The Laser-Raman and Infra-red Spectra of Poly(Methyl Methacrylate)

H. A. WILLIS, MRS V. J. I. ZICHY and P. J. HENDRA

The laser-Raman spectrum of poly(methyl methacrylate) complete with depolarization data is reported. A spectrum of powdered poly(ethyl methacrylate) is also given for reference purposes. Infra-red data on these polymers are included. The spectral data are fully assigned on a group-vibrational basis.

ALTHOUGH the infra-red spectra of several of the poly(alkyl methacrylates) have been recorded and assignments for poly(methyl methacrylate) have been proposed[1,2], no acceptable Raman spectra are available. Although fluorescence in these compounds is only moderate, it is sufficient to inundate Raman spectra recorded with the familiar mercury discharge type of source.

In this paper we report the laser-Raman spectra of poly(methyl methacrylate) (PMMA), with depolarization results, that of poly(ethyl methacrylate) (PEMA) powder, and infra-red absorption data on each compound. A complete assignment of the PMMA spectra is attempted on a group-vibrational basis. The depolarization data have been found particularly valuable in making this assignment.

EXPERIMENTAL

The sample of PMMA was prepared by free radical polymerization at about 50°C. High resolution proton n.m.r measurements showed that the syndiotactic configuration was the predominant species present. This is in agreement with the conclusions of other authors for PMMA prepared in this way[2,3]. For comparison purposes, a sample of the ethyl analogue, PEMA, was used, prepared under similar conditions, and it is presumed that this was predominantly syndiotactic in structure.

Raman spectra were recorded on a Cary 81 laser excited spectrometer. The continuous source emits at 6 328 Å (15 798·0 cm^{-1}) and has a power of about 60 mW. The beam was passed along the axis of a $5 \times \frac{3}{4}$ in diameter rod of the methyl polymer. The Raman radiation was collected at 180° to the exciting beam. Experience has shown that, using a large rod in this manner, the depolarization effects observed are likely to be reliable[4]. (The use of small diameter rods, although optically more satisfactory, relies on multiple reflection and gives misleading depolarization results.)

The sample of PEMA was in the form of a powder. This was examined in a small glass sample tube by illuminating and viewing through the wall. The spectrum was more complex than that of PMMA and was less well defined. Polarization results are, of course, not available from powder specimens and therefore the data were only used to assist in the analysis of the PMMA spectra. The spectrum of liquid methyl methacrylate was also recorded for comparison.

Infra-red spectra of PMMA and PEMA were recorded on a Grubb–Parsons Spectromaster (4 000–500 cm^{-1}) and Grubb–Parsons DM4 (500–250 cm^{-1}). Hot pressed or solvent-cast films were used, as appropriate, in the thicknesses indicated on the spectra.

The infra-red and Raman spectra of PMMA are given in *Figures 1* and *2*, and those of PEMA for comparison in *Figures 3* and *4*. *Figure 5* is the Raman spectrum of methyl methacrylate monomer.

RESULTS AND DISCUSSION

General comparison between infra-red and Raman spectra of PMMA

The bands in the Raman and infra-red spectra of PMMA are listed in *Table 1*, together with indications of their relative intensities, and the polarization of the Raman bands (where this could be observed). The infra-red data are from our own observations, but are, in general, in excellent agreement with those of Nagai[2].

Since PMMA has an unsymmetrical repeat unit and the sample examined was amorphous it is reasonable to expect the molecule to exist in a number of conformational states. Therefore, it is not surprising that the majority of vibrations give rise to bands in both the Raman and infra-red. The intensity distribution in the two spectra (*Figures 1* and *2*) is of course remarkably different. The most prominent bands in the one spectrum are almost invariably weak in the other. Our analysis of the spectra will suggest that this occurs because the asymmetric stretching modes of the ester group are strong in absorption and weak in Raman activity while the converse is

