Stretching and deformation vibrations of CH_2, $C(CH_3)$ and $O(CH_3)$ groups of poly(methyl methacrylate)

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Infrared and Raman spectra of atactic PMMA and infrared spectra of stereoregular PMMA and of its four deuterated derivatives $+CD_2C(CD_3)COOCD_3+_n$, $+CH_2C(CD_3)COOCD_3+_n$, $+CD_2C(CH_3)COOCD_3+_n$ and $+CD_2C(CD_3)COOCH_3+_n$, were measured. They were used to assign the bands of stretching and deformation vibrations of CH_2, $C-CH_3$ and OCH_3 groups in the infrared and Raman spectra and to discuss the effect of stereoregularity on these bands in the infrared spectra.

INTRODUCTION

Infrared and Raman spectra of poly(methyl methacrylate) (PMMA) have been studied by many authors[1–5]. Deuterated derivatives were used in the interpretation of infrared spectra by Nagai[2] who recorded the infrared spectra of PMMA with deuterated ester methyl groups (PMMA–OCD_3), of PMMA with deuterated methylene groups and C-methyl groups (PMMA–CD_2–CCD_3) and of fully deuterated PMMA (PMMA–D_8). On the other hand, deuterated derivatives were not used in the interpretation of Raman spectra by Willis[5]. The interpretation of PMMA spectra suggested by Nagai[2] and Willis[5] differs for a number of bands, and the existing experimental data provide no possibility of an unambiguous interpretation.

Since the interpretation of the stretching and deformation vibrations of methylene and methyl groups would gain much in precision if the Raman and infrared spectra were recorded for all deuterated derivatives of PMMA which contain each time only a single functional group with hydrogen atoms, we measured the infrared and Raman spectra of atactic samples $+CD_2C(CD_3)COOCD_3+_n$ (PMMA–D_8), $+CH_2C(CD_3)COOCD_3+_n$ (PMMA–CCD_3–OCD_3), $+CD_2C(CH_3)COOCD_3+_n$ (PMMA–CD_2–OCD_3), $+CD_2C(CD_3)COOCH_3+_n$ (PMMA–CD_2–CCD_3) and the infrared spectra of stereoregular forms of these derivatives We then attempted to use these spectra in a more precise interpretation of the characteristic vibrations of CH_2, $C-CH_3$ and OCH_3 groups and to examine the effect of stereoregularity on these bands in the infrared spectra.

EXPERIMENTAL

Sample preparation

Monomers. $CH_2{=}C(CD_3)COOCD_3$ was prepared from methyl-D_3-hydrogen methyl-D_3-malonate, formaldehyde and diethyl amine by the Mannich reaction[6] employing a procedure described in Reference 7. $CD_2{=}C(CH_3)COOCD_3$ was prepared from methyl-D_3 hydrogen methyl malonate, deuterated formaldehyde-D_2 and diethyl amine by a procedure described in Reference 8. $CD_2{=}C(CD_3)COOCH_3$ was prepared from deuterated acetocyanhydrin[9]. The deuterated acetone, methanol (CD_3OD) and formaldehyde $(CD_2O)_n$ used contained more than 99% of deuterium (Isocomerz GDR). $CD_2{=}C(CD_3)COOCD_3$ (Technosnabexport, USSR) contained 99.1% deuterium. All monomers were dried over CaH_2 and were freshly distilled prior to use.

Polymers. Atactic samples of PMMA and of its deuterated derivatives were prepared by polymerization of the respective monomers with 0.15% benzoyl peroxide. Isotactic samples were prepared in toluene at 0°C with phenylmagnesiumbromide as initiator[10]; syndiotactic samples were prepared in toluene[11] at −78°C with $TiCl_4$ and Et_3Al. All polymers were purified by twofold precipitation from dry acetone into distilled water and dried in a high vacuum at 60°C for 8 h.

Spectral measurements

The ^1H-n.m.r. spectra were recorded with a JEOL PS-100 spectrometer at 100 MHz in 10% solutions in an equimolar mixture of *ortho*dichlorobenzene and tetrachloroethylene at 135°C. The tacticity of polymers was determined from these n.m.r. spectra by a procedure introduced by Bovey[12] and the degree of deuteration was determined from integral intensities of the n.m.r. bands. The results are presented in *Table 1*. The infrared spectra were recorded with a Zeiss UR-20 infrared spectrometer by the method of KBr pellets. The Raman spectra were recorded using block-shaped samples with a CODERG LRDH-800 spectrometer. The 5145 Å line of the argon ion laser was used for the excitation. The intensity of radiation per sample was reduced to 250 mW to prevent decomposition of the sample.

