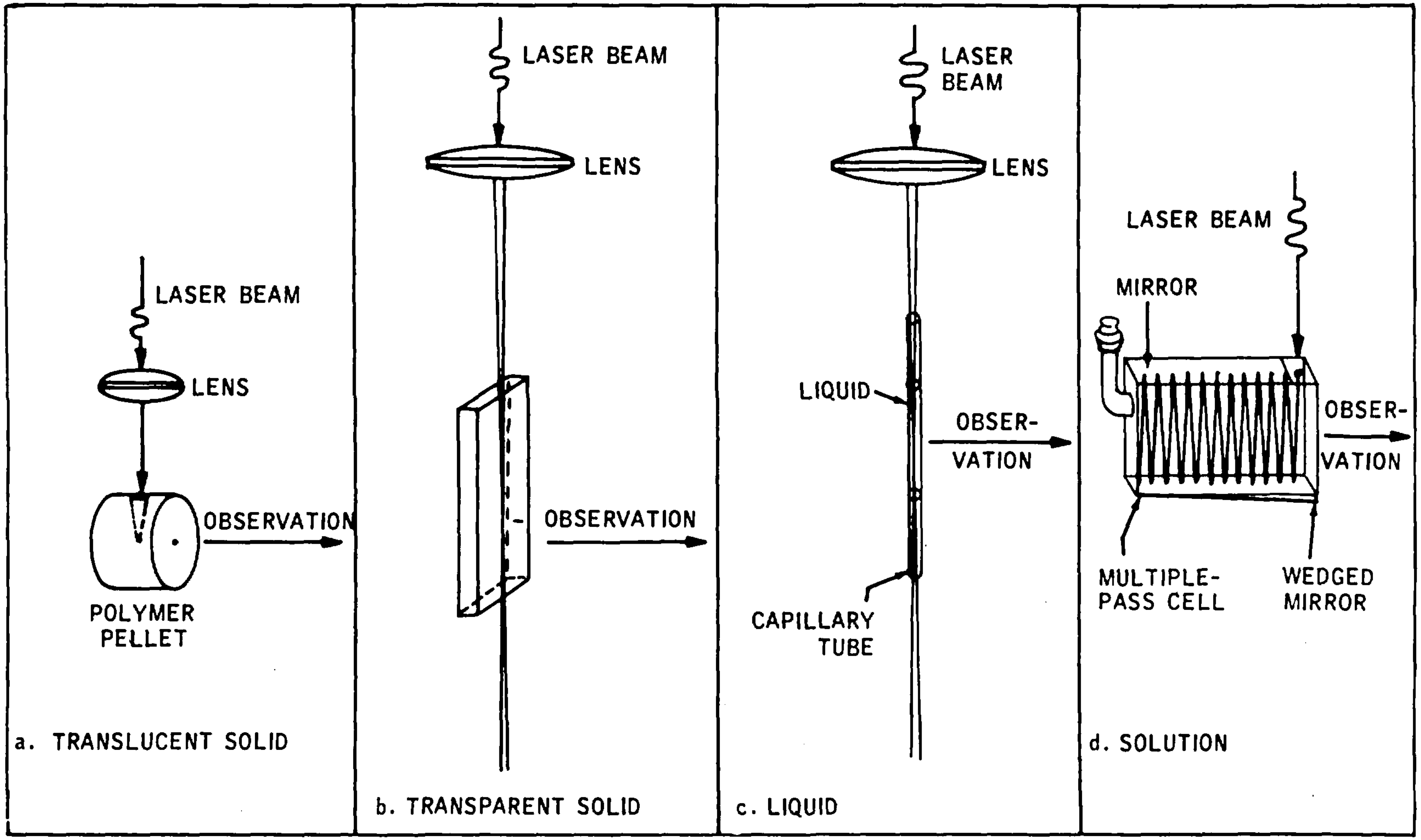
Koenig has been making extensive use of

FIGURE 15



Laser Raman instrumental arrangement of the Spectra-Physics Model 700.