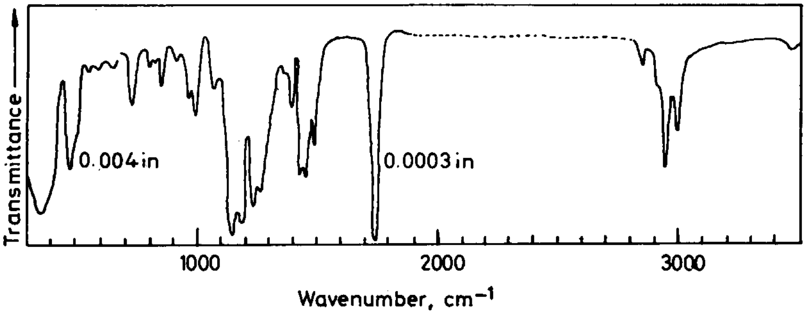


Figure 1—Infra-red spectrum of poly(methyl methacrylate)—liquid film

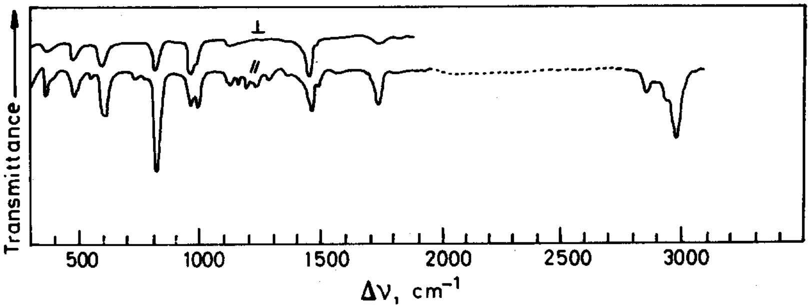


Figure 2—Raman spectrum of poly(methyl methacrylate)—solid rod

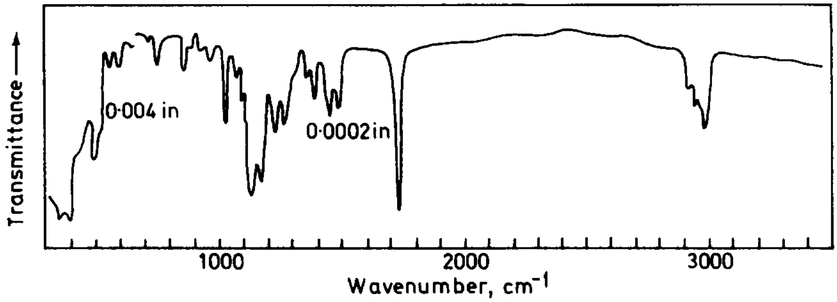


Figure 3—Infra-red spectrum of poly(ethyl methacrylate)—liquid film

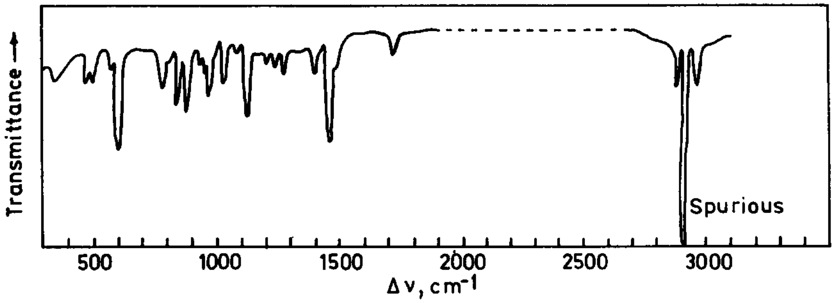


Figure 4—Raman spectrum of poly(ethyl methacrylate)—powder

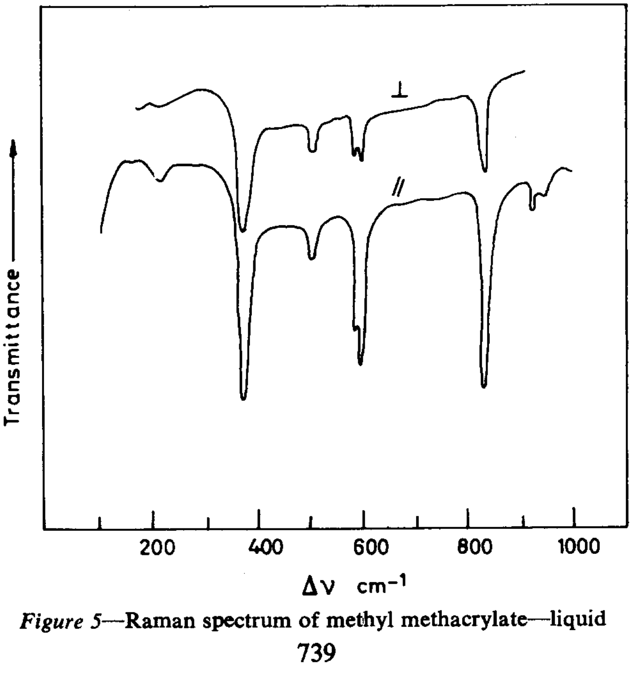


Figure 5—Raman spectrum of methyl methacrylate—liquid

Table 1. Poly(methyl methacrylate)—infra-red and Raman spectra

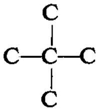
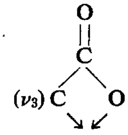
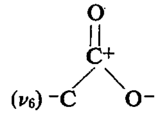
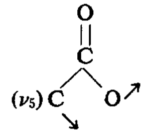
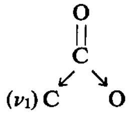
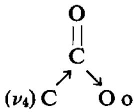
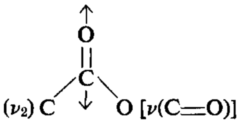
Infra-red cm^{-1}	*Raman* cm^{-1}	P.	*Assignment*
295 vw			
320 sh	304 w	p	δ(C—C—C) of  group
360 s	370 m	p	 (δ_s in plane)
400 sh	400 vw	?	δ(C—O—C)
484 m	487 m	dp	 (o.o.p. deformation)
505 wsh	504 vw	?	 (δ_a in plane, or C═O in plane deformation)
552 vw	537 w	p	δ(C—C—C) skeletal mode
598 vw	604 s	p	 ν_s(C—C—O)
658 vw	—	–	?
749 m	736 vw	?	ν(C—C) skeletal mode
807 vw	796 vw	?	?
828 vw	818 vs	sp	ν_s(C—O—C)
842 m	833 vw	?	CH_2 rock
910 vw	—	–	?
967 m	970 ms	dp	α-CH_3 rock
988 m	991 ms	p	O—CH_3 rock
1 063 m			ν(C—C) skeletal mode
	1 125 mw	?	ν(C—C) skeletal mode
1 150 vs	1 161 w	?	ν_a(C—O—C—)
1 190 vs	1 188 mw	?	
1 240 s	1 234 w	?	 or C—O stretch
1 270 s	1 276 vw	?	