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Table 1 Stereoregularity and deuteration of PMMA and deuterated derivatives

	dyads		triads			D content* in		
PMMA	r (%)	m (%)	I (%)	H (%)	S (%)	OCH_3 (%)	CH_2 (%)	CCH_3 (%)
	Isotactic samples							
i-PMMA	97	3	96	3	1	–	–	–
i-PMMA-CD_2-CCD_3	–	–	–	–	–	–	95	97
i-PMMA-CD_2-OCD_3	–	–	91	6	3	99	98	–
i-PMMA-CCD_3-OCD_3	98	2	–	–	–	99	–	97
	Syndiotactic samples							
s-PMMA	7	93	1	12	87	–	–	–
s-PMMA-CD_2-CCD_3	–	–	–	–	–	–	97	96
s-PMMA-CD_2-OCD_3	–	–	4	14	82	99	95	–
s-PMMA-CCD_3-OCD_3	15	85	–	–	–	99	–	96
	Atactic samples							
a-PMMA	24	76	6	36	58	–	–	–
a-PMMA-CD_2-CCD_3	–	–	–	–	–	–	95	95
a-PMMA-CD_2-OCD_3	–	–	5	36	59	99	95	–
a-PMMA-CCD_3-OCD_3	22	78	–	–	–	99	–	95
a-PMMA-D8	–	–	–	–	–	99	99	99

*The deuterium content is not less than the values listed

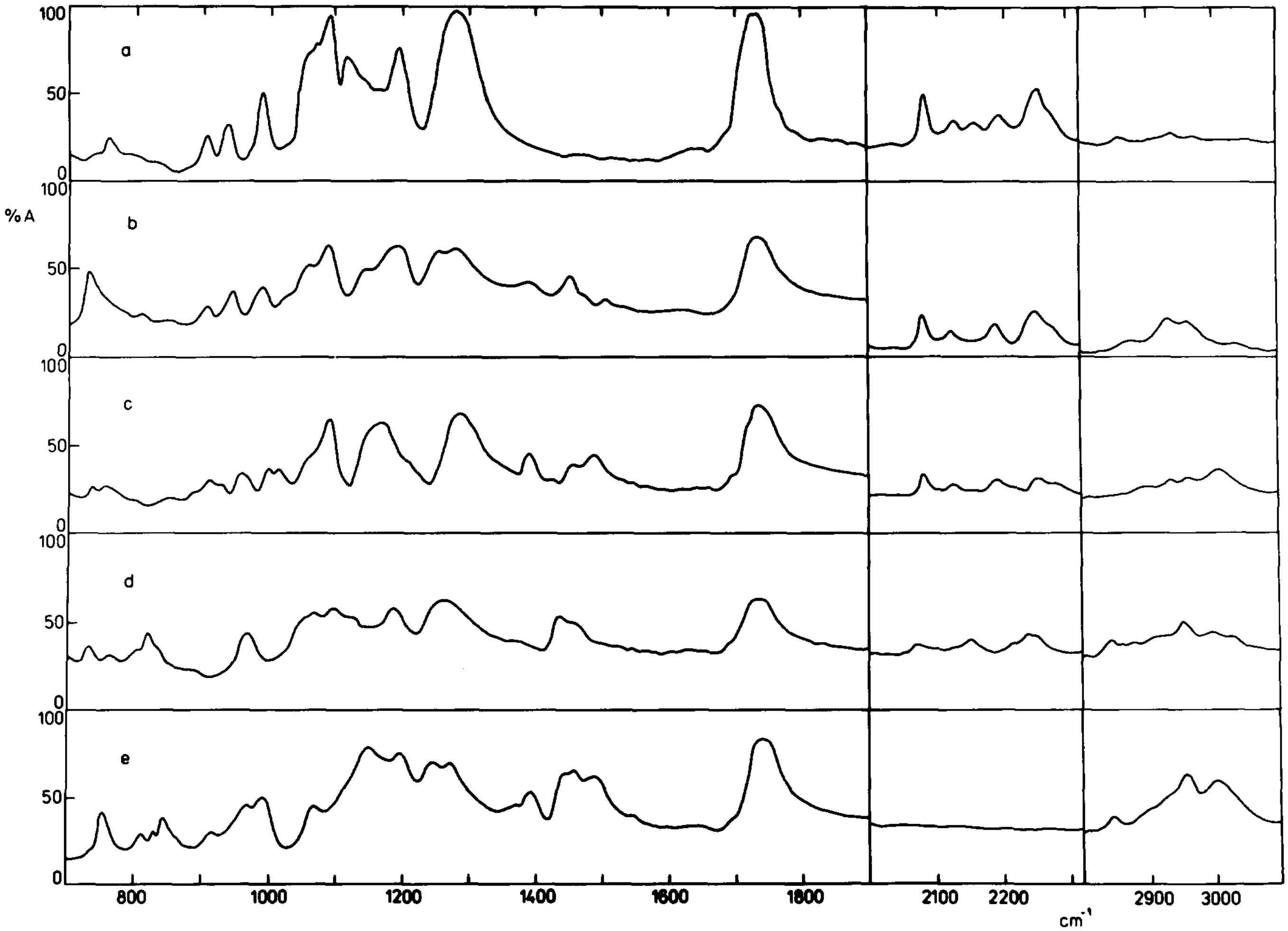

Figure 1 Infrared spectra of atactic PMMA and its deuterated derivatives
A PMMA-D_8
B PMMA-CCD_3-OCD_3
C PMMA-CD_2-OCD_3
D PMMA-CD_2-CD_3
E PMMA

