

**MODEL COMPOUNDS OF POLY(METHYL METHACRYLATE).
CONFORMATIONAL STRUCTURE OF METHYL
3-METHOXY-2-METHYLPROPIONATE**

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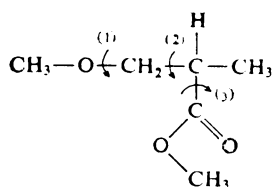
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By analysis of ^1H and ^{13}C NMR spectra, and of infrared and Raman spectra of methyl 3-methoxy-2-methylpropionate, the formation of conformers generated by rotation about the bonds $\text{CH}_3\text{O}-\text{CH}_2$, CH_2-CH and $\text{C}-\text{C}=\text{O}$ was studied. The structure of the most highly populated conformer is proposed.

In spite of considerable effort, conformational forms of poly(methyl methacrylate) (PMMA) and of its oligomers formed during anionic polymerization have not been unambiguously determined so far. Using model molecules which can form conformational structures occurring in PMMA oligomers we are trying¹⁻⁴ to refine the procedures of conformational analysis based on NMR and vibrational spectra, and to find the rules of formation of rotational isomers in these molecules.

One of the simplest models of this group of compounds is methyl 3-methoxy-2-methylpropionate (*I*).



I

Assuming that the ester group has a planar structure with *syn* orientation of the carbonyl with respect to the CH_3 group^{5,6} the compound *I*, similarly as the PMMA oligomers, can generate conformers by rotation about the bonds $\text{O}-\text{CH}_2$ (*1*), CH_2-C (*2*) and $\text{C}-\text{C}=\text{O}$ (*3*). In the staggered approximation, rotation about the bond *1* generates the structures \bar{t} , \bar{g}^+ and \bar{g}^- (Fig. 1*a*), rotation about the bond *2* the structures *t*, g^+ and g^- (Fig. 1*b*) and rotation about the bond *3* the structures

syn-CH₃, *syn*-H, *syn*-CH₂, *anti*-CH₃, *anti*-CH₂ and *anti*-H (Fig. 1c). Rotation about the bonds 1 and 2 can be followed by ¹³C and ¹H NMR spectra. In vibrational spectra, conformers generated by rotation about all three bonds can in principle be observed. Therefore we have tried to determine the complete conformational structure of this compound by combination of NMR and vibrational spectroscopic methods. At this we have made use of previously studied vibrational spectra of 1-methoxy-2-methylpropane³ (*II*) as model of conformational structures generated by rotation about the bonds 1 and 2, and of methyl 2-methylpropanoate⁷ (*III*) as model of structures generated by rotation about bond 3.