1 376 wsh	—	–	δ_s(C—H) of α-CH_3
1 388 m	—	–	δ_s(C—H) of α-CH_3
	1 400 vw	?	CH_2 twist or wag
1 438 s	—	–	δ_s(C—H) of O—CH_3

Table 1—continued

Infra-red	*Raman*		*Assignment*
cm^{-1}	cm^{-1}	P.	
1 452 s	1 456 ms	dp	δ_a(C—H) of α-CH$_3$
1 465 sh			δ_a(C—H) of O—CH$_3$
1 483 m	1 490 w	?	δ(CH$_2$)
1 730 vs	1 736 mw	p	
2 850 vw	2 849 vw	?	Combination band involving O—CH$_3$
2 915 w	2 920 vw	?	Combination band involving O—CH$_3$ and ν_s(CH$_2$)
2 920 sh			
2 948 m	2 957 m	?	ν_s(C—H) of O—CH$_3$ with ν_s(C—H) of α-CH$_3$ and ν_a(CH$_2$)
2 995 m	—	-	ν_a(C—H) of O—CH$_3$ ν_a(C—H) of α-CH$_3$
3 460 vw	—	-	(2ν_2) Overtone of 1 730 cm^{-1}

Abbreviations: vs=very strong; s=strong; m=medium; w=weak; vw=very weak; sh=shoulder; p=polarized; dp=depolarized; sp=strongly polarized; ?=polarization doubtful; o.o.p.=out of plane; P.=polarization.

true of the corresponding symmetrical stretching modes. Bands which may reasonably be attributed primarily to C—C stretching and deformation of the polymer backbone are medium or weak in intensity in both infra-red and Raman spectra. In particular, there are several bands in the absorption spectrum of syndiotactic PMMA which are absent from the spectrum of the isotactic species. We agree with other authors[2, 5] that these are due to skeletal modes of the polymer backbone. In almost all cases these bands are very weak or are absent in the Raman spectrum. This observation is a little surprising, since it has been widely held as a general rule that the Raman spectrum is dominated by features due to skeletal modes.