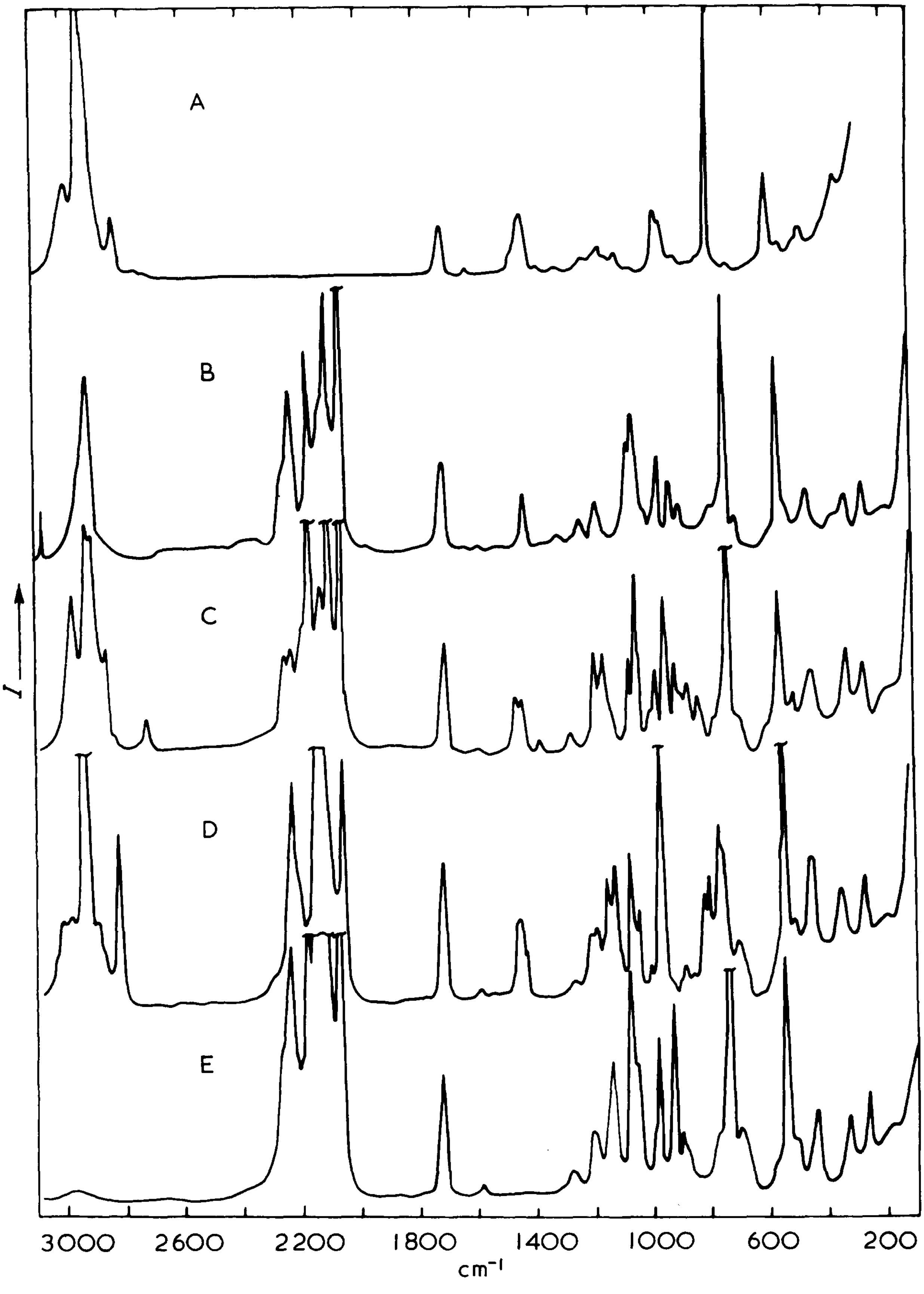

Figure 2 Raman spectra of atactic PMMA and its deuterated derivatves

A PMMA
B PMMA-CCD_3-OCD_3
C PMMA-CD_2-OCD_3
D PMMA-CD_2-CCD_3
E PMMA-D_8

Table 2 C–H Deformation and stretching vibrations of CH$_2$ group of PMMA-CCD$_3$-OCD$_3$