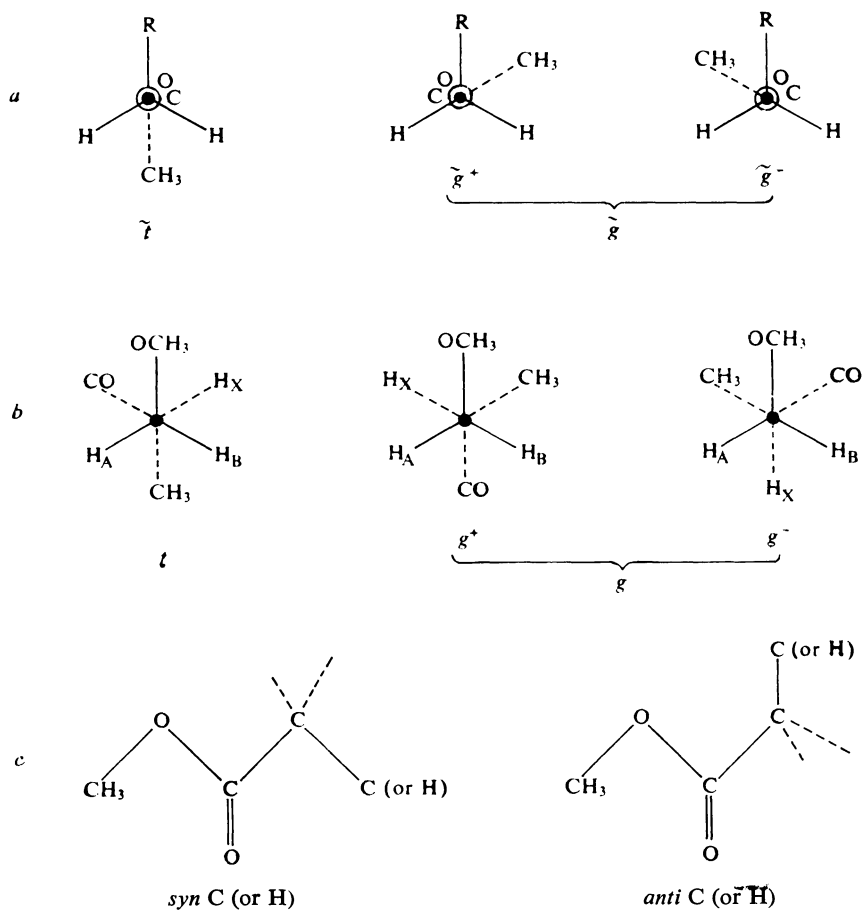


FIG. 1

Isomers of *I* formed by rotation about the bond O-CH₂ (a); CH₂-C (b); C-C=O (c)

EXPERIMENTAL

Methyl 3-methoxy-2-methylpropionate (*I*), together with other anionic oligomers, was prepared by reaction of sodium methanolate with methyl methacrylate in methanol solution, in the presence of 2,4,6-tris(dimethylaminomethyl)phenol as inhibitor of radical polymerization⁸. Rectification of the crude product on a Perkin-Elmer column PE 200 (200 TP) yielded the chromatographically pure product (b.p. 419.5 K, $n_D^{20} = 1.4053$, $d_{25} = 0.97185 \text{ g cm}^{-3}$; lit.⁸ b.p. 420.2 K, $n_D = 1.4055$).

¹H NMR spectra were measured on the PS-100 (JEOL) spectrometer at 100 MHz. In variable temperature measurements, temperature values were calibrated by means of methanol and ethylene glycol chemical shifts⁹. ¹³C NMR spectra were measured on the XL-200 (Varian) spectrometer at 50 MHz, with a digital resolution of 0.3 Hz and pulse repetition rate 5.2s, in the gated decoupling mode preserving full coupling, with NOE. Resolution enhancement by exponential weighting and apodization was used to achieve resolution better than 1 Hz in fully coupled ¹³C NMR spectra. Samples for NMR measurements were prepared as solutions in CDCl₃ (approximately 50% *v/v* in ¹³C NMR; 10% *v/v* with hexamethyldisilane as internal standard in ¹H NMR). Measurements of neat samples gave poorer resolution, but qualitatively similar results were obtained.

Raman spectra of the neat samples were measured on the spectrometer Coderg LRDH-800 connected on-line with the multichannel analyzer TN-11 in the Tracor system. Spectra were excited by the line 514.5 nm of the argon laser CR-3 (Coherent Radiation). Spectra were measured in the 90° arrangement and were usually obtained by accumulation of several scans. Low-temperature spectra were measured in a cell with an evacuated jacket.

Infrared spectra of the neat samples were measured on the spectrometer Perkin-Elmer 580 B connected on-line with the multichannel analyzer Tracon Northern TN-4000, and on the spectrometer Perkin-Elmer 621. All spectra were treated by the TN-4000 analyzer.

RESULTS AND DISCUSSION

NMR Spectra

By rotation about the bond O—CH₂, *I* can form isomers which in the staggered approximation are shown in Fig. 1a. The conformational structure on bond *I* was determined, similarly as in previous papers on model ethers^{2,3} from the value of the vicinal carbon-proton coupling constant, ³*J*_{CH₃OCH₂}, measured in the fully coupled ¹³C NMR spectra (Fig. 2) and the relation

$$x_{\bar{\gamma}} = \frac{(J_{\bar{\gamma}} + J_{\bar{\delta}}) - 2^3 J_{\text{CH}_3\text{OCH}_2}}{(J_{\bar{\gamma}} - J_{\bar{\delta}})}$$

with $10.4 < J_{\bar{\gamma}} < 11.1 \text{ Hz}$ and $2.2 < J_{\bar{\delta}} < 2.6 \text{ Hz}$ (ref.³).