Assignment of the vibrational spectra of PMMA

(i) C—H *stretching modes*—In the 3 000 cm^{-1} region there is one prominent band in the Raman spectrum at $\Delta\nu = 2\,957$ cm^{-1} (depolarized) and two weak features at $\Delta\nu = 2\,920$ and 2 849 cm^{-1}. These correspond closely to absorption bands at 2 948, 2 920 and 2 848 cm^{-1}. The infra-red spectrum has a further prominent band at 2 995 cm^{-1}, missing from the Raman spectrum. Nagai[2] has assigned the infra-red bands by comparing the spectrum of syndiotactic PMMA with those of the partially and fully deuterated polymers. This assignment places ν_a(CH$_2$)* with ν_a(O—CH$_3$) at 2 995 cm^{-1}, while ν_s(O—CH$_3$)*, ν_a(α-CH$_3$) and ν_s(α-CH$_3$) occur together with ν_s(CH$_2$) at 2 948 cm^{-1}. This suggestion seems a little unsatisfactory, since ν_a and ν_s of the α-methyl group are made to coincide, and further, the CH$_2$ modes are said to occur at higher frequency than the corresponding methyl modes, contrary to the assignments usually accepted for hydrocarbons[6]. In the infra-red spectrum of the methoxy deuterated species, PMd$_3$MA, Nagai

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*ν_a denotes asymmetric stretching mode; ν_s denotes symmetric stretching mode.

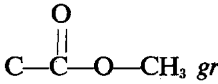
finds that a PMMA band at 2 920 cm^{-1} (ascribed to a combination mode of the ester group) is shifted to lower frequency, revealing a weak feature at 2 915 cm^{-1}. The latter might well be assigned to $\nu_s(CH_2)$; $\nu_a(CH_2)$ may then be assigned to the 2 948 cm^{-1} band, together with $\nu_s(\alpha\text{-}CH_3)$ and $\nu_s(O{-}CH_3)$, leaving the absorption at 2 995 cm^{-1} to $\nu_a(\alpha\text{-}CH_3)$ and $\nu_a(O{-}CH_3)$. This explanation would appear to be consistent with Nagai's experiments, and would leave the relevant positions of the bands more in keeping with their widely accepted order in hydrocarbon spectra[6].

Irrespective of which explanation may be correct, the 2 995 cm^{-1} band in the infra-red spectrum is attributed only to asymmetric C—H stretching modes. It is encouraging to note that this is absent from the Raman spectrum. The remaining band in this spectral region ($\Delta\nu = 2\,849$ cm^{-1}, 2 850 cm^{-1}, infra-red) is well accounted for as a combination mode, following Nagai's argument[2].

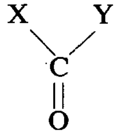
(ii) C—H *deformations in the 1 500* cm^{-1} *to 1 350* cm^{-1} *region*—The Raman spectrum has a prominent band at $\Delta\nu = 1\,456$ cm^{-1} (depolarized) and weak bands (polarization doubtful) at $\Delta\nu = 1\,490$ and 1 400 cm^{-1}. The infra-red bands at 1 438 cm^{-1} and 1 388 cm^{-1} have no equivalent in the Raman spectrum. These latter are assigned by Nagai[2] as $\delta_s(O{-}CH_3)$ and $\delta_s(\alpha\text{-}CH_3)$ respectively in agreement with the proposals of Katritzky *et al*[7]. The Raman observations may be taken to confirm this assignment, since the symmetrical methyl deformation mode is usually missing from the Raman spectra of saturated hydrocarbons[6]. The weak Raman band at $\Delta\nu = 1\,400$ cm^{-1} is not observed in the infra-red spectrum. This would suggest its assignment to a CH_2 wagging or twisting mode, since these are known to be more prominent in the Raman effect than in the absorption spectra of hydrocarbons[9].

