

Infrared Spectra of Stereoregular Polymethyl Methacrylate

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I. INTRODUCTION

The stereoregular polymerization of methyl methacrylate was reported in 1958 by Fox et al.,¹ Miller et al.,² and Watanabe et al.³ The crystal structure of isotactic polymethyl methacrylate (PMMA) was reported by Stroupe et al.,⁴ but the differences between the structures of isotactic and syndiotactic polymers have not been reported in detail.

Infrared spectra were used by Baumann et al.⁵ to measure the tacticity of the polymer, but further details concerning the nature of the absorption bands characteristic of stereoregular PMMA have not yet been reported.

In a previous communication,⁶ we have reported the preparation of three kinds of deuterated methyl methacrylates and the spectra of their stereoregular polymers. In the present work, the spectra of PMMA are considered and discussed on the results obtained from the spectral changes with deuteration and crystallization, and from the infrared dichroic measurements of stereoregular PMMA, $\left[\text{CH}_2\text{C}(\text{CH}_3)(\text{COOCH}_3) \right]_n$; PM- d_3 ,MA, $\left[\text{CH}_2\text{C}(\text{CH}_3)(\text{COOCD}_3) \right]_n$; PMMA- d_6 , $\left[\text{CD}_2\text{C}(\text{CD}_3)(\text{COOCH}_3) \right]_n$; and PM- d_3 ,MA- d_6 , $\left[\text{CD}_2\text{C}(\text{CD}_3)(\text{COOCD}_3) \right]_n$.

II. EXPERIMENTAL

Preparation of the deuterated monomers has been described previously,⁶ and the polymerization conditions are summarized in Table I.

Ethyl methacrylate (EMA) and *n*-butyl methacrylate (*n*-BMA), which are members of the methacrylic ester series, were polymerized stereoregularly by the same conditions as those used for MMA. Polymers prepared with the phenylmagnesium bromide catalyst are viscous substances and are not crystalline. Radical polymers are also not crystallizable. We call the former the isotactic and the latter the syndiotactic, based on the later discussion.

The infrared spectra were obtained with a Hitachi EPI-2 infrared spectrophotometer equipped with NaCl and KBr prisms and a Perkin-

TABLE I
Polymerization Conditions of PMMA Samples

Type of stereoregularity	Catalyst	Polymerization temp. °C.	Polymerization system
Atactic	KPS + NaHSO ₃	50	Emulsion polymerization
Isotactic	C ₆ H ₅ MgBr	20	Solution in toluene ^a
Syndiotactic	B(<i>i</i> -C ₄ H ₉) ₃	-30	Bulk polymerization ^b

^a Data of Watanabe et al.⁷

^b Data of Ashikari.⁸

Elmer Model 221 spectrophotometer equipped with grating, NaCl and CsBr prisms, a AgCl polarizer being used for the dichroic measurements.

The crystallization of samples was carried out as follows. The isotactic samples were stretched to an elongation of about 12 times in hot water at 60–65°C. and the atactic (or the syndiotactic) samples to 8 times at 80–85°C. and annealed for several days at that temperature, the samples being clamped so as to retain their length. The isotactic samples can readily be crystallized, but the atactic (or the syndiotactic) samples cannot. The x-ray diffraction pattern of isotactic PMMA, shown in Figure 1, is the same as that of type II polymer, reported by Fox et al.¹

The infrared spectra of isotactic and syndiotactic polymers (PMMA, PM-*d*₃,MA, PMMA-*d*₅, PM-*d*₃,MA-*d*₅, and PEMA) in the 4000–400 cm.⁻¹ region are shown in Figure 2. The polarized spectra of isotactic polymers are shown in Figures 3 and 4, and those of syndiotactic polymers in Figure 5.

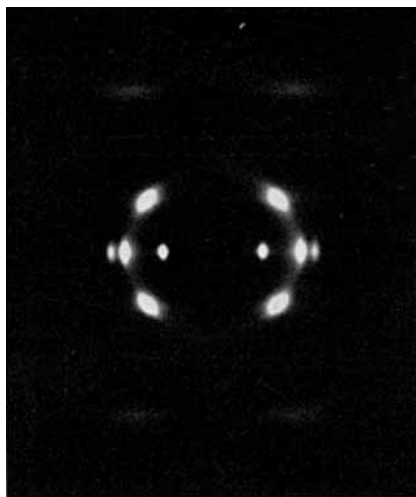


Fig. 1. X-ray diffraction photograph of crystallized isotactic PMMA.