Raman atactic			Infrared atactic		Infrared syndio		Infrared iso		Region
cm^{-1}	ρ	*I*	cm^{-1}	*I*	cm^{-1}	*I*	cm^{-1}	*I*	
–			2860^c	w	2860^c	w	2860^c	w	stretching vibrations
2939	0.04	vs	2932	m	2934	m	2930	m	
2960	0.28	sh	2958	m	2958	m	2958	m	
1450	0.87	m	1448	m	1448	m	1448	m	bending vibrations
–			460^b	sh	1460^b	sh	1460^b	sh	
1330	0.70	w	–^{a}		–^{a}		–^{a}		wagging or twisting vibrations
–			1385	w	1385	w	1385	vw	
–			732	m	732	m	753	s	rocking vibration

[a] Possible overlapping with the very strong band at 1280 cm^{-1}
[b] Harmonic vibration
[c] Probably a result of Fermi resonance

RESULTS AND DISCUSSION

The infrared spectra of atactic samples PMMA-D$_8$, PMMA–CCD$_3$–OCD$_3$, PMMA–CD$_2$–OCD$_3$, PMMA–CD$_2$–CCD$_3$ and PMMA are given in *Figure 1*; the Raman spectra of atactic samples of these derivatives are given in *Figure 2*. Interpretation of the spectra was made much easier owing to the high isotopic purity of the individual samples (*Table 1*), due to which bands of stretching and deformation vibrations of the CH bonds of methyl and methylene groups in which the hydrogen atom has been replaced by deuterium could be assumed not to appear in the measured spectra.

Methylene vibrations

A suitable model for the study of the methylene vibrations of PMMA is PMMA–CCD$_3$–OCD$_3$. We therefore checked interpretations of characteristic vibrations of the methylene group of PMMA given in the literature[2,3,5] by comparing these data with the measured vibrational spectra of this deuterated derivative shown in *Figures 1b* and *2b* (cf. also *Table 2*).

Stretching vibrations of C–H bonds of the methylene group. The methylene C–H bond stretching vibrations of PMMA are usually cited[2,5] to lie at 2995, 2948 and 2915 cm^{-1}.

In the range 2700–3100 cm^{-1} the infrared spectrum of atactic PMMA–CCD$_3$–OCD$_3$ exhibits three absorption bands with the wavenumbers 2860, 2932 and 2958 cm^{-1} (*Figure 1b, Table 2*), while the Raman spectrum contains only two bands with the wavenumbers 2939 and 2960 cm^{-1} (*Figure 2b, Table 2*). Bands with the wavenumbers 2932 and 2958 cm^{-1}, which can be observed in the infrared and in the Raman spectrum of PMMA–CCD$_3$–OCD$_3$, are assigned to the stretching vibrations of the C–H bands of the methylene group. In the Raman spectrum the more intensive and polarized band with wavenumber 2939 cm^{-1} obviously corresponds to the symmetric stretching vibration of the CH bonds. The band with wavenumber 2960 cm^{-1}, which possesses a higher depolarization factor, corresponds to the antisymmetric mode. The weaker band in the infrared spectrum with wavenumber 2960 cm^{-1} is either a harmonic vibration, or due to the Fermi resonance between the stretching vibration of the CH$_2$ bonds and the bending vibration of the CH$_2$ group situated at 1448 cm^{-1} (*Table 2*). Nakanishi[14] expects the band of the symmetric stretching vibration of the CH bonds of the CH$_2$ groups to be in the range about 2850 cm^{-1}. The position of this band found by us in PMMA–CCD$_3$–OCD$_3$ at wavenumber 2932 cm^{-1} could indicate that the band has been shifted from its position by the Fermi resonance.

CH$_2$ bending vibrations. In PMMA the bending vibration of the CH$_2$ group has been assigned to a band[2,3] at 1445–1452 cm^{-1} and to a band[5] at 1483 cm^{-1}. In the range 1400–1500 cm^{-1} the infrared spectrum of PMMA–CCD$_3$–OCD$_3$ exhibits an absorption band at 1448 cm^{-1} with a shoulder at 1460 cm^{-1}. In the same range the Raman spectrum also exhibits one band with wavenumber 1450 cm^{-1}. Since in this range there is no band in the infrared and Raman spectrum of PMMA–D$_8$ (*Figure 1a*) in the spectrum of PMMA–CCD$_3$–OCD$_3$ we assign the band at 1448 cm^{-1} to the bending vibration of the CH$_2$ group and the shoulder at 1460 cm^{-1}, observed only in the infrared spectra, to the harmonic vibration of some vibrational mode of the CH$_2$ group.