The weak Raman band at $\Delta\nu = 1\,490$ cm^{-1} is presumably equivalent to the absorption band at 1 483 cm^{-1}, a band assigned by Nagai[2] as $\delta_a(\alpha\text{-}CH_3)$. However, this frequency is outside the range quoted by Sheppard and Simpson[9] (1 470 to 1 440 cm^{-1}) typical for deformations of an isolated methyl group on a carbon skeleton, whilst Salomon *et al*[1] consider that this band is due to the methylene scissoring mode. Since $\delta_a(CH_3)$ vibrations give rise to strong Raman bands in the spectra of hydrocarbons[9] while the $\delta(CH_2)$ band is frequently relatively weak. We favour Salomon's suggestion.

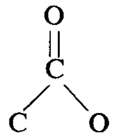
Nagai's assignment of the infra-red band at 1 465 cm^{-1} to a $\delta_a(O{-}CH_3)$ mode agrees with that of Katritzky *et al.*[7a] and thus the absorption at 1 452 cm^{-1} may be reasonably assigned to $\delta_a(\alpha\text{-}CH_3)$. There is only one Raman band in this region (at $\Delta\nu = 1\,456$ cm^{-1}) and since we expect both methyl deformations to be active, we presume this band to represent both $\delta_a(O{-}CH_3)$ and $\delta_a(\alpha\text{-}CH_3)$.



(iii) *Bands associated with the* $C{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}CH_3$ *group*—Analysis of the vibrational spectra of the unsymmetrical carbonyl halide F—CO—Cl has been achieved by comparison with the spectra of the symmetrical halides F—CO—F and Cl—CO—Cl both of which have C_{2v} symmetry[10, 11]. Nyquist and Potts[12] have extended this treatment to other molecules of the general form



Further, Hummel[12a] has suggested more specifically that the group

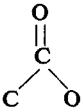
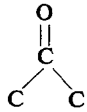


in esters may be usefully described as having C_{2v} symmetry. We shall therefore consider this group to have the six fundamental modes of Y—XZ—Y designated and illustrated by Herzberg[13a].

The fundamental ν_2 is substantially the carbonyl stretching mode which is easily identified as the weak polarized Raman band at $\Delta\nu = 1\,736$ cm^{-1} (infra-red 1 730 cm^{-1}, strong). The vibration ν_4, ν_a(C—C—O) is also easily assigned, following Nagai[2], to the weak pair of Raman bands at $\Delta\nu = 1\,234$ and 1 276 cm^{-1}, analogous to the very prominent infra-red bands at 1 240 cm^{-1} and 1 270 cm^{-1}. The 'doubling' of this vibration frequency has been elegantly explained by Havriliak and Roman[5] as resulting from rotational isomerism about the C—O bond. The assignment of the remaining fundamentals presents more difficulty, and therefore at this stage, it appears better to consider these alongside the vibrations of the C—O—C group. The latter has three fundamental modes, ν_a(C—O—C), ν_s(C—O—C) and δ(C—O—C).

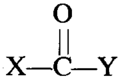
ν_a(C—O—C) gives rise to a very strong band in the infra-red spectra of ethers at about 1 100 cm^{-1}, and is found as a weak band in the Raman spectrum of dimethyl ether[13b] also at $\Delta\nu = 1\,100$ cm^{-1}. With PMMA, it seems likely that the band may appear as a doublet due to rotational isomerism. Havriliak and Roman[5] consider that the strong pair of infra-red bands 1 190 cm^{-1} and 1 150 cm^{-1} are ester bands, hence we assign these, and the corresponding weak Raman bands at $\Delta\nu = 1\,188$ and 1 161 cm^{-1} as ν_a(C—O—C). This is not in agreement with the proposals of Nagai[2] who considers these to be due to skeletal stretching modes, but the latter seems an unlikely explanation as the same bands appear, almost unaltered, in the infra-red spectra of both methyl methacrylate and methyl acrylate monomer[12b]. The 'splitting' of the vibrational frequencies ν_a(C—O—C) slowly disappears with increasing length of the alkoxy chain[12b], leading to the argument that rotational isomerism is involved, since with an increasing number of possible rotational forms the 'structure' of the band would disappear, leaving a single broad peak.