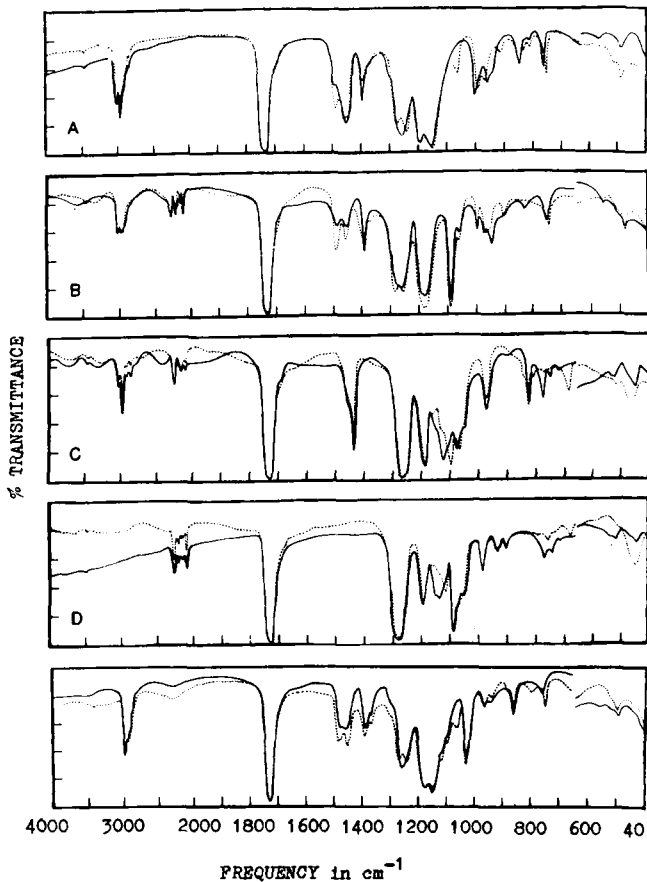


Fig. 2. Infrared spectra of isotactic and syndiotactic (A) PMMA, (B) PM- d_3 ,MA, (C) PMMA- d_6 , (D) PM- d_3 ,MA- d_6 , and (E) PEMA: (—) isotactic polymer; (---) syndiotactic polymer.

The frequency, relative intensity, polarization and the tentative assignment for the infrared spectra of stereoregular PMMA are listed in Table II, and the frequency, relative intensity, and polarization of deuterated polymers are listed in Tables III-V.

III. RESULTS AND DISCUSSION

As was reported in a previous communication,⁶ it may be noticed that qualitative differences between the spectra of atactic and syndiotactic PMMA were not observed. Baumann et al.⁵ reported quantitative differences between the spectra of these two polymers, and indicated a method for measuring the syndiotacticity of PMMA owing to the absorption intensities of the 9.45μ band, which is characteristic in the spectra of atactic and syndiotactic PMMA, but not in the spectra of isotactic

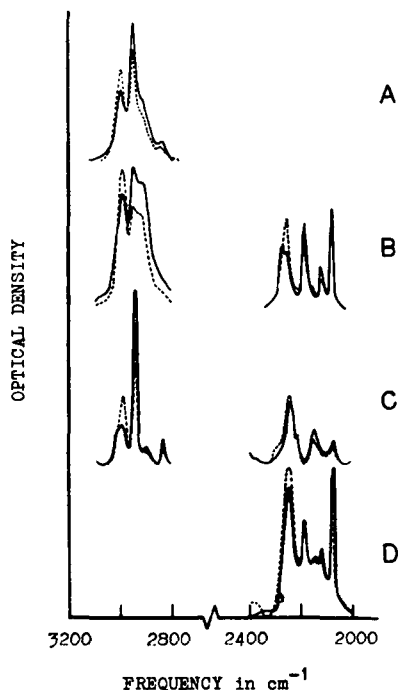


Fig. 3. Polarized spectra of isotactic (A) PMMA, (B) PM- d_3 ,MA, (C) PMMA- d_6 , and (D) PM- d_3 ,MA- d_6 in the C-H and C-D stretching region: (—) electric vector perpendicular to direction of stretch; (---) electric vector parallel to direction of stretch.

PMMA. In the spectra of deuterated polymers, these quantitative differences (and also qualitative differences) are not observed. For example, we compared the spectra of atactic PMMA- d_6 with that of the syndiotactic polymer, but there were no such differences.

On the other hand, Nishioka et al.⁹ reported a method for measuring the tacticity of PMMA by NMR spectroscopy. On the results of their works, it is demonstrated the syndiotactic polymers of our samples have 85% syndiotacticities and the atactic polymers 70% syndiotacticities. Such facts suggest that the polymers prepared with KPS + NaHSO₃ catalyst at 50°C. in emulsion may be considered to be polymers having syndiotactic structure. All polymers recorded as syndiotactic in this work are those prepared by the method mentioned above, unless otherwise indicated.

As it is very difficult to crystallize the syndiotactic polymers, their infrared dichroism is not very pronounced. On the contrary, the isotactic polymers are easily crystallized, and the intensity changes of several bands due to the crystallization can be observed, as reported previously.⁶ In the spectrum of isotactic PMMA, these intensity changes are not clearly observed, because of overlapping by other strong bands, but the spectra of isotactic PM- d_3 ,MA and PM- d_3 ,MA- d_6 show distinct intensity

changes. These bands are as follows; 1483, 1388, 1249, 825, and 759 cm^{-1} bands of PMMA, 1486, 1388, 1260, and 756 cm^{-1} bands of PM-d_3 -MA, 771 cm^{-1} band of PMMA-d_6 , and 1144 and 770 cm^{-1} bands of PM-d_3 , MA-d_6 . It is believed that these are groups of essentially four