Twisting and wagging vibrations of the CH$_2$ group. In PMMA twisting and wagging vibrations of the CH$_2$ group have been related to the infrared band[13] at 1370 cm^{-1} and to the Raman band[5] at 1400 cm^{-1}. Bands of the twisting and wagging vibrations of the methylene group in PMMA can be expected in the range from 1200 to 1400 cm^{-1}. More detailed information is obtained from the comparison of various deuterated PMMA samples. The infrared band at 1370 cm^{-1} in PMMA is also observed in the infrared spectra of PMMA with deuterated C-methyl groups[15] (at 1380 cm^{-1}) and in PMMA–CCD$_3$–OCD$_3$ (at 1385 cm^{-1}) (*Figure 1b, Table 2*). This band disappears in the infrared spectra of PMMA with the deuterated methylene group [PMMA–CD$_2$[13] PMMA–CD$_2$–CCD$_3$ (*Figure 1d*), PMMA–CD$_2$–OCD$_3$ (*Figure 1c*) and PMMA–D$_8$ (*Figure 1a*)]. The band in the Raman spectra of PMMA at 1327 cm^{-1} appears also in the Raman spectra of PMMA with deuterated C-methyl groups[16] (at 1328 cm^{-1}), in PMMA with deuterated ester groups[16] (at 1332 cm^{-1}), in PMMA with deuterated ester groups[16] (at 1332 cm^{-1}) and in PMMA–CCD$_3$–OCD$_3$ (at 1330 cm^{-1}, *Figure 2b*). This band disappears in the Raman spectra of PMMA with deuterated methylene groups, PMMA–CD$_2$ [16], PMMA–CD$_2$–CCD$_3$ (*Figure 2d*), PMMA–CD$_2$–OCD$_3$ (*Figure 2c*) and in PMMA–D$_8$ (*Figure 2e*). In the infrared spectra this band cannot be detected, obviously since at

Table 3 C–H Deformation and stretching vibrations of C–CH_3 group of PMMA-CD_2-OCD_3

Ramam atactic			Infrared						Region
			atactic		syndio		iso		
cm^{-1}	ρ	*I*	cm^{-1}	*I*	cm^{-1}	*I*	cm^{-1}	*I*	
2857[b]	0.33	w	2855[b]	vw	2855[b]	vw	–		
2890[b]	0.06	s	2890[b]	w	2890[b]	w	2890[b]	w	stretching
2928	0.06	vs	2930	m	2928	m	2928	wsh	vibrations
2954	0.06	vs	2958	m	2956	m	2958	mbroad	
3004	0.45	vs	3000	s	2996	s	3002	s	
1385	0.20	w	1385	s	1385	s	1385	vwsh	
1393	0.25	w	1395	wsh	1395	wsh	1393	s	bending
1460	0.70	s	1450	m	1450	m	1468[a]	m	vibrations
1480	0.68	s	1483	s	1483	s	1485[a]	m	
953	0.18	s	957	m	957	m	957	sh	rocking
967	0.18	vs	968	sh	968	wsh	968	s	vibrations

[a] The strong overlapping between the bands at 1468 cm^{-1} and 1483 cm^{-1} does not allow establishment of the exact wavenumbers of their maxima
[b] Harmonic or combination vibrations probably due to the Fermi resonance

1280 cm^{-1} it is overlapped by a very strong band corresponding to the vibration of the C–O group. The described behaviour of the infrared active band of PMMA at 1370 cm^{-1} and of the Raman-active band of PMMA at 1327 cm^{-1} in the deuteration of the individual groups indicates that both bands are related to the characteristic vibrations of the CH_2 group and more specifically to the wagging or twisting vibrations of this group[17].

Rocking vibration of the CH_2 group. In infrared spectra of PMMA, CH_2 group rocking vibrations are assumed to correspond to the band[2] at 749 and the band[18,19] at 842 cm^{-1}; in Raman spectra, the corresponding band is thought to appear at 833 cm^{-1}. Our recent measurements of the infrared and Raman spectra of PMMA–CCD_3–OCD_3 (*Figures 1b, 2b*) show that this compound has no band in the range 800–900 cm^{-1} and that the band lying in the infrared spectra of PMMA at 749 cm^{-1} is shifted to 732 cm^{-1} for PMMA–CCD_3–OCD_3 (*cf. Table 2, Figure 1b*). This suggests that the bands of PMMA at 749 and 842 cm^{-1} cannot be simple rocking vibrations of the CH_2 groups. Willis[5] assumes that the band in the infrared spectrum of PMMA at 749 cm^{-1} corresponds in the Raman spectrum to a PMMA band at 733 cm^{-1} and assigns it to skeletal vibrations. When comparing the infrared and Raman spectra of variously deuterated PMMA samples, we found that the PMMA band lying in the infrared spectra at 749 cm^{-1} was shifted to 695, 735, 746 and 667 cm^{-1} for PMMA–CD_2[13], PMMA–CCD_3[15], PMMA–OCD_3[2] and PMMA–D_8[2] respectively, while the PMMA band observed in the Raman spectra at 733 cm^{-1} was shifted only very little after deuteration of PMMA, namely, to 714, 715, 726 and 705 cm^{-1} in PMMA–CD_2, PMMA–CCD_3, PMMA–OCD_3 and PMMA–D_8, respectively[16]. We assume, therefore, that the band in PMMA at 749 cm^{-1} is given by the skeletal vibrational motion affected by the rocking vibration, while the PMMA band at 733 cm^{-1} represents skeletal vibration.

