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Stereoregular Oligomers of Methyl Methacrylate. V. X-Ray Single Crystal Analysis of Isotactic Pentamer and Syndiotactic Tetramer

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STEREOREGULAR OLIGOMERS OF METHYL METHACRYLATE. V. X-RAY SINGLE CRYSTAL ANALYSIS OF ISOTACTIC PENTAMER AND SYNDIOTACTIC TETRAMER†

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ABSTRACT

Stereostructures of the isotactic pentamer (*meso-meso-meso-meso* isomer) and the syndiotactic tetramer (*racemo-racemo-meso* isomer) of MMA were determined by x-ray single crystal analysis. The *mmmm*-pentamer and the *rrm*-tetramer were isolated by HPLC from the oligomer mixtures prepared with t-C_4H_9MgBr and with t-$C_4H_9Li/(C_2H_5)_3Al$ in toluene, respectively. The melting point of the *mmmm*-pentamer was 59.0–60.0°C, which was lower than that of the *rrm*-tetramer (99.4–100.2°C). Monoclinic crystals of the *mmmm*-pentamer and the *rrm*-tetramer grown from heptane solution belonged to the space groups $P2_1/n$ and $P2_1$, respectively. The conformation of the main chain (t-C_4H_9—$(C-C)_n$—H) of the *mmmm*-pentamer was *tttttgtg* and that of the *rrm*-tetramer was *tttttg*.

†Dedicated to Professor Otto Vogl on the occasion of his 65th birthday with our warmest wishes.

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INTRODUCTION

Stereoisomers of oligomers are good model compounds of stereoregular polymers. However, isolation of pure stereoisomers from an oligomer mixture becomes exceedingly difficult as the degree of polymerization increases. Few papers have reported the isolation of stereoisomers of oligomers as a single crystal: the stereoregular all-*ortho* ethylidene-linked trinuclear phenolic compounds [1], the tetramer of 2-(2-pyridyl)propene [2], the dimer of phenyl vinyl sulfoxide [3], the tetramer of methyl methacrylate (MMA) with head-to-head linkage [4], and the linear isotactic dimer [5] and trimer of MMA [6] were studied by x-ray crystallographic analysis. Recently, the structures of the purely isotactic chloral oligomers up to the hexamer level were determined by x-ray single crystal analysis [7, 8].

As reported previously [9, 10], purely isotactic and purely syndiotactic MMA oligomers from dimer to octamer can be isolated effectively by HPLC from the oligomer mixtures prepared by the living isotactic polymerization of MMA initiated with t-C_4H_9MgBr and by the living syndiotactic polymerization initiated with t-$C_4H_9Li/(C_2H_5)_3Al$. Although the chain propagation in the polymerization systems is highly stereospecific, the termination reaction with methanol is almost nonstereospecific. Consequently, the isotactic oligomer mixture consists of two series of stereoisomers, $mm\cdots mm$ and $mm\cdots mr$, and the syndiotactic mixture consists of $rr\cdots rm$ and $rr\cdots rr$, where m and r represent *meso* and *racemo* diads, respectively.

meso-terminal   *racemo*-terminal
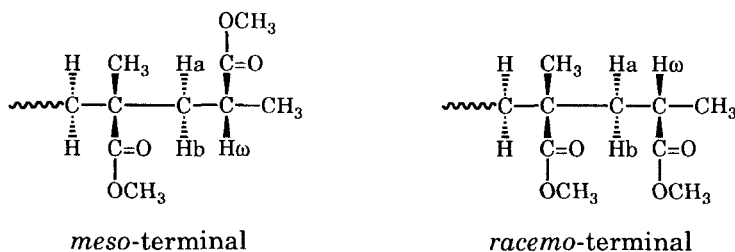
The m/r assignment for the Hω terminal of the isotactic oligomers can be made by ^{1}H-NMR spectroscopy as follows [10]: the chemical shift difference between the nonequivalent methylene protons (H_a and H_b) in the terminal monomeric unit is larger for the r diad than for the m diad because the Hω terminal of the isotactic oligomers in solution assumes *trans-gauche* (tg) conformation along the skeletal sequence C—C—C—C—Hω. This assignment was confirmed by the crystallographic determination of the isotactic (mm) trimer [6]. However, it has not been conclusive whether the above m/r assignment is true for the Hω terminal of the syndiotactic oligomers.