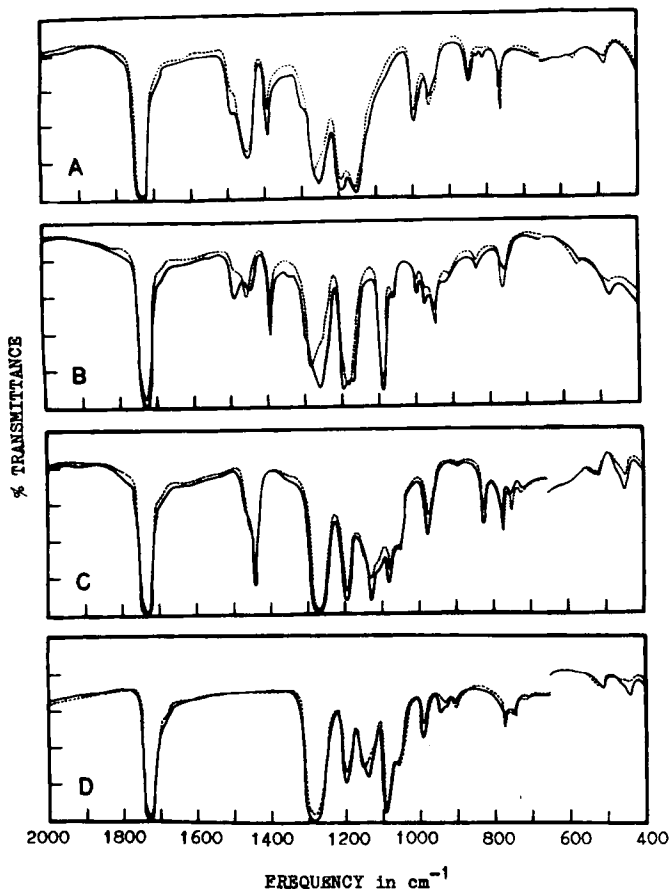


Fig. 4. Polarized spectra of isotactic (A) PMMA, (B) PM-d_3 ,MA, (C) PMMA-d_6 , and (D) PM-d_3 , MA-d_6 : (—) electric vector perpendicular to direction of stretch; (---) electric vector parallel to direction of stretch.

clusters of bands originating from the deformation vibrations of the $\alpha\text{-CH}_3$ group, the skeletal stretching vibrations, the stretching vibrations of C—C—O side chain, and the CH_2 rocking vibrations.

1. C—H and C—D Stretching Regions

It is noticed that the C—H and C—D stretching regions of isotactic polymers are the same as those of syndiotactic polymers with respect to the frequency, the relative intensity, and the polarized nature of the bands.

TABLE II
 Infrared Spectra of Stereoregular Polymethyl Methacrylate

Isotactic			Syndiotactic			Tentative assignment ^c
Fre- quency, cm. ⁻¹	Rela- tive inten- sity ^a	Polar- ization ^b	Fre- quency, cm. ⁻¹	Rela- tive inten- sity ^a	Polar- ization ^b	
3460	w	—	3460	w	—	2ν(C=O)
2995	m	π	2995	m	π	ν _s (CH ₃ —O) + ν _s (CH ₂)
2948	m	σ	2948	m	σ	ν _s (CH ₃ —O) + ν _s (α-CH ₃) + ν _s (α-CH ₃) + ν _s (CH ₂)
2920	sh	—	2920	sh	—	Combination band asso- ciated with ester CH ₃ group
2835	vw	σ	2835	vw	σ	Combination band asso- ciated with ester CH ₃ group
1730	vs	σ	1730	vs	σ	ν(C=O)
1483	w sh	σ	1483	m	σ	δ _s (α-CH ₃)
1465	s	—	1465	sh	—	δ _s (CH ₃ —O)
			1452	s	π	δ(CH ₂)
1445	s	σ				δ(CH ₂) overlapped with δ _s (CH ₃ —O)
			1438	s	σ	δ _s (CH ₃ —O)
1388	m	σ	1388	m	σ	δ _s (α-CH ₃)
1370	w sh	—	1370	w sh	—	δ _s (α-CH ₃) (amorphous)
1295	w sh	σ				
			1270	s	σ	
1260	s	π				} ν _s (C—C—O) coupled with ν(C—O) (see text)
1252	s	σ				
			1240	s	σ	} Skeletal stretching coupled with internal C—H deformation vibration (see text)
1190	vs	σ	1190	vs	σ	
1150	vs	σ	1150	vs	σ	
			1063	w	σ	Band arises from intra- molecular interaction (see text)

(continued)

In PMMA we can observe bands at 2995, 2948, and 2835 cm.⁻¹, with an additional inflection at 2920 cm.⁻¹. These bands are all associated with C—H vibrations, as the fully deuterated polymers show no absorption in this region.

On deuteration with the CH₂ and α-CH₃ groups, the intensities of the bands in this region are reduced, but the bands at 2995, 2948, and 2835 cm.⁻¹ are not shifted, and the 2920 cm.⁻¹ band appears clearly (Fig. 2).

On the other hand, the intensities of the bands at 2995 and 2948 cm.⁻¹ are found to decrease very much on deuteration of the ester CH₃ group, and the bands at 2920 and 2835 cm.⁻¹ disappear.

TABLE II (Continued)

Isotactic			Syndiotactic			Tentative assignment ^c
Fre- quency, cm. ⁻¹	Rela- tive inten- sity ^a	Polar- ization ^b	Fre- quency, cm. ⁻¹	Rela- tive inten- sity ^a	Polar- ization ^b	
996	m	σ	988	m	σ	} $\nu_s(\text{C—O—C})$ coupled with $\gamma(\text{CH}_3\text{—O})$ (see text)
			967	m	π	
951	m	π	910	w	—	$\gamma(\alpha\text{—CH}_3)$
842	w	σ	842	w	σ	
			828	vw	σ	
825	vw	—				
810	vw	σ	807	vw	—	
759	w	π				Skeletal stretching coupled with $\gamma(\text{CH}_2)$ (see text)
			749	w	π	$\gamma(\text{CH}_2)$ coupled with skeletal stretching (see text)
560	vw	π	554	vw	—	
			510	vw	—	
484	w	σ	484	w	σ	$\delta(\text{C—C—O})$

^a The following abbreviations have been used: s = strong, m = medium, w = weak, v = very, and sh = shoulder.