FIGURE 16

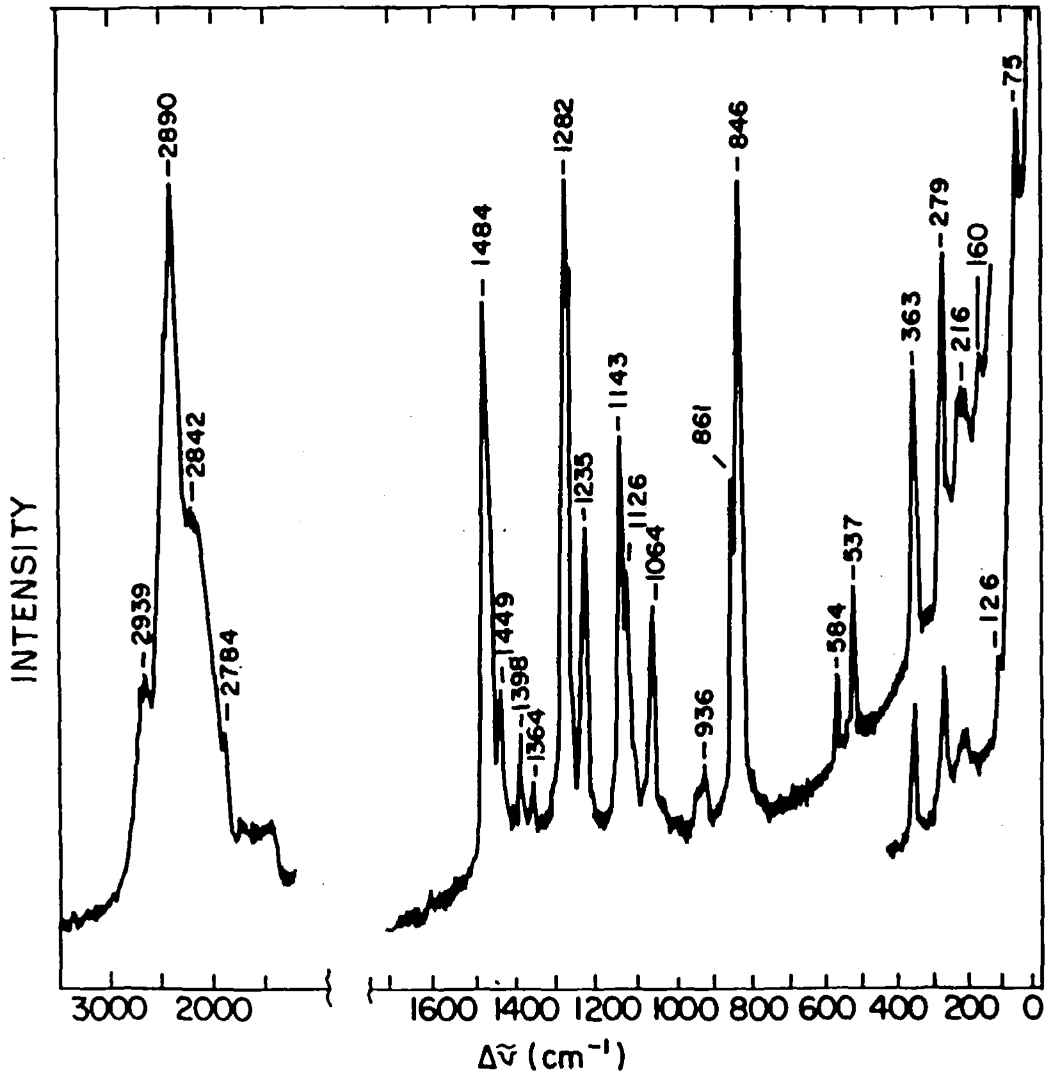


Sample systems for Laser Raman studies.[35]

laser Raman in the vibrational analysis of a number of polymer systems being conducted at Case Western Reserve University. A computer program has been developed for normal coordinate analysis by Hannon et al.[39] based upon the force fields presented by Snyder and Schachtschneider[40, 41] in their very excellent work on polyethylene and polypropylene. According to Koenig, with this computer program plus laser Raman spectroscopy and IR spectroscopy, a complete vibrational analysis can be made in a matter of days or weeks if no unusual complications arise. Prior to these developments, many years of effort may have been required and the analysis would not have been complete. Cornell and Koenig[42] successfully applied laser-excited Raman scattering to the characterization of polybutene-1 which is complicated by the fact that it exists in three crystalline forms.

Laser Raman scattering will continue to find many applications in the field of polymer analysis and characterization. This technique has the advantage that aqueous systems can be studied. Therefore, biological systems (polysaccharides, polypeptides, etc.) will undoubtedly come under the scrutiny of laser Raman instrumentation.