In this work we obtained single crystals of the syndiotactic tetramer suitable for x-ray crystallographic determination; the crystalline tetramer had been identified as the rrm-isomer according to the ^{1}H-NMR spectrum [9]. X-ray studies on the crystal gave a clear certification for the m/r assignment of the syndiotactic oligomers. X-ray single crystal analysis of the $mmmm$-pentamer was also carried out. The $mmmm$-pentamer is, of course, a better model of isotactic PMMA than the mm-trimer.

EXPERIMENTAL

The isotactic and the syndiotactic oligomers of MMA were prepared as reported previously [9]. Living isotactic polymerization of MMA [11, 12] was initiated with t-C_4H_9MgBr ([MMA]/[t-C_4H_9MgBr] = 50 mol/mol) in toluene at $-78\,°C$, and the reaction was terminated 75 min after initiation by adding a small amount of methanol to the polymerization mixture. The yield of the polymerization products was 20.7% and the number-average molecular weight, $\overline{M}_n$, was 1014. Living syndiotactic polymerization of MMA [13, 14] was carried out with t-C_4H_9Li/ $(C_2H_5)_3Al$ complex ([Al]/[Li] = 2 mol/mol, [MMA]/[t-C_4H_9Li] = 5 mol/mol) in toluene at $-78\,°C$. The polymerization reaction was terminated with methanol 3 h after initiation. The yield of the polymerization products was 92% ($\overline{M}_n$ = 759). The tetramer to octamer fractions were isolated from the oligomer mixtures by GPC (column size: 2 × 50 cm), and subsequently each fraction was subjected to HPLC on a column (0.75 × 50 cm) packed with silica gel using the butyl chloride and acetonitrile mixtures as an eluent (n-C_4H_9Cl/CH_3CN = 96/4 − 88/12) [15] to give pure diastereomers. Single crystals of the *mmmm*-pentamer and the *rrm*-tetramer were grown from heptane solution.

Crystallographic details for the *mmmm*-pentamer and the *rrm*-tetramer are given in Table 1. All x-ray data were collected with a Rigaku AFC-5R automated four-circle diffractometer using CuK_α radiation (λ = 1.5418 Å). Three standard reflections, monitored every 100 reflections during data collection, indicated no appreciable decay. No absorption correction was made. The structures were solved by the direct method [16] and by the weighted Fourier synthesis. The structure of the *mmmm*-pentamer was refined by the full-matrix least-squares procedure with anisotropic thermal parameters. For the *rrm*-tetramer, positions of oxygen atoms were refined anisotropically and those of carbon atoms isotropically. Positions of hydrogen atoms were idealized for both oligomers.

RESULTS AND DISCUSSION

Crystals of the *mmmm*-pentamer melted at 59.0–60.0°C. The melting point (mp) was lower than those of the *mm*-trimer (61.1–62.3°C) and isotactic PMMA (138°C) [17] (Table 1). The calculated crystal density of the *mmmm*-pentamer (1.176 g·cm^{-3}) was intermediate between those of the *mm*-trimer (1.123 g·cm^{-3}) [6] and isotactic PMMA (1.21 g·cm^{-3}) [18]. The differences of the density indicate that the packing of the molecules in a unit cell is improved as the degree of polymerization increases, and the result is that the end groups become less significant. The difference of the mp between the isotactic (*mmmm*-) pentamer and the syndiotactic (*rrm*-) tetramer (ca. 40°C) was relatively large as compared with the difference in their density (0.011 g·cm^{-3}). This suggests that the *rrm*-tetramer has a less flexible molecular structure than the *mmmm*-pentamer.

Figure 1(a) shows the x-ray molecular structure of the *mmmm*-pentamer. The crystal symmetry demands the crystal to consist of a racemic mixture of the ($R,R,-S,S,R$) and (S,S,R,R,S) isomers; only the (R,R,S,S,R) isomer is shown in the figure. Repetition of the five monomeric units between C5 and C26 produces an isotactic