^b The symbol π indicates that the variation of dipole moment associated with the band is along the chain axis; σ indicates that the dipole moment changes are perpendicular to the chain axis.

^c The following abbreviations have been used: ν_a = asymmetric stretching, ν_s = symmetric stretching, δ_a = asymmetric bending, δ_s = symmetric bending, δ = bending, and γ = rocking.

Spectral behavior in this region on deuteration with several groups is similar to that of methyl acetate ($\text{CH}_3\text{COOCH}_3$), examined by Nolin and Jones.¹⁰ In the case of methyl acetate, they found the bands at 3026, 2995, 2957, 2905, and 2846, cm.^{-1} , and assigned the bands at 2957 and 2846 cm.^{-1} as the $\nu_a(\text{CH}_3)$ and the $\nu_s(\text{CH}_2)$ vibrations of the ester CH_3 group respectively, because of the band shift on deuteration and the general position of these vibrations, and they concluded that the other bands may be assigned as the overtone or the combination bands associated with the ester CH_3 group.

In the case of PMMA, the bands at 2995, 2948, 2920, and 2835 cm.^{-1} are all associated with the ester CH_3 group. The intensities of the former two are much larger than those of the latter two, so the former two may be fundamental vibrations of the ester CH_3 group. Moreover polarized spectra of isotactic polymers have distinct parallel and perpendicular dichroic nature, respectively.

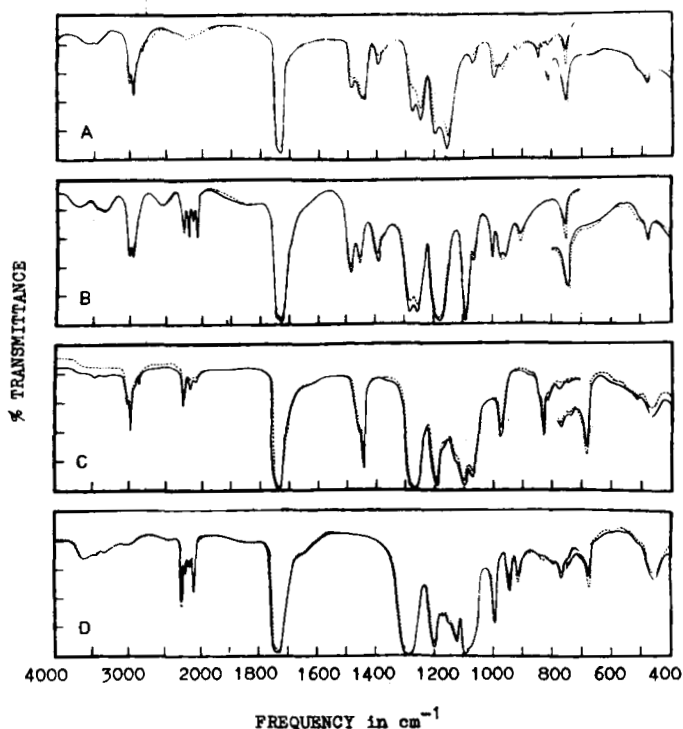


Fig. 5. Polarized spectra of syndiotactic (A) PMMA, (B) PM- d_3 ,MA, (C) PMMA- d_5 , and (D) PM- d_3 ,MA- d_5 : (—) electric vector perpendicular to direction of stretch; (---) electric vector parallel to direction of stretch.

Such facts are consistent with the assignment of the bands at 2995 and 2948 cm^{-1} as the $\nu_a(\text{CH}_3)$ and the $\nu_s(\text{CH}_3)$ vibrations of the ester CH_3 group, respectively. The other bands in the spectra of PMMA- d_5 may be associated with the overtone or the combination vibrations of the ester CH_3 group.

In PM- d_3 ,MA we observe one parallel band at 2995 cm^{-1} and two perpendicular bands at 2948 and 2915 cm^{-1} . As the theory of molecular vibration allows four fundamental C—H stretching vibrations in this region for an isolated PM- d_3 ,MA molecule, the overlapping of several bands must occur. The parallel band at 2995 cm^{-1} must shift to the band at 2240 cm^{-1} in the spectra of PMMA- d_5 . This band is probably assigned to the $\nu_a(\text{CH}_2)$ vibration. Because its frequency is higher than that expected for the $\nu_a(\text{CH}_2)$ mode of hydrocarbons, this assignment may rather be questionable, but its polarized nature is consistent with that of the rocking vibration of CH_2 group, mentioned later.

The perpendicular bands at 2948 and 2915 cm^{-1} are associated with the CH_2 and $\alpha\text{-CH}_3$ groups, and are separated at 2212, 2150, and 2075 cm^{-1} in the spectra of PMMA- d_5 . The intensities of the bands associated with the stretching vibrations of the CH_3 group attached to the carbon

atom are very much lower than those of the CH_3 group attached to the oxygen atom. As this conclusion is also consistent with the behavior of the C—D stretching bands of the CD_3 group,¹⁰ the shoulder at 2212 cm.^{-1} and the weak band at 2075 cm.^{-1} may be assigned as the $\nu_s(\alpha\text{-CD}_3)$ and