FIGURE 17



Laser Raman spectrum of polyoxyethylene.[35]

B. Other Spectrometric Methods

1. *General Discussion*

No attempt will be made in the following discussion to cover all of the remaining spectrometric methods. It would not be possible to cover each method in depth because of space nor is it the intent of this review to so do. In fact some of the more commonly used techniques will be omitted. For example, a technique such as ultraviolet-visible spectrophotometry which is useful for determination of residual monomers, antioxidants, UV screening agents, surface active agents, etc. will not be discussed. The recently translated work of Fikhtengol'ts et al.[43] covers this topic rather thoroughly. Likewise, spectrophotofluorometry and phosphorimetry, which the writer[44] has used to determine inhibitors in polymers, will not be discussed. Instead, some promising new developments in only a few other fields will be mentioned. These will not be treated in depth but are included because they are new noteworthy techniques which will probably advance the field of polymer characterization and analysis in the near future. This section will be short in comparison to section A, the main critical review covering IR and Raman spectroscopy.

2. *C^{13} Nuclear Magnetic Resonance Spectrometry*

Most polymer studies by NMR to date have involved proton magnetic resonance, and Bovey[45] has covered the application of this technique to the characterization of polymers in a section of his recent book on NMR. On the other hand, it would be advantageous if one could study the basic backbone (carbon skeleton of the polymer). This would be roughly equivalent to the use of Raman scattering as a complementary technique to provide information concerning the polymer backbone while IR provides data regarding the C—H bonds. C^{13} NMR will provide such information. Unfortunately, C^{13} has a relatively small magnetogyric ratio and its natural abundance is only 1.1%. Therefore, in order to obtain a usable spectrum, with acceptable signal-to-noise ratio, one must use a computer of average transients (CAT) and accumulate the signal for as long as 12 hr or more. Farrar[46] has reviewed the field of pulsed and Fourier Transform NMR and has pointed out the advantages of Fourier Transform NMR over continuous wave NMR.

The new Fourier transform pulse accessory available from Varian Associates for high resolution NMR spectrometers should make C^{13} NMR studies much more practical. This technique of multichannel excitation can improve the sensitivity for a given observation time by as much as a factor of 10 or more over conventional sweep methods. Thus, Fourier transform C^{13} NMR spectra of a polymer can now conceivably be obtained in about an hour of scan time. In order to obtain a relatively simple spectrum, heteronuclear spin decoupling of the protons must be made. Unfortunately, the band areas for C^{13} resonance are not in direct 1:1 correspondence with the concentrations as in the case of proton NMR. This could make quantitative measurements somewhat complicated. One distinct advantage is the fact that polymers may not have to be completely melted or in solution to obtain good spectra. Partial melting or softening achieves sufficient segmental motion to obtain sharp bands. One disadvantage is the fact that this instrumentation is rather expensive (probably over $100,000) at the present time and not within the means of all laboratories. Digilab (Block Engineering, Inc.) now have a Fourier transform system for IR and NMR spectroscopy and they will probably develop modifications to determine proton-decoupled C^{13} resonance spectra. In summary, application of these new Fourier transform techniques will provide an excitingly new means of studying the C—C skeleton of polymers in the near future.

3. *Mass Spectrometry*

Even though polymers have been studied by mass spectrometry, pyrolysis is normally required to make them amenable for study. Thus, the volatile fragments from pyrolysis of copolymers have been analyzed by MS to provide information as to the monomers present and even the monomer sequence distribution (no further discussion of pyrolysis-mass spectrometry will be presented). However, the undegraded polymer has a vapor pressure much too low to be examined by conventional MS techniques (e.g., a polyethylene of 14,000 MW would have the amazingly low vapor pressure of only 10^{-480} atm at room temperature). Bendix has developed a polymer mass spectrometer in collaboration with Dole and colleagues,[47] and it is to be introduced as a prototype in 1970. Although it is capable of measuring macroions, it is still a research tool and is not suitable for routine laboratory characterization of high polymers of unknown or variable MW distribution according to Bendix.