TABLE 1.   Crystal Data of the *mmmm*-Pentamer and
rrm-Tetramer[a] of MMA

	mmmm-5	*rrm*-4
Formula	$C_{29}H_{50}O_{10}$	$C_{24}H_{42}O_8$
Formula weight	558.7	458.3
Melting point/°C	59.0–60.0	99.4–100.2
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1$
$a/\text{Å}$	31.461 (5)	17.941 (14)
$b/\text{Å}$	6.416 (2)	11.740 (8)
$c/\text{Å}$	15.793 (3)	12.227 (9)
β/deg	98.11 (1)	94.92 (7)
$V/\text{Å}^3$	3156 (1)	2566 (3)
Z	4	4
$D_{calcd}/\text{g}\cdot\text{cm}^{-3}$	1.176	1.187
Crystal size/mm	$0.5 \times 0.1 \times 0.1$	$1.0 \times 0.3 \times 0.1$
Scan mode	$2\theta\text{-}\omega$	ω
Total unique data	5383	4243
Obsd. data ($|F| > 3\sigma(|F|)$)	2701	3091
No. of parameters	352	336
R^b	0.132	0.154
Rw^c	0.117	0.137

[a]Estimated standard deviations in the least significant digits are given in
parentheses.
[b]$R = \Sigma \,||F_o| - |F_c||/\Sigma|F_o|$.
[c]$Rw = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, $w = 1/\sigma(F)^2$.

PMMA chain, and therefore the pentamer is surely assigned to the *mmmm*-isomer.
It should be noted that the R/S notation depends on the order of priority of the end
groups.

The crystal of the *rrm*-tetramer contained two independent molecules in a unit
cell, since four molecules [two (R,R,S,R) and two (S,S,R,S) isomers] are included
for two equivalent positions. The (R,R,S,R) and (S,S,R,S) isomers had essentially
the same (enantiomeric) conformation. Figure 1(b) shows the ORTEP drawing of
the (R,R,S,R) isomer. The present x-ray study has proved the validity of the *m/r*
assignment by ^{1}H NMR for the Hω terminal of the syndiotactic oligomers; the
chemical shift difference between the nonequivalent methylene protons in the Hω
terminal of both the isotactic and syndiotactic MMA oligomers is smaller for the *m*
diad than for the *r* diad. It is well known that the opposite is the case for the
methylene protons in an *m/r* diad embedded in a PMMA chain [19, 20]; the methyl-
ene protons of isotactic PMMA are nonequivalent whereas those of syndiotactic
PMMA are equivalent.

The (R,R,S,S,R) pentamer adopted the $tttttg^+tg^+$ conformation along the
skeletal   sequence   *t*-C_4H_9—C5—C6—C10—C11—C15—C16—C20—C21—C25—
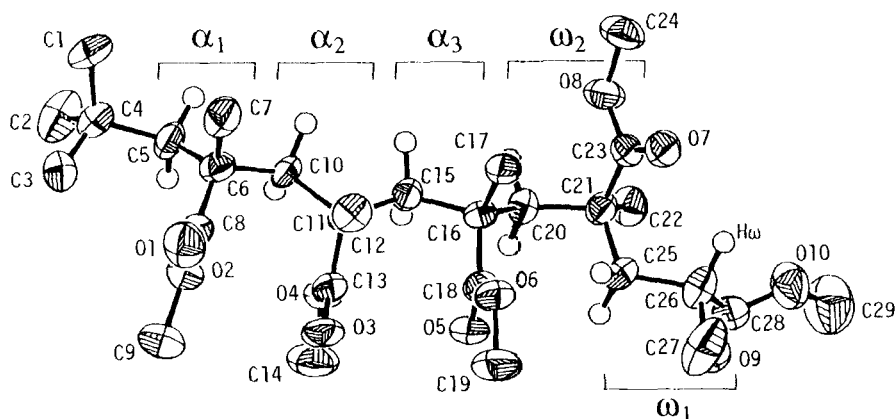C26—Hω (Table 2). The conformation of the three monomeric units from the Hω