TABLE III
Infrared Spectra of Stereoregular Polymethyl- d_3 Methacrylate

Isotactic			Syndiotactic		
Frequency, cm. ⁻¹	Relative intensity ^a	Polar- ization ^b	Frequency, cm. ⁻¹	Relative intensity ^a	Polar- ization ^b
2995	m	π	2995	m	π
2948	m	σ	2948	m	σ
2915	sh	σ	2915	sh	σ
2270	sh	σ	2270	sh	σ
2254	m	π	2254	m	π
2185	m	σ	2185	m	σ
2120	m	σ	2120	m	σ
2080	m	σ	2080	m	σ
1730	vs	σ	1730	vs	σ
1486	m	σ	1483	s	σ
1450	m	π	1450	s	π
1442	m	σ			
1388	s	σ	1388	m	σ
1370	vw	—	1370	w sh	—
			1280	s	σ
1276	s	π			
1259	s	σ			
			1251	s	σ
1194	vs	σ			
1177	vs	π	1178	vs	σ
1167	vs	σ			
1085	vs	σ	1088	vs	σ
1054	vw	π	1054	vw	—
994	w	σ	994	w	σ
971	w	σ			
946	m	π	965	m	π
			950	sh	$\pi?$
903	sh	π	903	w	π
832	w	σ			
756	w	π			
			746	w	π
556	vw	$\pi?$	554	vw	—
			504	w sh	—
477	w	σ	477	w	σ

^a Abbreviations as given in Table II.

$\nu_s(\alpha\text{-CD}_3)$ vibrations, respectively. The band at 2150 cm.^{-1} is tentatively assigned to the $\nu_s(\text{CD}_2)$ vibration. As the polarized nature of this absorption is inconsistent with that of $\delta(\text{CH}_2)$ vibration, this assignment is rather questionable.

TABLE IV
Infrared Spectra of Stereoregular Polymethyl Methacrylate-*d*₆

Isotactic			Syndiotactic		
Frequency, cm. ⁻¹	Relative intensity ^a	Polar- ization ^a	Frequency, cm. ⁻¹	Relative intensity ^a	Polar- ization ^a
2995	m	π	2995	m	π
2948	m	σ	2948	m	σ
2920	sh	—	2920	sh	—
2835	w	σ	2835	w	σ
2240	m	π	2240	m	π
2212	w sh	—	2212	w sh	—
2150	w	σ	2150	w	σ
2075	w	σ	2075	w	σ
1730	vs	σ	1730	vs	σ
1460	w sh	—	1460	w sh	—
1438	s	σ	1438	s	σ
1265	vs	σ	1265	vs	σ
1190	s	σ	1188	s	σ
1124	s	σ			
			1160	sh	—
1150	sh	σ			
1102	sh	σ			
1074	s	σ	1096	s	σ
			1067	s	σ
			1050	w sh	—
1044	w sh	—			
972	m	σ	972	m	σ
895	vw	—			
			880	vw	—
855	w sh	—			
			835	w sh	—
823	m	σ	823	m	σ
			806	w	σ
771	m	π			
			764	vw	σ
742	vw	π			
			734	vw	—
717	vw	π			
			677	w	π
530	vw	π			
520	vw	$\sigma?$			
			512	vw	$\sigma?$
450	w	σ	465	w	σ

^a Abbreviations as given in Table II.

2. C—H Bending Vibrations

In the spectrum of isotactic PMMA, we have observed bands at 1483, 1445, and 1388 cm.⁻¹ and a weak shoulder at 1465 cm.⁻¹. Syndiotactic PMMA exhibits bands at 1483, 1452, 1438, 1388, and 1370 cm.⁻¹ and a weak shoulder at 1465 cm.⁻¹. These bands disappear in the spectra of

TABLE V
Infrared Spectra of Stereoregular Polymethyl- d_3 Methacrylate- d_6

Isotactic			Syndiotactic		
Frequency, cm. ⁻¹	Relative intensity ^a	Polar- ization ^a	Frequency, cm. ⁻¹	Relative intensity ^a	Polar- ization ^a
2250	m	π	2250	m	π
2212	w	—	2212	w	—
2185	m	σ	2185	m	σ
2150	w	σ	2150	w	σ
2120	w	σ	2120	w	σ
2080	m	σ	2080	m	σ
1730	vs	σ	1730	vs	σ
1275	vs	σ	1275	vs	σ
1192	s	σ	1192	s	σ
			1162	w sh	σ
1149	sh	π			
			1135	sh	σ
			1113	s	σ
1085	vs	σ	1087	vs	σ
			1067	sh	—
1050	sh	—	1052	sh	—
987	m	σ	987	m	σ
940	w	σ			
			932	w	σ
925	w	σ			
905	w	π	905	w	π
			830	vw	—
			778	vw	$\sigma?$
770	w	π			
			756	w	σ
746	vw	π			
			736	vw	$\pi?$
715	vw	π			
			674	w	π
530	vw	$\pi?$			
514	vw	—	510	vw	—
443	w	σ	450	w	σ

^a Abbreviations as given in Table II.

PM- d_3 ,MA, and the corresponding C—D vibration of the former is recognized at about 1085 cm.⁻¹. The reasonable value of 1.323 is found for the ratio of the C—H vibrational frequency to that of its corresponding C—D mode. Therefore the bands at 1438 and 1460 cm.⁻¹ in the spectra of PMMA- d_5 can certainly be assigned to the $\delta_s(\text{CH}_3)$ and $\delta_a(\text{CH}_3)$ vibrations of the ester CH_3 group, respectively.