Vibrations of the C–CH_3 group

To revise the interpretation of the characteristic vibrations of the C–CH_3 groups, we mainly used the infrared and Raman spectra of PMMA–CD_2–OCD_3 given in *Figures 1c* and *2c* and in *Table 3.*

Stretching vibrations of CH bonds of C–CH_3 groups. In the literature, the PMMA band[2] at 2948 or the band[5] at 2995 are assigned to these vibrations.

In the range of stretching vibrations of the CH bonds the infrared spectra of PMMA–CD_2–OCD_3 exhibit three rather strong bands at 3000, 2958 and 2930 cm^{-1} and two weaker bands at 2890 and 2855 cm^{-1} (*Figure 1c, 2c*). The Raman spectra of this derivative contain four rather strong bands at 3004, 2954, 2928 and 2890 cm^{-1} and a weak band at 2857 cm^{-1} (*Figure 2c*). The strong bands at 2890, 2928, 2954 cm^{-1} in the Raman spectra are strongly polarized ($\rho \doteq 0.06$). The bands at 2857 and 3004 cm^{-1} have a depolarization factor approximately 0.4 (*Table 3*).

Since it may be expected that the C–CH_3 group lies in the plane of the ester group[18], it obviously has two fundamental stretching vibrations of the CH bonds lying in the plane of the ester group, strongly polarized in the Raman spectra, and one out-of-plane fundamental stretching vibration of the CH bonds unpolarized in the Raman spectra[20]. In the vibrational spectra of PMMA–CD_2–OCD_3 three bands which are strong both in the Raman and in the infrared spectrum are assigned to the fundamental frequencies of stretching vibrations of the CH bonds. Of these three bands, two bands at 2928 and 2954 cm^{-1} are polarized, while the band at 3004 cm^{-1} is unpolarized.

The band lying at 2890 cm^{-1}, strongly polarized and relatively strong in the Raman spectra and weak in the infrared spectrum, may be assigned to a harmonic vibration of the C–CH_3 group, the intensity of which is enhanced by Fermi resonance. The band at 2857 cm^{-1}, which is unpolarized in the Raman spectrum and weak both in the Raman and in the infrared spectrum, may be a combination frequency. The assignment of these two bands is very uncertain and confirmation would require a more detailed theoretical analysis.

C–methyl bending vibrations. C–methyl symmetrical bending vibrations of PMMA have been related to the infrared bands[2,3,5] at 1388 and 1370 cm^{-1} and to the Raman band[5] at 1400 cm^{-1}.

As has been shown in the discussion of the CH_2 vibrations, the band in the infrared spectrum of PMMA at 1370 cm^{-1} is related to the wagging or twisting vibration of the CH_2 group. In the Raman spectra of PMMA measured by us (*Figure 2a*) we found a weak band at 1390 cm^{-1} accompanied by an inflection at 1400 cm^{-1}. In the infrared and Raman spectra of PMMA–CD_2–OCD_3 (*Figures 1c, 2c, Table 3*) a doublet at 1385 and 1393 cm^{-1} can be observed. Both these bands are assigned to the deformation vibration

Table 4 C–H Deformation and stretching vibrations of -OCH$_3$ group of PMMA-CD$_2$-CCD$_3$

Raman atactic			Infrared atactic		Infrared syndio		Infrared iso		Region
cm^{-1}	ρ	*I*	cm^{-1}	*I*	cm^{-1}	*I*	cm^{-1}	*I*	
2847	0.07	vs	2844	w	2842	w	2845	w	stretching vibrations
2880[a]	0.06	sh	2890[a]	vw	2890[a]	vw	2890[a]	vw	
2915[a]	0.16	s	2910[a]	w	2910[a]	w	2910[a]	w	
2955	0.07	vs	2952	s	2952	s	2956	s	
3002	0.47	s	2997	m	2995	m	3004	m	
3031[a]	0.58	s	3025[a]	sh	3025[a]	vwsh	3025[a]	sh	
1440	0.64	s	1436	s	1436	s	1436	s	bending vibrations
1456	0.68	s	1456	sh	1456	m	1458	m	
1465	0.70	s	1472	sh	1472	wsh	1475	wsh	
972	0.28	vs	972	s	972	s	973	s	rocking vibration

[a] Harmonic or combination vibrations probably affected by the Fermi resonance

of the C–CH$_3$ groups. Such interpretation is also supported by the fact[15] that in PMMA–C–CD$_3$ the doublet disappears in this range. The fact that this deformation vibration of the C–CH$_3$ group in the spectra of atactic samples as a doublet is obviously connected with the position of the band being dependent on stereoregularity. In the infrared spectrum of syndio-PMMA–CD$_2$–OCD$_3$ (*Table 3*) this band is lying at 1385 cm^{-1}, while only an inflexion appears at 1395 cm^{-1}; in the infrared spectrum of the isotactic sample (*Table 3*) the band has a maximum at 1393 cm^{-1}, with only an inflection appearing at 1385 cm^{-1}.