Dole and associates[47] produced molecular beams of macroions as follows. By electrospraying a dilute polymer solution into an evaporation chamber, negative macroions were produced and a molecular beam formed by sampling the gaseous mixture of macroions, solvent, and nitrogen molecules with a nozzle-skimmer system of the Kantrowitz-Gray type. The macroion current was detected by a Faraday cage after the light ions were repelled from the beam by negative voltages on a repeller grid. Definite mass to charge states were produced. It is interesting that polystyrene macroions of 51,000 MW tended to form dimers and trimers in the beam while those of 411,000 MW tended to appear mostly as multiply-charged single species. Undoubtedly, once instrumentation becomes available this extremely new and novel technique will find use in polymer characterization.

4. *Electron Spectrometry*

Another relatively new technique which may prove useful for polymer analysis and characterization is electron spectrometry, sometimes referred to through common usage as ESCA (electron spectrometry for chemical analysis as developed by Siegbahn[48]). Basically, electron spectroscopy is the technique of measuring the binding energies of electrons ejected by the interactions of a molecule with a monoenergetic beam of x-rays (or photons). Because excitation must occur in an evacuated chamber, the technique is particularly suited to substances of low vapor pressure, i.e., inorganic compounds, organic molecules adsorbed on catalysts, polymers, etc. Unfortunately, chemical shifts would probably be too small to allow one to see many significant features in hydrocarbon homopolymers or copolymers. However, polymers containing heteroatoms, oxidation of homopolymers, the presence of additives, vulcanization mechanisms, etc. may be amenable to study by ESCA. Application to practical problems such as this must await the commercial development of suitable instruments. Fortunately, several companies have now developed some rather practical instruments. Advances through application of this technique are exciting in prospect.

III. SUMMARY

Several spectrometric techniques for the analysis and characterization of polymers are critically reviewed. Infrared spectrophotometric methods for the determination of ethylene and propylene sequence distributions in ethylene-propylene copolymers (EPM) are discussed. Major problems are the evaluation of group absorptivities and the resolution of overlapped bands in the $—CH_2—$ and $—CH_3$ rocking and wagging region of the spectrum used for these measurements. The relative merits of using digitized spectra and a least squares curve-fitting technique for resolving the absorption band parameters are presented. Various infrared spectrophotometric methods for determination of EPM composition are discussed and compared. Advantages of using the new laser Raman scattering techniques for the characterization and vibrational analysis of polymers are mentioned. Some very new techniques which offer exciting promises in the analysis and characterization of polymers are cited. These include C^{13} nuclear magnetic resonance by Fourier transform pulsed techniques, a new polymer mass spectrometer for studying macroions, and electron spectrometry (ESCA).

Acknowledgment

The author gratefully acknowledges permission to use the drawings provided by R.F. Schaufele shown in Figures 16 and 17. The author also thanks Esso Research Laboratories for permission to publish this review.