The found values of ³*J*_{CH₃OCH₂} equal to 6.2 Hz (298 K) and 6.5 Hz (333 K) yield $0.84 < x_{\bar{\gamma}} < 0.87$ and $0.80 < x_{\bar{\gamma}} < 0.83$, respectively. These values are practically identical to those found³ for the model ether *II*.

Conformational structure generated by rotation about the bond $\text{CH}_2\text{—C}$ in the staggered approximation is shown in Fig. 1*b*. Conformer populations on bond 2 can be determined *a*) from the vicinal ${}^3J_{\text{HH}}$ coupling constants $J_{\text{AX}}, J_{\text{BX}}$ obtained by analysis of the methylene proton band in proton NMR spectra (Fig. 3); *b*) from vicinal ${}^3J_{\text{CH}_3\text{CHCH}_2} = {}^3J_{\text{CH}}$ carbon–proton coupling constant measured in the fully coupled ${}^{13}\text{C}$ NMR spectrum (Fig. 2).

${}^1\text{H}$ NMR spectra were measured in the range 333 to 218 K. The methylene proton band was analyzed as the AB part of an ABX system¹⁰. From the two AB patterns, the sum ($J_{\text{AX}} + J_{\text{BX}}$) and the geminal coupling J_{AB} could be directly read off. The difference ($J_{\text{AX}} - J_{\text{BX}}$), together with the shift δ_{AB} , were calculated from the line spacings with the use of the primarily determined J_{AB} . Conformer populations $x_{\text{t}}, x_{\text{g}}^+, x_{\text{g}}^-$ can be derived from the ${}^1\text{H}$ NMR spectral parameters by means of the relations

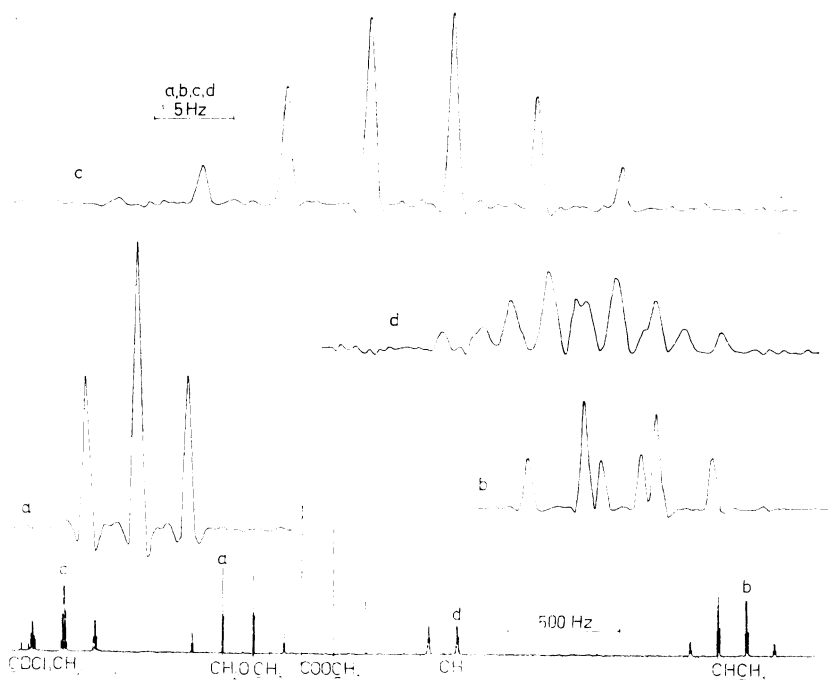


FIG. 2
 ${}^{13}\text{C}$ NMR spectra of *I*, 50% *v/v* in CDCl_3 , 333 K, fully coupled, with NOE

$$\begin{aligned}
 J_{AX} + J_{BX} &= (x_t + x_g^+)(J_T^H + J_G^H) + x_g^-(2J_G^H), \\
 J_{AX} - J_{BX} &= (x_t - x_g^+)(J_T^H - J_G^H), \\
 x_g^- &= \frac{(J_T^H + J_G^H) - (J_{AX} + J_{BX})}{J_T^H - J_G^H}; \quad x_t - x_g^+ = \frac{(J_{AX} - J_{BX})}{J_T^H - J_G^H}.
 \end{aligned}
 \tag{1}$$