Antisymmetrical bending vibrations of the C–CH$_3$ group in PMMA are identified with the band at[2,3] 1483 cm^{-1} or with the band[5] at 1452 cm^{-1}. According to our measurements, the infrared spectrum of PMMA–CD$_2$–OCD$_3$ exhibits two bands at 1450 and 1483 cm^{-1} in this range (*Figure 1c, Table 3*), while the Raman spectrum (*Figure 2c, Table 3*) exhibits two unpolarized bands at 1460 and 1480 cm^{-1}.Since no band can be observed in this range in the infrared and Raman spectra of fully deuterated PMMA (PMMA–D$_8^2$) (*Figure 2*), we believe that both these bands in the spectra of PMMA–CD$_2$–OCD$_3$ are bending vibrations of the C–CH$_3$ group.

For the C–CH$_3$ group lying in the plane of the ester group, three fundamental deformation vibrations of the C–CH$_3$ group may be expected, namely, two in-plane and one out-of-plane with respect to the plane of the ester group. By analogy with the spectra of methyl acetate[20], we assign the band at 1390 cm^{-1} (often called symmetric deformation vibration) and the band at 1480 cm^{-1} as planar deformation vibrations of the C–CH$_3$ group, while the band at 1450 cm^{-1} is assigned in this respect as out-of-plane deformation vibration.

Rocking vibration of the C–CH$_3$ group. The rocking vibration of the C–CH$_3$ group in the infrared and Raman spectra was assigned to bands[2,3,5,15] with the wavenumbers 951 and 967 cm^{-1}. According to Nagai[2], the band at 967 cm^{-1} should be attributed to syndiotactic sequences and that at 951 cm^{-1} to isotactic sequences. The infrared and Raman spectra of PMMA–CD$_2$–OCD$_3$ fully support such interpretation. The infrared spectra of syndiotactic PMMA–CD$_2$–OCD$_3$ exhibit a band at 957 cm^{-1}, while the isotactic sample exhibits a band at 968 cm^{-1} (cf. *Table 3*). In the infrared and Raman spectrum of the atactic sample of PMMA–CD$_2$–OCD$_3$ one can see a doublet near these wavenumbers (*Figures 1c, 2c*).

Vibration of the methyl group in ester groups

The assignment of vibrations of the ester methyl group in PMMA is based predominantly on measurements performed by Nagai[2] and on the interpretation of the infrared spectra of PMMA–CD$_2$–CCD$_3$. To verify this assignment, we measured the infrared spectra of PMMA–CD$_2$–CCD$_3$ once again and extended experimental data by including the Raman spectra of this sample.

Stretching vibrations of CH bonds. Nagai[2] observed in the infrared spectrum of PMMA–CD$_2$–CCD$_3$ four bands in the range of stretching vibrations of the CH bonds, namely, at 2995, 2948, 2920, and 2835 cm^{-1}; of these, the intensive bands at 2995 and 2948 cm^{-1} were assigned to the asymmetric and symmetric stretching vibrations of the CH bonds respectively. In our measurements of the infrared spectra of PMMA–CD$_2$–CCD$_3$, we found two rather strong bands at 2952 and 2997 cm^{-1}, three weaker bands at 2844, 2890 and 2910 cm^{-1} and an inflection at 3025 cm^{-1} (*Figures 1d, 2d, Table 4*). In the Raman spectra one can observe five intensive bands at 2847, 2915, 2955, 3002 and 3031 cm^{-1} and one weak band at 2880 cm^{-1}; of these, the bands at 3031 and 3002 cm^{-1} are less polarized (*Table 4*), while the other bands are strongly polarized. The wavenumbers and relative intensities of all these bands correspond to values found in the infrared and Raman spectra of deuterated methyl acetate[20], CD$_3$COOCH$_3$. From comparison of intensities of the Raman and infrared spectra, and of the depolarization factors (*Table 4*) and from the interpretation of the spectra of CD$_3$COOCH$_3$[20] we infer that the band of PMMA–CD$_2$–CCD$_3$ at 3002 cm^{-1} and denoted by Nagai[2] as an asymmetric vibration is an out-of-plane vibration with respect to the plane of the ester group, while the band at 2955 cm^{-1} and denoted as symmetric vibration is an in-plane vibration of the CH bonds. Another in-plane vibration of the CH bonds is probably the band at 2847 cm^{-1}, judging by the intensity and depolarization factor. Further bands of PMMA–CD$_2$–CCD$_3$ observed in this range are obviously harmonic, or combination frequencies of deformation vibration of the ester OCH$_3$ group, the intensity of which is affected by the Fermi resonance.