REFERENCES

1. Drushel, H.V., Ellerbe, J.S., Cox, R.C., and Lane, L.H., *Anal. Chem.*, 40, 370 (1968).
2. Veerkamp, T.A. and Veermans, A., *Makromol. Chem.*, 50, 147 (1961).
3. Natta, G., Mazzanti, G., Valvassori, A., Sartori, G., and Morero, D., *Chim. Ind.* (Milan), 42, 125 (1960).
4. Bucci, G. and Simonazzi, T., *J. Polym. Sci.*, Part C, 7, 203 (1964).
5. Natta, G., Valvassori, A., Ciampelli, F., and Mazzanti, G., *J. Polym. Sci.*, Part A, 3, 1 (1965).
6. Ciampelli, F. and Valvassori, A., *J. Polym. Sci.*, Part C, #16 (1), 377 (1967).
7. Stone, H., *J. Opt. Soc. Amer.*, 52, 998 (1962).
8. Pitha, J. and Jones, R.N., *Can. J. Chem.*, 44, 3031 (1966).
9. Seshadri, K.S. and Jones, R.N., *Spectrochim. Acta*, 19, 1013 (1963).
10. Abramowitz, S. and Bauman, R.P., *J. Chem. Phys.*, 39, 2757 (1963).
11. Meiron, J., *J. Opt. Soc. Amer.*, 55, 1105 (1965).
12. Koenig, J.L., Wolfram, L.E., and Grasselli, J.G., *Spectrochim. Acta*, 22, 1233 (1966).
13. Tosi, C., Corradini, P., Valvassori, A., and Ciampelli, F., *J. Polym. Sci.* Part C, #22(2), 1085 (1969).
14. Noble, F.W. and Hayes, J.E., Jr., *Ann. N.Y. Acad. Sci.*, 115, 644 (1964).
15. Noble, F.W. and Abel, K., *Anal. Chem.*, 36, 1855 (1964).
16. Drushel, H.V. and Iddings, F.A., *Anal. Chem.*, 35, 28 (1963).
17. Corish, P.J. and Tunnicliffe, M.E.T., *J. Polym. Sci.*, Part C, #7, 187 (1964).
18. Natta, G., Massanti, G., Valvassori, A., and Pajaro, G., *Chim. Ind.* (Milan), 39, 733 (1957).
19. Gössl, T., *Makromol. Chem.*, 42, 1 (1960).
20. Ciampelli, F., Bucci, G., Simonazzi, T., and Santambrogio, A., *Chim. Ind.* (Milan), 44, 489 (1962).
21. Wei, P.E., *Anal. Chem.*, 33, 215 (1961).
22. Stoffer, R.L. and Smith, W.E., *Anal. Chem.*, 33, 1112 (1961).
23. Folt, V.L., Shipman, J.J., and Krimm, S., *J. Polym. Sci.*, 61, S17 (1962).
24. Lomonte, J.N., *J. Polym. Sci.*, B1, 645 (1963).
25. McMurry, H.L. and Thornton, V., *Anal. Chem.*, 24, 318 (1952).
26. Kennedy, J.P., Elliott, J.J., and Groten, B., *Macromol. Chem.*, 77, 26 (1964).
27. Ketley, A.D. and Harvey, M.C., *J. Org. Chem.*, 26, 4649 (1961).
28. Liang, C.Y. and Watt, W.R., *J. Polym. Sci.*, 51, S14 (1961).
29. Jones, R.N., *Spectrochim. Acta*, 9, 235 (1957).
30. Bucci, G. and Simonazzi, T., *Chim. Ind.* (Milan), 44, 262 (1962).
31. Bly, R.M., Kiener, P.E., and Fries, B.A., *Anal. Chem.*, 38, 217 (1966).
32. Takeuchi, T., Tsuge, S., and Sugimura, Y., *Anal. Chem.*, 41, 184 (1969).
33. Veerkamp, T.A., De Kock, R.J., Veermans, A., and Lardinoye, M.H., *Anal. Chem.*, 36, 2277 (1964).

34. Nielsen, J.R., *J. Polym. Sci.*, 7C, 19 (1964).

35. Schaufele, R.F., *Trans. N.Y. Acad. Sci.*, 30, 69 (1967).

36. Schaufele, R.F., *J. Opt. Soc. Amer.*, 57, 105 (1967).

37. Schaufele, R.F. and Weber, M.J., *Phys. Rev.*, 152, 705 (1966).

38. Matsui, Y., Kubota, T., Tadokoro, H., and Yoshihara, T., *J. Polym. Sci.*, Part A, 3, 2275 (1965).

39. Hannon, M.J., Boerio, F.J., and Koenig, J.L., *J. Chem. Phys.*, 50, 2829 (1969).

40. Schachtschneider, J.H. and Snyder, R.G., *Spectrochim. Acta*, 19, 117 (1963).

41. Snyder, R.G. and Schachtschneider, J.H., *Spectrochim. Acta*, 20, 853 (1964).

42. Cornell, S.W. and Koenig, J.L., *J. Polym. Sci.*, Part A-2, 7, 1965 (1969).

43. Fikhtenfol'ts, V.S., Zolotareva, R.V., and L'vov, Yu., *Ultraviolet Spectra of Elastomers and Rubber Chemicals*, translated from Russian, Plenum Press, New York, 1966.

44. Drushel, H.V. and Sommers, A.L., *Anal. Chem.*, 36, 836 (1964).

45. Bovey, F.A., *Nuclear Magnetic Resonance Spectroscopy*, Academic Press, New York, 1969.

46. Farrar, T.C., *Anal. Chem.*, 42, 109A (1970).

47. Dole, M., Mack, L.L., Hines, R.L., Mobley, R.C., Ferguson, L.D., and Alice, M.B., *J. Chem. Phys.*, 49, 2240 (1968).

48. Siegbahn, K. et al., ESCA *Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy*, Almquist and Wiksells, Uppsala, 1967.