By change of assignment of the protons H_A, H_B in Fig. 1b, the values of J_{AX}, J_{BX} in the structures t and g^+ are interchanged. The value x_g^- obtained from the relations (1) is independent of the H_A, H_B assignment, $x_t - x_g^+$ changes sign with change of assignment. For the coupling parameters J_T^H, J_G^H (corresponding to the dihedral angles 180° and 60° , respectively) the ranges $11.4 < J_T^H < 12.2$ Hz, and $2.85 >$

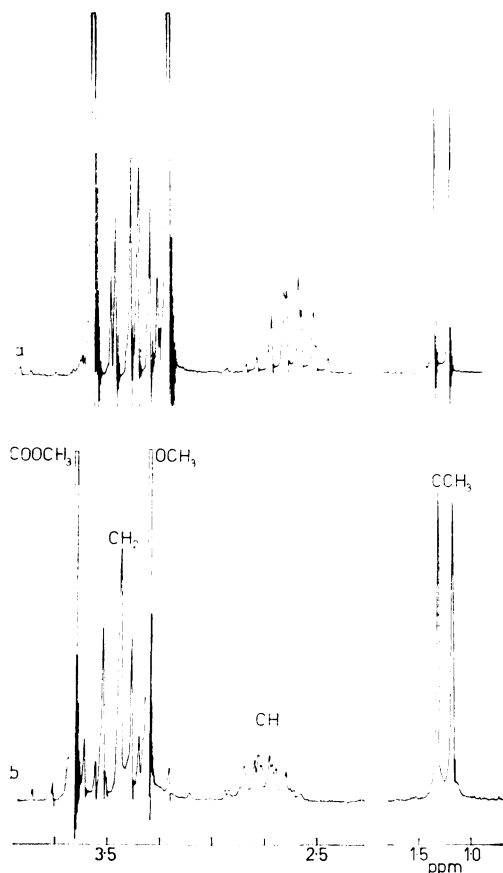


FIG. 3

^1H NMR spectra of I, 10% v/v in CDCl_3 a 331 K; b 219 K

$> J_G^H > 2.44$ Hz were derived for *II* in ref.³. For the present calculation, the mean of these ranges was used, with $J_T^H = 11.8$ Hz and $J_G^H = 2.65$ Hz; the extremes of the ranges yielded conformer mole fractions differing by ± 0.01 from the mean. The resulting conformer populations, based on the assignment shown in Fig. 1b are summarized in Table I. Here x_t appears as the most abundant conformer, and its population decreases with increasing temperature.

The choice of the assignment of H_A, H_B shown in Fig. 1b can be verified from ^{13}C NMR spectra. Therefore ^{13}C NMR spectra were measured at room temperature and at 333 K. The fine structure of the components of the CCH_3 quartet was analyzed as the C band of an $H_A H_B H_X C$ system^{10,11}. As seen in Fig. 2, this C band has the appearance of a pair of triplets. The pair spacing of 4.5 Hz is independent of temperature and we assume that it corresponds to the ${}^2J_{\text{CH}}$ coupling, and that the spacing of the outer components of each triplet corresponds to the sum ${}^3J_{\text{CHA}} + {}^3J_{\text{CHB}}$. The lack of splitting of the central components of the triplets indicates that ${}^3J_{\text{CHA}} \approx {}^3J_{\text{CHB}}$. Conformer populations are related to the ${}^3J_{\text{CH}}$ couplings by means of the relations

$$\begin{aligned} J_{\text{CHA}} &= x_t J_G^C + x_g^+ J_T^C + x_g^- J_G^C, \\ J_{\text{CHB}} &= x_t J_G^C + x_g^+ J_G^C + x_g^- J_T^C, \\ x_t &= \frac{(J_T^C + J_G^C) - (J_{\text{CHA}} + J_{\text{CHB}})}{J_T^C - J_G^C}. \end{aligned} \quad (2)$$