a) mmmm-pentamer

b) rrm-tetramer
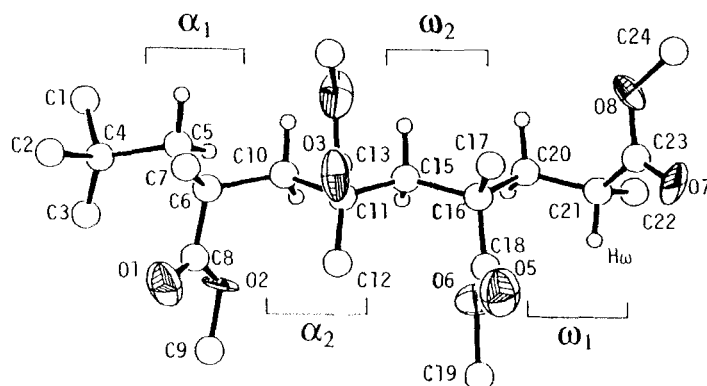
FIG. 1. The ORTEP diagrams of a) the *mmmm*-pentamer (R,R,S,S,R) and b) the *rrm*-tetramer (R,R,S,R) of MMA. Methyl hydrogen atoms are omitted in the figures for clarity.

terminal was the same as that of the (R,S,R) trimer (ttg^+tg^+) [6]. The backbone of the (R,R,S,R) tetramer assumed the $tttttg^+$ form along t-C_4H_9—C5—C6—C10—C11—C15—C16—C20—C21—Hω (Table 3). Both the *mmmm*-pentamer and *rrm*-tetramer tend to take *trans* zigzag conformation along the main chain and tg^+ conformation in the Hω terminal.

All the ester groups in the oligomers take planar *cis* geometry. The plane of the ester groups occurs perpendicular to the tt zigzag backbone with the carbonyl group oriented to the same side (*syn*) of the α-methyl group, except for the α_3-unit of the *mmmm*-pentamer in which the carbonyl group was in the *anti* geometry.

TABLE 2. Selected Bond Lengths, Angles, and Torsional Angles for the *mmmm*-Pentamer (R,R,S,S,R)[a] of MMA

Monomeric units	Bond lengths, Å		Bond angles, degrees		Torsional angles, degrees	
α_1	C4—C5	1.58	C4—C5—C6	122	C4—C5—C6—C10	−174
	C5—C6	1.55	C5—C6—C10	103	C5—C6—C10—C11	−161
	C6—C7	1.57	C7—C6—C8	109	C7—C6—C8=O1	−1
	C6—C8	1.48	C6—C8—O2	110	O1=C8—O2—C9	−3
	C8—O1	1.19	O1—C8—O2	122		
	C8—O2	1.36	C8—O2—C9	116		
	C9—O2	1.51				
α_2	C6—C10	1.58	C6—C10—C11	120	C6—C10—C11—C15	−168
	C10—C11	1.58	C10—C11—C15	103	C10—C11—C15—C16	164
	C11—C12	1.54	C12—C11—C13	108	C12—C11—C13=O3	2
	C11—C13	1.52	C11—C13—O4	111	O3=C13—O4—C14	−4
	C13—O3	1.19	O3—C13—O4	123		
	C13—O4	1.35	C13—O4—C14	118		
	C14—O4	1.48				
α_3	C11—C15	1.60	C11—C15—C16	119	C11—C15—C16—C20	161
	C15—C16	1.60	C15—C16—C20	102	C15—C16—C20—C21	168
	C16—C17	1.56	C17—C16—C18	114	C17—C16—C18=O5	−174
	C16—C18	1.50	C16—C18—O6	112	O5=C18—O6—C19	−1
	C18—O5	1.19	O5—C18—O6	123		
	C18—O6	1.34	C18—O6—C19	117		
	C19—O6	1.50				
ω_2	C16—C20	1.56	C16—C20—C21	118	C16—C20—C21—C25	55
	C20—C21	1.59	C20—C21—C25	109	C20—C21—C25—C26	174
	C21—C22	1.58	C22—C21—C23	106	C22—C21—C23=O7	−118
	C21—C23	1.47	C21—C23—O8	113	O7=C23—O8—C24	−2
	C23—O7	1.21	O7—C23—O8	120		
	C23—O8	1.33	C23—O8—C24	118		
	C24—O8	1.46				
ω_1	C21—C25	1.56	C21—C25—C26	115	C21—C25—C26—Hω	41
	C25—C26	1.61	C25—C26—Hω	109	C27—C26—C28=O9	74
	C26—C27	1.60	C27—C26—C28	105	O9=C28—O10—C29	0
	C26—C28	1.46	C26—C28—O10	110		
	C28—O9	1.22	O9—C28—O10	123		
	C28—O10	1.32	C28—O10—C29	118		
	C29—O10	1.45				

[a]The estimated standard deviations for bond lengths, bond angles, and torsional angles involving only nonhydrogen atoms are 0.01–0.02 Å, 0.7–1.2°, and 0.7–1.8°, respectively.