The symmetrical stretch ν_s(C—O—C) is assigned in the Raman spectrum of dimethyl ether to a feature at $\Delta\nu = 918$ cm^{-1} (strong, polarized)[13b]. The vibration evidently moves to lower frequency with increasing size of the alkyl groups, since it is found at $\Delta\nu = 843$ cm^{-1} (strong, polarized) in diethyl ether, and in ethyl isopropyl ether it occurs at 831 cm^{-1}[17]. Thus, the strong polarized band of PMMA at $\Delta\nu = 818 \text{ cm}^{-1}$ seems the best choice for this mode, especially as this corresponds closely with $\Delta\nu = 830 \text{ cm}^{-1}$ (strong, polarized) in methyl methacrylate monomer, and $\Delta\nu = 843 \text{ cm}^{-1}$ in PEMA. The remaining band of the —C—O—C skeleton, δ(C—O—C), is assigned to a band at $\Delta\nu = 414 \text{ cm}^{-1}$ in dimethyl ether (weak, polarized)[13b]. A weak band near 400 cm^{-1} in both the Raman and infra-red may possibly be δ(C—O—C) in the PMMA spectra.

Table 2. Low frequency modes of  $C{-}\overset{\overset{O}{\|}}{C}{-}O$ and  $C{-}\overset{\overset{O}{\|}}{C}{-}C$ skeleton

Methyl methacrylate monomer (liquid)		*Poly(methyl methacrylate)*		*Poly(ethyl methacrylate)*		*Polyethyl acrylate*		*Acetone (See ref. 14)*		*Assignment*
i.r.	R	i.r.	R	i.r.	R	i.r.	R (See ref. 18)	i.r.$_{(gas)}$	R$_{(liquid)}$	
374	376 p	360	370 p	355	348	345	375	385	393	ν_3
503	506 dp	484	487 dp	493	483	445	490	484	493	ν_6
		505	504*	513	498			530	530	ν_5
598	599 p	598	604 p	—†	604	—†	609	777	787	ν_1

p=polarized; dp=depolarized.
*Polarization not measured.
†Band not identified in i.r. spectrum.

The more prominent low frequency bands of a number of acrylate and methacrylate monomers and polymers (with those of acetone for comparison) are shown in *Table 2*. The only common structural feature in these molecules is the  $X{-}\overset{\overset{O}{\|}}{C}{-}Y$ group, hence it is probable that the bands are due to ν_1, ν_3, ν_5 and ν_6 of this group. Of these modes, ν_1 and ν_3 should give polarized Raman bands, and hence they are assigned at $\Delta\nu = 604$ and 370 cm^{-1} respectively in the spectrum of PMMA. ν_6 and ν_5 are associated with depolarized bands and must correspond to bands at $\Delta\nu = 487$ and 504 cm^{-1}. These latter four suggestions are in agreement with those for acetone[18]. ν_6 and ν_5 apparently coincide in the spectrum of methyl methacrylate monomer, whilst the proposal that ν_1 has a frequency close to 600 cm^{-1} calls for comment, since the corresponding mode in acetone appears as a very strong polarized band at 787 cm^{-1}. However, in an examination of the Raman spectra of a series of methyl ketones Braun *et al*[17] showed that a very prominent polarized band drifts downwards in the frequency as the ketone becomes more asymmetrical, i.e.

$CH_3{-}CO{-}CH_3$	787 cm^{-1}
$CH_3{-}CO{-}C_2H_5$	762 cm^{-1}
$CH_3{-}CO{-}CH(CH_3)_2$	723 cm^{-1}
$CH_3{-}CO{-}CH_2CH(CH_3)_2$	592 cm^{-1}

This lends support to the assignment of ν_1 at such a low frequency.