Similarly as in our previous studies³, the ${}^3J_{\text{CH}}$ coupling parameters J_T^C, J_G^C were derived for $4J_G^C < J_T^C < 4.4J_G^C$ Hz, and considering the substituent parameters

TABLE I

${}^1\text{H}$ NMR coupling parameters of *I* and population of isomers formed by rotation about the bond CH_2-C

<i>T</i> K	J_{AB} Hz	$J_{\text{AX}} + J_{\text{BX}}$ Hz	$J_{\text{AX}} - J_{\text{BX}}$ Hz	x_t	x_g^+	x_g^-
331	9.2	12.7	1.9	0.51	0.30	0.19
313	9.2	13.0	1.8	0.52	0.32	0.16
297	8.9	12.8	2.0	0.52	0.30	0.18
264	8.9	13.1	3.6	0.62	0.23	0.15
237	8.6	13.0	3.4	0.61	0.23	0.16
228	8.6	13.2	4.1	0.65	0.21	0.14
219	8.7	13.5	4.4	0.69	0.21	0.10

of Spoomaker^{12,13} yielding $8.1 < J_T^C < 8.25$ Hz and $2.02 > J_G^C > 1.73$ Hz. With these parameters, the experimental values of $(^3J_{\text{CH}_A} + ^3J_{\text{CH}_B}) = 6.7$ Hz at 298 K and 7.1 Hz at 333 K yield $0.56 > x_t > 0.54$ and $0.49 > x_t > 0.475$, respectively. These values and their temperature trend are in very good agreement with the results of ¹H NMR analysis based on the H_A, H_B assignment in Fig. 1b. Such agreement is not obtained for the alternative interpretation of the structure of the CCH₃ band, with $^3J_{\text{CH}_A} \neq ^3J_{\text{CH}_B}$, $^3J_{\text{CH}_A} \approx ^2J_{\text{CH}_X}$, with any of the two H_A, H_B assignments. Combined ¹H and ¹³C NMR evidence thus establishes *x_t* as the major conformer. The difference in the population of the minor conformers is not revealed in ¹³C NMR spectra measured at 298 and 333 K.

Vibrational Spectra

In Fig. 4 Raman and infrared spectra of *I* are shown measured at room temperature where the substance is liquid, and at 133 K, where it is in the glassy state (the compound could not be crystallized). During cooling the following bands appear as conformationally sensitive: infrared and Raman bands at 968, 953, 912, 898, 762, 748, 650, 618 and 596 cm⁻¹, Raman bands at 846, 837, 826, 812, 372 and 333 cm⁻¹, and infrared bands at 1055 and 1065 cm⁻¹. Band intensity changes are observed even during cooling of the glassy state indicating that even there changes of conformational equilibria take place.

The conformationally sensitive doublets at 968, 953 cm⁻¹ and at 912, 898 cm⁻¹, active both in infrared and in Raman spectra, exhibit an equal temperature trend and both lie in a range where also bands of *II* appear³ and where *III* does not exhibit any prominent bands⁷. Therefore we assume that these conformationally sensitive doublets correspond to conformers generated by rotation about bonds *1* or *2*. Based on the results of NMR analysis, the doublet components at 953 and 898 cm⁻¹, the intensity of which increases with cooling, are assigned primarily to conformers with *ī* or *t* structure (Fig. 1a,b). Conformers generated by rotation about bond *1* are usually manifested in Raman spectra³ by strong bands about 800 cm⁻¹. In compound *I* this range of Raman spectra cannot be used in studies of rotation about bond *1* because it is overlapped by a very strong conformationally insensitive band of the ester group.