The intensity of the $\delta_s(\text{CH}_3)$ vibration of the ester CH_3 group is much larger than that of the $\delta_a(\text{CH}_3)$ vibration. This is consistent with the fact found for the corresponding vibrations of methyl acetate.¹⁰

In the spectra of PM- d_3 ,MA, we have observed one parallel band at 1450 cm.⁻¹ and two perpendicular bands near 1483 and 1388 cm.⁻¹.

These bands all disappeared on the deuteration of the CH_2 and $\alpha\text{-CH}_3$ groups but not on the deuteration of the ester CH_3 group. The two perpendicular bands near 1483 and 1388 cm.^{-1} can be assigned to the $\delta_a(\alpha\text{-CH}_3)$ and $\delta_s(\alpha\text{-CH}_3)$ vibrations, respectively. The parallel band at 1450 cm.^{-1} is certainly the frequency of the $\delta(\text{CH}_2)$ vibration.

As reported previously,⁶ the intensity of the band at 1483 cm.^{-1} is lower in the spectrum of isotactic PMMA than that of the syndiotactic polymer, and the intensity of the band at 1388 cm.^{-1} is higher and sharper in the spectrum of isotactic PMMA than that of syndiotactic polymer. These bands in the spectrum of isotactic PMMA increase somewhat in intensity owing to the crystallization. These facts are also recognized in the spectrum of isotactic PM- d_3 ,MA.

The relationship between the intensity of band and the molecular structure is in general not known, but the facts mentioned above show that the sterical configuration of polymer chain affects sensitively the bending vibrations of the $\alpha\text{-CH}_3$ group, but not the CH_2 or the ester CH_3 groups.

The weak band at 1370 cm.^{-1} in the spectrum of syndiotactic PMMA may be the amorphous band associated with the $\delta_s(\alpha\text{-CH}_3)$ vibration. The corresponding band in the spectrum of isotactic polymer is observed at the same frequency, and this disappears on crystallization. The syndiotactic polymer can not readily crystallize, and the intensity of this absorption must still remain as the weak shoulder in the spectrum of oriented polymer.

3. Absorption in the $1300\text{--}1200\text{ cm.}^{-1}$ Region

Carboxylic esters have characteristic absorption in this region. Belamy¹¹ reported that the bands were much less stable than the corresponding carbonyl vibration, and they were sensitive to changes in the mass and nature of the attached groups. He also assigned them as C—O stretching vibrations, and emphasized that it was not to be expected that the bands would arise from a pure C—O stretching motion, and the movements of other atoms were undoubtedly involved.

In methyl acetate and its deuterated analogues and many steroids, Jones et al.¹² assigned this characteristic band as the $\nu_a(\text{C—C—O})$ vibration. Kawasaki et al.¹³ assigned the band at about 1250 cm.^{-1} in polybutyl acrylates as the $\nu_a(\text{C—O—C})$ vibration.

In the spectra of isotactic and syndiotactic PMMA, strong bands are observed in this region. They shift progressively to a higher frequency with increasing deuterium contents in the monomer unit. This is consistent with the observation in the spectra of methyl acetate.¹⁰

The spectra of MMA and its deuterated analogues in gas state have exhibited corresponding bands in the $1330\text{--}1280\text{ cm.}^{-1}$ region. The frequencies of these bands are about 50 cm.^{-1} higher than those of the corresponding polymer bands. These data are summarized in Table VI.

It must be expected that MMA has conjugation between the $\text{C}=\text{C}$ bond and the $\text{C}=\text{O}$ bond. As a result of polymerization the conjugation

TABLE VI
Displacement of C—C—O Stretching Frequencies of Polymers and Monomers
with Deuteration

Polymer	Frequency, cm. ⁻¹	Monomer	Frequency, cm. ⁻¹
PMMA			
Isotactic	1249	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C} \\ \\ \text{COOCH}_3 \end{array}$	1327, 1308
Syndiotactic	1270, 1240		
PM- <i>d</i> ₃ ,MA			
Isotactic	1260	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C} \\ \\ \text{COOCD}_3 \end{array}$	1330, 1315
Syndiotactic	1280, 1251		
PMMA- <i>d</i> ₆			
Isotactic	1265	$\begin{array}{c} \text{CD}_2 \\ \\ \text{CD}_2=\text{C} \\ \\ \text{COOCH}_3 \end{array}$	1315, 1280
Syndiotactic	1265		
PM- <i>d</i> ₃ ,MA- <i>d</i> ₆			
Isotactic	1275	$\begin{array}{c} \text{CD}_3 \\ \\ \text{CD}_2=\text{C} \\ \\ \text{COOCD}_3 \end{array}$	1315, 1287
Syndiotactic	1275		

is destroyed, and there will be some decrease in the force constant of the C—C stretching vibration of bond III (see Fig. 6). If this is true, there is some contribution to the bands from the C—C stretching vibration of bond III.

The behavior of the bands on deuteration and polymerization suggests the bands arise from the C—C—O stretching vibration. Also the contribution from the C—O stretching vibration of the alcohol residue can not be neglected.

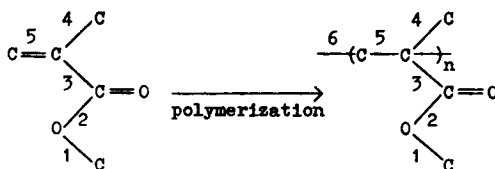


Fig. 6. Bond notation.

In the spectra of syndiotactic PMMA, PM-*d*₃,MA, and PEMA, two strong bands are observed near 1270 and 1240 cm.⁻¹. These two bands are both perpendicularly polarized. On the other hand, the corresponding isotactic polymers have only one strong absorption in this region. These bands in isotactic polymers are separated into two absorption maxima in

the polarized spectra; the one at higher frequency shows parallel dichroism, and the other at lower frequency perpendicular dichroism.