(iv) *Other* C—H *modes and* C—C *skeletal modes*—A detailed analysis of the band structure in the infra-red spectrum of syndiotactic PMMA between 1 300 and 1 050 cm^{-1} [5] suggests that bands at 1 125 and 1 063 cm^{-1} are essentially ν(C—C) modes of the polymer backbone. The band at 1 125 cm^{-1} could not be observed directly in the infra-red spectrum. However, the structure in the 1 300 cm^{-1} to 1 050 cm^{-1} region was resolved by a computer method into a series of Lorenzian bands. This revealed a band at 1 125 cm^{-1}, which was previously hidden by the ν(C—O) structure. It is therefore particularly valuable that the band at $\Delta\nu = 1\,125$ cm^{-1} may be observed directly in the Raman spectrum. Presumably this is so because the ν(C—O) mode gives rise to relatively weak bands in this region of the Raman spectrum. The prominence of the $\Delta\nu = 1\,125$ cm^{-1} band would substantiate Havriliak and Roman's contention[5] that this band is of a different origin to the overlapping ester bands. Thus, we may confidently assign that at 1 125 cm^{-1} to a skeletal mode (either a pure C—C stretch as suggested by Krimm *et al*[19], or a combination of CH_3 (rock), CH_2 (wag) and C—C stretch, as observed by Schachtschneider and Snyder[20] at 1 130 cm^{-1} for the *trans* form of syndiotactic polypropylene). The band at 1 063 cm^{-1} behaves conversely to that at 1 125 cm^{-1}, in that it appears in the infra-red spectrum, but is not observed in the Raman. Nagai[2] and Havriliak and Roman[5] agree that this is a backbone mode. This band is present in the infra-red spectrum of syndiotactic PMMA, and is absent from that of the isotactic species. If indeed it arises from the C—C stretch of the planar zig-zag backbone this would lend support to Havriliak and Roman's contention that this prominent difference between the infra-red spectra of the two stereoisomers arises from the predominantly planar conformation of the backbone of the syndiotactic polymer, and the preferred coiled form of the isotactic species. Nagai[2] considers that the infra-red bands at 991 cm^{-1} arises from ν_s(C—O—C) and γ(CH_3—O). We have placed ν_s(C—O—C) at 818 cm^{-1}, but that of γ(CH_3—O) appears to be a reasonable assignment for the 991 cm^{-1} band ($\Delta\nu = 988$ cm^{-1} in the Raman spectrum), and agrees well with the proposals of Katritzky *et al*[7a]. Similarly, 970 cm^{-1} infra-red and $\Delta\nu = 967$ cm^{-1} appear reasonable for the (α-CH_3) rocking mode. Nagai[2] assigns the CH_2 rocking mode to a band at 749 cm^{-1}, but this seems a very low value for the single —CH_2— group, and we would prefer 842 cm^{-1} ($\Delta\nu = 833$ cm^{-1} in Raman spectrum).

There is no evidence to permit an assignment of the band at $\Delta\nu = 796$ cm^{-1} in the Raman spectrum (807 cm^{-1} in the infra-red), but that at $\Delta\nu = 736$ cm^{-1} (749 cm^{-1} in the infra-red) is more interesting since the band is sensitive to tacticity (759 cm^{-1} in the spectrum of the isotactic species). This suggests that it may be a skeletal mode, and indeed Sheppard and Simpson[9] suggest that there should be a ν(C—C) mode in this region in paraffins with an internal quaternary carbon atom. The $\Delta\nu = 537$ cm^{-1} band in the Raman spectrum (552 cm^{-1} in the infra-red) may be another skeletal mode found by the same authors near 500 cm^{-1}. They suggest that a further polarized band of the C_5 unit should appear in the Raman spectrum between 350 and 305 cm^{-1}, thus the polarized band at $\Delta\nu = 304$ cm^{-1} would seem to correspond to this mode in the PMMA spectrum. The suggested assignments are collected together in *Tables 1* and *2*.

It is apparent that the modes causing most bands can be described fairly accurately. The ability to record a first class Raman spectrum of poly(methyl methacrylate) complete with depolarization data has proved most valuable in clarifying the previous suggested vibrational assignments for the polymer.

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