O–CH$_3$ bending vibrations. Nagai[2] assigned two bands at 1438 and 1465 cm^{-1} in the infrared spectrum of PMMA–CD$_2$–CCD$_3$ to the symmetric and asymmetric bending, vibration of the OCH$_3$ groups, respectively. According to our measurements, this compound has three bands at

Table 5 C-H Deformation and stretching vibrations of PMMA

Raman			Infrared						Assignment
atactic			atactic		syndio		iso		
cm^{-1}	ρ	I	cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	
1327	0.63	m	–[a]		–[a]		–[a]		wagging or twisting CH_2
–			1370	w	1370	w	1370	vw	wagging or twisting CH_2
1390	0.30	m	1388	m	1390	m	1390	m	CCH_3 bending
1436	0.78	s	1438	s	1438	s	1438	s	OCH_3 bending
1451	0.70	vs	1452	s	1452	s	1452	s	CH_2 bend., CCH_3 bend., OCH_3 bend.
1460	0.62	s	1465	sh	1465	sh	1465	sh	CH_2 bend., CCH_3 bend., OCH_3 bend.
1487	0.71	s	1483	s	1483	s	1483	m	CCH_3 bend.
2845	0.02	s	2845	w	2845	w	2842	w	OCH_3[a]
2893	0.04	s	2885	wsh	2885	sh	2890	wsh	OCH_3[a], CCH_3[a]
2938	0.03	s	2930	vwsh	2930	vwsh	2925	vwsh	CH_2, CCH_3 stretching vibrations
2950	0.06	vs	2953	s	2952	s	2953	s	CCH_3, OCH_3, CH_2 stretching vibrations
3002	0.42	s	2998	s	2998	s	3000	s	CCH_3, OCH_3 stretching vibrations
3031	–	sh	–		–		3030	vwsh	OCH_3[a]

[a] Harmonic or combination vibrations probably affected by the Fermi resonance

1436, 1456 and 1472 cm^{-1} in this range, both in the infrared and in the Raman spectrum (*Figures 1d, 2d, Table 4*): none of these bands is polarized in the Raman spectrum. All the three bands have been assigned by us to bending vibrations of the OCH_3 group. The frequencies and relative intensities of these bands correspond to those found by George[20] in the infrared and Raman spectra of CD_3COOCH_3 George's interpretation also suggests that the band at 1436 cm^{-1} in the infrared and Raman spectra of PMMA–CD_2–CCD_3 is in fact an in-plane deformation vibration with respect to the plane of the ester group. Such interpretation of the band is in agreement with temperature changes of the shape of this band[21].

Rocking vibrations. For isotactic and syndiotactic PMMA Nagai[2] assigned bands at 996 and 988 cm^{-1} to rocking vibrations of the ester CH_3 group, which interact with the stretching vibration of the COC group. In the infrared and Raman spectrum of PMMA–CD_2–CCD_3 (*Figures 1d, 2d*) we detected in this region one band at 972 cm^{-1}, which in agreement with Nagai[2] is assigned by us as the rocking vibration of the ester CH_3 group in PMMA–CD_2–CCD_3.

Effect of stereoregularity on the characteristic frequencies of the CH_2 and CH_3 group

Tables 2–4 show the effect of stereoregularity on the deformation and stretching vibrations of methyl and methylene groups in the infrared spectra of PMMA with a single undeuterated group. The results show that the wavenumbers and intensities of some bands corresponding to the characteristic vibrations of the CH_2, CH_3 and OCH_3 depend on the tacticity of the polymer (see, for example, the bands of CH_2 rocking vibrations in PMMA–CCD_3–OCD_3 (*Table 2*) and CCH_3 rocking and bending vibrations in PMMA–CD_2–OCD_3 (*Table 3*)). It can be seen that the C–CH_3 bending and stretching vibrations depend on the tacticity of PMMA more strongly than the respective vibrations of methylene or OCH_3 groups. In the infrared spectrum of PMMA, where the bands of the CH_2, C–CH_3 and OCH_3 groups overlap, the effect of tacticity is reflected only as a change in the ratio of intensities of some bands.

CONCLUSIONS

As can be seen in *Table 5*, all intensive bands of the deformation and stretching vibrations of the CH bonds in the infrared and Raman spectra of three deuterated polymers with one undeuterated group, i.e. PMMA–CCD_3–OCD_3, PMMA–CD_2–OCD_3 and PMMA–CD_2–CCD_3 appear in the infrared and Raman spectra of PMMA. Small shifts observed for some bands are obviously due to a simple overlapping of the bands. The fact that in the range of the deformation and stretching vibrations of methyl and methylene groups the spectrum of PMMA can be composed from the particular spectra of PMMA derivatives with a single undeuterated methyl or methylene group suggests that the CH_2, C–CH_3 and OCH_3 bending and stretching vibrations do not interact with each other, and that also their interactions with the other vibrations of PMMA is small. This allows interpretation valid for deuterated derivatives to be used in the interpretation of the spectrum of PMMA. This interpretation for deformation and stretching vibrations of the CH bonds is given in *Table 5*.

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