Bands clearly corresponding with these are observed at 1265 and 1275 cm.^{-1} in the spectra of PMMA- d_6 and PN- d_3 ,MA- d_6 , respectively, and they are not separated in isotactic and syndiotactic polymers even in the polarized spectra, and show weak perpendicular dichroism.

The differences of the bands in frequency and polarized nature between isotactic and syndiotactic polymers indicate that the C—C—O group in each polymer have different sterical configurations.

4. Skeletal Vibrations

The strong bands at 1190 and 1150 cm.^{-1} observed in the spectra of PMMA are characteristic bands of carboxylic esters similar to the bands in the 1300–1200 cm.^{-1} region. These bands are perpendicularly polarized

TABLE VII
Displacement of Characteristic Absorptions of Esters with Deuteration

	Frequency, cm.^{-1}	
CH ₃ (CH ₂) ₉ CH ₂ COOCH ₃	1248	1196, 1169
CH ₃ (CH ₂) ₉ CD ₂ COOCH ₃	1252	
CH ₃ (CH ₂) ₉ CH ₂ COOCD ₃	1256	1196
CH ₃ (CH ₂) ₉ CD ₂ COOCD ₃	1275	
CD ₃ (CH ₂) ₉ CH ₂ COOCH ₃	1246	1192, 1167
PMMA		
Isotactic	1260, 1252	1190, 1150
Syndiotactic	1270, 1240	1190, 1150
PM- d_3 ,MA		
Isotactic	1276, 1259	1178
Syndiotactic	1280, 1251	1178
PMMA- d_6		
Isotactic	1265	1190, 1124
Syndiotactic	1265	1190, 1096
PM- d_3 ,MA- d_6		
Isotactic	1275	1192, 1149, 1135
Syndiotactic	1275	1192, 1113

TABLE VIII
Displacement of C—C—O Stretching and Deformation Vibrations with Deuteration

	Frequency, cm.^{-1}					
	Isotactic			Syndiotactic		
PMMA	(1260) ^a	(1252)	484	1270	1240	484
		1249				
PM- d_3 ,MA	(1276)	(1259)	477	1280	1251	477
		1260				
PMMA- d_6		1265	450		1265	465
PM- d_3 ,MA- d_6		1275	443		1275	450

^a The values in parentheses are those observed in polarized spectra.

in the spectra of isotactic and syndiotactic polymers. In the spectra of PEMA, these bands are observed at 1175 and 1145 cm^{-1} and also show perpendicular polarization.

On deuteration of several groups, the 1190 cm^{-1} band seems to remain essentially unchanged. This behavior is consistent with that of the band near 1190 cm^{-1} of methyl laurate,¹⁴ as shown in Table VII.

On the other hand, the 1150 cm^{-1} band shows complex changes on deuteration as shown in Table VII.

These bands may be associated with the mixed vibrations of the following modes: skeletal stretching, CH_2 twisting, and the other internal carbon-hydrogen deformation modes. The more specific assignments of these bands to particular modes of vibrations are difficult because of their complex behavior on deuteration.

The band at 484 cm^{-1} in the spectra of isotactic and syndiotactic PMMA may be assigned to the C—C—O deformation vibration (Table VIII). This absorption is shifted progressively to a lower frequency with increasing deuterium content of the monomer unit.

5. CH_2 and CH_3 Rocking Vibrations

In the spectra of isotactic and syndiotactic PMMA, a perpendicular band is observed at 996 and 988 cm^{-1} , respectively. The behavior of this absorption on deuteration is very complex, and the band corresponding to this absorption can not be assigned for the deuterated species. However, it may tentatively be assigned to the coupled vibration of C—O—C symmetric stretching and $\gamma(\text{CH}_3)$ vibration of the ester CH_3 group. It is reasonable to consider that these vibrations are easily coupled with each other.

In the spectra of isotactic and syndiotactic PMMA, a parallel band is observed at 951 and 967 cm^{-1} , respectively. This band is not affected both in isotactic and syndiotactic polymers on deuteration of the ester CH_3 group and is observed at 946 and 965 cm^{-1} in isotactic and syndiotactic PM- d_3 ,MA, respectively. As this band is not observed in the spectra of PMMA- d_6 and PM- d_3 ,MA- d_6 , it is reasonable to assign the band to the $\gamma(\alpha\text{-CH}_3)$ vibration.

On crystallization, the isotactic band increases somewhat in intensity. Such behavior is consistent with that found for the deformation vibrations of the bands originating from the $\alpha\text{-CH}_3$ group.

The bands near 750 cm^{-1} in the spectra of isotactic and syndiotactic PMMA are both parallelly polarized. It is observed that the isotactic bands are always higher in frequency than the corresponding syndiotactic bands in the spectra of PMMA, PEMA, and P n -BMA, as shown in Figure 7. Therefore it seems reasonable that their frequencies reflect the configurational regularity of the methacrylate polymer series.