Conformationally sensitive bands of compound *I* appearing both in Raman and in infrared spectra at 762, 748, 650, 618 and 596 cm⁻¹ lie in a range where *II* has no prominent band³ and where *III* exhibits relatively well pronounced conformationally sensitive bands⁷. Therefore we assume that also in compound *I* these bands are characteristic of structures generated by rotation about the bond C—C=O. As not only the positions, but also the intensities and the temperature trend of these bands in compound *I* are very similar⁷ as in *III*, we assume that the corresponding conformational structures are the same in *I* and *III*, and that also the population

of these structures is similar in both these molecules. The conformational structure of *III* has not been unambiguously determined so far. In agreement with our previous paper we assume that also in *I* the structure described in the staggered approximation

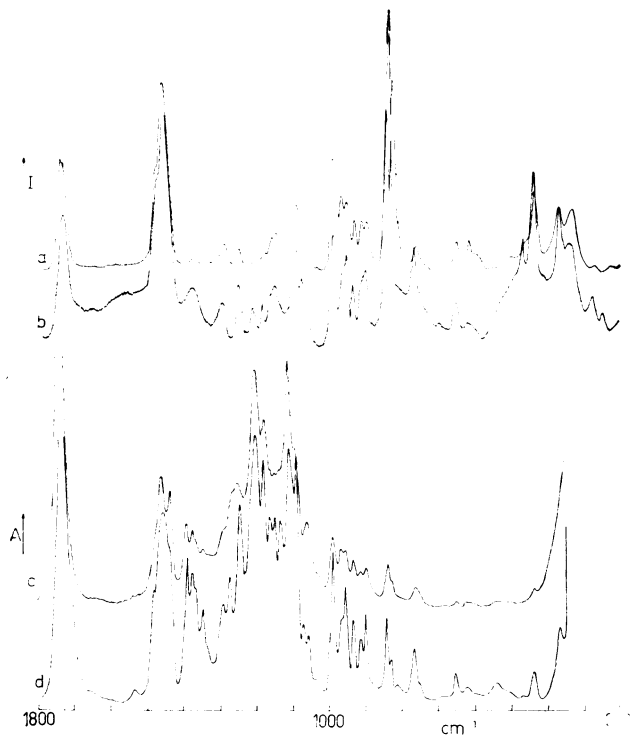


FIG. 4
Raman (*a, b*) and infrared (*c, d*) spectra of *I* *a, c* liquid; *b, d* glass (133 K)

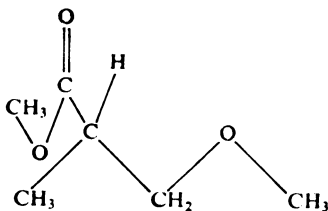


FIG. 5
The preferred conformational structure of *I*

as *syn*-H is the most favoured of the conformers generated by rotation about the bond 3. This structure corresponds to vibrational bands at 762 and 650 cm^{-1} the intensities of which increase with cooling. Vibrational bands at 748, 618 and 596 cm^{-1} the intensities of which decrease at cooling, are supposed to correspond to *syn*-C structures. As in methyl 2,2-dimethylpropanoate² the *anti*-CH₃ structures are energetically strongly disfavoured with respect to *syn*-CH₃ structures ($\Delta H = 8 \text{ kJ/mol}$), we do not expect *anti* structures to be manifested in vibrational spectra of *I*.

In addition to the above discussed conformationally sensitive bands, Raman spectra exhibit further sensitive bands at 372 and 333 cm^{-1} and infrared spectra at 1 055 and 1 065 cm^{-1} . We have not found sufficient evidence for assigning these bands to some conformational structures of compound *I*.

CONCLUSION

As indicated in the introduction, in the studied molecule various conformational structures can be generated by independent rotations about three single bonds. Even if *anti*-structures on the C—C=O bond are excluded, this leaves 27 conformers to be considered. As none of the bands in vibrational spectra can be simply assigned to a single one of these 27 forms, ΔH values cannot be extracted from the temperature dependence of vibrational band intensities^{14,15}. Conformational preferences on two of the three bonds can be characterized quantitatively from NMR spectra. However, even here each of the cited mole fractions (*e.g.* x_1 , x_2) corresponds to a sum over the forms generated by rotation about the other two bonds, and their temperature dependence likewise cannot be used for the determination of ΔG . Nevertheless, combination of the conformational preferences on the various bonds permits us to define the most highly populated form of the studied molecule which is designated as (i) (t) (*syn*-H) in the presently used nomenclature, and shown schematically in the staggered approximation in Fig. 5.

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