TABLE 3. Selected Bond Lengths, Angles, and Torsional Angles for the *rrm*-Tetramer $(R,R,S,R)^a$ of MMA

Monomeric units	Bond lengths, Å		Bond angles, degrees		Torsional angles, degrees	
α_1	C4—C5	1.67	C4—C5—C6	118	C4—C5—C6—C10	162
	C5—C6	1.56	C5—C6—C10	99	C5—C6—C10—C11	167
	C6—C7	1.53	C7—C6—C8	107	C7—C6—C8=O1	7
	C6—C8	1.54	C6—C8—O2	112	O1=C8—O2—C9	9
	C8—O1	1.18	O1—C8—O2	131		
	C8—O2	1.30	C8—O2—C9	114		
	C9—O2	1.42				
α_2	C6—C10	1.60	C6—C10—C11	122	C6—C10—C11—C15	175
	C10—C11	1.62	C10—C11—C15	103	C10—C11—C15—C16	−173
	C11—C12	1.52	C12—C11—C13	98	C12—C11—C13=O3	4
	C11—C13	1.40	C11—C13—O4	111	O3=C13—O4—C14	−4
	C13—O3	1.15	O3—C13—O4	112		
	C13—O4	1.37	C13—O4—C14	116		
	C14—O4	1.47				
ω_2	C11—C15	1.55	C11—C15—C16	123	C11—C15—C16—C20	179
	C15—C16	1.59	C15—C16—C20	102	C15—C16—C20—C21	−173
	C16—C17	1.55	C17—C16—C18	105	C17—C16—C18=O5	−6
	C16—C18	1.46	C16—C18—O6	115	O5=C18—O6—C19	7
	C18—O5	1.18	O5—C18—O6	118		
	C18—O6	1.27	C18—O6—C19	125		
	C19—O6	1.50				
ω_1	C16—C20	1.62	C16—C20—C21	112	C16—C20—C21—Hω	38
	C20—C21	1.53	C20—C21—Hω	105	C22—C21—C23=O7	−95
	C21—C22	1.51	C22—C21—C23	111	O7=C23—O8—C24	9
	C21—C23	1.47	C21—C23—O8	113		
	C23—O7	1.26	O7—C23—O8	122		
	C23—O8	1.30	C23—O8—C24	122		
	C24—O8	1.47				

[a]The estimated standard deviations for bond lengths, bond angles, and torsional angles involving only nonhydrogen atoms are 0.02–0.05 Å, 1.0–2.7°, and 1.8–4.4°, respectively.

There is disagreement in recent x-ray diffraction studies [18, 21, 22] and conformational energy calculations [23, 24] as to the *syn/anti* orientation of ester groups in PMMA. Kusanagi et al. [18] adopted the *anti* orientation in the double strand helix model of isotactic PMMA. Bosscher et al. [22] suggested that the ester groups with the *anti* orientations were placed opposite the ester groups with the *syn* orientations in the double strand helix of isotactic PMMA. Other papers [23, 24] reported that the ester groups prefer the *syn* orientation in the *tt* state of *m* and *r* diads in

PMMA. Our results of x-ray single crystal analysis on the isotactic pentamer and the syndiotactic tetramer indicate that the orientation of the ester group is predominantly *syn*, although the *anti* form was also found to exist. This suggests that the energy difference between the *syn/anti* orientations should be very little.

Relatively large values for the *intradiad* bond angles, $\angle C-CH_2-C$, which were described in the literature [18, 21, 24], were also observed in the present work (Tables 2 and 3). The *interdiad* bond angles, $\angle CH_2-C-CH_2$, were 99–103° in the *tt* states and 109° in the *tg*⁺ states.

The isotactic pentamer and the syndiotactic tetramer are the largest MMA oligomers among those whose structures have been solved by x-ray single crystal analysis. X-ray crystallographic analysis on the oligomers with the higher degree of polymerization would allow determination of the long-range structures such as a double-stranded 10/1 helix [18, 22] of isotactic PMMA. It has become possible to isolate pure stereoisomers of MMA oligomers exceeding the decamer level by supercritical fluid chromatography [25, 26].

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