In the spectra of syndiotactic polymers, it is observed that the band shifts to 677 cm^{-1} on deuteration with CH_2 and $\alpha\text{-CH}_3$ groups. As seen in Figure 2, the deuteration of the ester CH_3 group of PMMA and

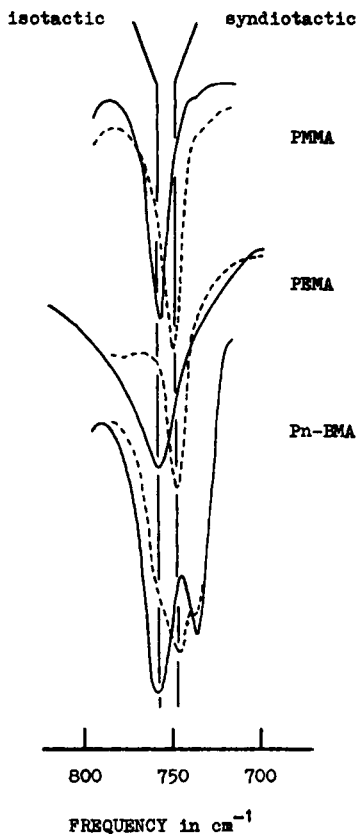


Fig. 7. Stereoregularity-sensitive bands near 750 cm.^{-1} .

PMMA- d_5 does not affect the band position, and the bands are observed at 746 and 674 cm.^{-1} in the spectra of PM- d_3 ,MA and PM- d_3 ,MA- d_5 , respectively. The ratios of 749 to 677 cm.^{-1} and 746 to 674 cm.^{-1} are both 1.107 , and these values are much smaller than those estimated by Krimm.¹⁵ These facts indicate that the bands are not pure γCH_2 vibration, but are coupled with skeletal stretching vibration.

In the spectra of isotactic polymers, the 759 cm.^{-1} band is not shifted on deuteration of the ester CH_3 group. On deuteration of the CH_2 and $\alpha\text{-CH}_3$ groups, the band disappears, but a band corresponding is not observed at the expected region.

As already mentioned, it is observed that the bands near 750 cm.^{-1} of PMMA and PM- d_3 ,MA increase in intensity owing to the crystallization. In the spectra of isotactic PMMA- d_5 and PM- d_3 ,MA- d_5 , a variation in intensity on crystallization is also observed for the bands at 771 and 770 cm.^{-1} , respectively. As these bands have parallel polarization, it seems probable that these bands correspond to the 759 cm.^{-1} band of isotactic PMMA.

A shift to higher frequency on deuteration is not expected for the pure C—H vibration, but it is expected for the coupled vibration. If the band arises from the skeletal stretching vibration coupled with $\gamma(\text{CH}_2)$ vibration, the one component originating mainly from the skeletal vibration may shift to a higher frequency, and the other originating from the C—H vibration to a lower frequency. It seems reasonable that the 759 cm.^{-1} band of isotactic PMMA is assigned to the skeletal C—C stretching vibration coupled with $\gamma(\text{CH}_2)$ vibration. Unlike the syndiotactic band, the isotactic band is mainly attributed to the skeletal vibrations.

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Synopsis

Stereospecific polymerization of deuterated methyl methacrylates, $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCD}_3$, $\text{CD}_2=\text{C}(\text{CD}_3)\text{COOCH}_3$, and $\text{CD}_2=\text{C}(\text{CD}_3)\text{COOCD}_3$, which were prepared by the acetone-cyanohydrin method, were carried out. From the polarized infrared study of polymethyl methacrylate and its deuterated analogue, the spectra of stereoregular polymethyl methacrylates were tentatively assigned in the $4000\text{--}400\text{ cm.}^{-1}$ region. The isotactic polymers are easily crystallized and show intensity variations of bands. These bands originate mainly from the deformation vibrations of the $\alpha\text{-CH}_2$ group, the stretching vibrations of the C—C—O side chain, and the skeletal stretching vibration coupled with CH_2 rocking vibration.

Résumé

On a effectué des polymerisations stereospecifiques des methacrylates de methyle deutérés, $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCD}_3$, $\text{CD}_2=\text{C}(\text{CD}_3)\text{COOCH}_3$ et $\text{CD}_2=\text{C}(\text{CD}_3)\text{COO-CD}_3$, par la methode d'aceton-cyanhydrin. Les spectres infrarouges dans la region 4000–400 cm^{-1} du polyméthacrylate de methyle stereoregulier sont interpretées par des etudes de l'infrarouge polarisée sur le polymethacrylate de methyle et ses analogues deutérés. Les polymers isotactiques cristallisent facilement et ils demontrent des variations des intensités des bandes. Les bandes sont principalement originaires des vibrations de l'elongation de la groupe $\alpha\text{-CH}_3$, des vibrations de l'elongation de squellete couplée avec la vibration de balancement de CH_2 .

Zusammenfassung

Stereospezifische Polymerisation von deuterierten Methyl Methacrylaten, $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCD}_3$, $\text{CD}_2=\text{C}(\text{CD}_3)\text{COOCH}_3$ und $\text{CD}_2=\text{C}(\text{CD}_3)\text{COOCD}_3$, die wurden mittels der Azeton-Cyanhydrinmethode dargestellt, wurde durchgeführt. Aus den polarisierten Infrarotmessungen über Polymethylmethacrylaten und die entsprechenden deuterierten wurden die Spektren der stereoregularen Verbindungen im Bereich von 4000–400 cm^{-1} vorläufig gedeutet. Die isotaktische Polymeren sind leicht kristallisiert und zeigen untereinander Intensitätsdifferenz der Infrarotbanden. Die Banden sind vornehmlich daraus zu entstehen, die Deformierungsschwingung der $\alpha\text{-CH}_3$ Gruppe, die Dehnungsschwingung der C—C—O Seitenkette und die Skelett-dehnungsschwingung gekuppelt mit CH_2 -Rockingschwingung.

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