NOTES

Crystal Structure of Methyl Methacrylate Dimer. Revised *meso/racemo* Assignment for the Dimer

Tamaki NAKANO, Koichi UTE, Yoshio OKAMOTO,
Yoshiki MATSUURA,* and Koichi HATADA

Department of Chemistry, Faculty of Engineering Science,
Osaka University, Toyonaka, Osaka 560, Japan

* Institute for Protein Research, Osaka University,
Suita, Osaka 565, Japan

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Triphenylmethyl methacrylate (TrMA) is a monomer which can give an optically active polymer having the chirality due to only helicity.¹ Recently, we carried out the asymmetric oligomerization of TrMA initiated with a complex of (–)-sparteine and 9-fluorenyl-lithium (Sp-FILi) to elucidate the mechanism of the asymmetric polymerization, and clarified that the oligomer anions with certain specific structures propagate to the higher oligomer anions in the early stage of asymmetric polymerization.² This study is based on the results of analysis of the oligo(methyl methacrylate) [oligo(MMA)] derived from the oligo(TrMA) having a 9-fluorenyl group at the beginning of the polymer chain (α -end),³ and ¹H NMR peak assignments for stereoisomers were made according to the previous report⁴ based on the ¹H NMR spectra of the oligo(MMA) having a *t*-butyl group at the α -end. Recently, the molecular structure of the MMA-trimer having a *t*-butyl group at the α -end³ was studied by X-ray analysis and the previous *meso/racemo* assignment for the dyad sequence at the terminal chain end (ω -end)³ was found to be incorrect.^{5,6}

In this work, the crystal structure of one of

the two diastereomers of MMA-dimer having a 9-fluorenyl group at the α -end⁷ derived from TrMA-dimer⁸ was determined, and it was found that the difference in the chemical shifts between the methylene protons in the ω -end unit of the *racemo* isomer is larger than that of the *meso* isomer.

MMA-dimer having a 9-fluorenyl group at the α -end

Oligo(MMA) was derived from oligo(TrMA) prepared with Sp-FILi complex at [TrMA]/[FILi]=2 in the same manner as described previously.^{2,9} The diastereomers of oligo(MMA) were separated by HPLC columns (25 × 0.46 (i.d.) cm, 50 × 0.72 (i.d.) cm) packed with silica gel (5 μ m diameter) using a butyl chloride–acetonitrile (97:3) mixture as the eluent.²

A single crystal of the *meso* dimer (the minor isomer) was grown from a hexane solution. The crystal data are as follows: molecu-

Table I. Bond lengths, bond angles, and torsional angles in MMA units^a

Bond length/Å		Bond angle/°					
C1–C14	1.653 (3)	C15–C19	1.681 (3)	C1–C14–C15	120.5 (1)	C15–C19–C20	120.4 (2)
C14–C15	1.555 (3)	C19–C20	1.557 (3)	C14–C15–C19	108.9 (1)	C19–C20–H23	108.9 (15)
C15–C16	1.545 (3)	C20–C21	1.638 (5)	C16–C15–C17	107.7 (2)	C21–C20–C22	105.1 (2)
C15–C17	1.533 (3)	C20–C22	1.511 (3)	C15–C17–O2	112.0 (2)	C20–C22–O4	111.7 (2)
		C20–H23	1.002 (26)	C17–O2–C18	116.4 (2)	C22–O4–C23	116.5 (2)
C17–O1	1.209 (3)	C22–O3	1.206 (3)	O1–C17–O2	122.6 (2)	O3–C22–O4	122.5 (2)
C17–O2	1.339 (2)	C22–O4	1.333 (3)				
O2–C18	1.451 (3)	O4–C23	1.446 (4)				
Torsional angle/°							
C1–C14–C15–C19	–164.5 (1)	C15–C19–C20–H23	34.9 (16)				
C14–C15–C19–C20	–57.3 (2)						
C16–C15–C17–O1	–19.9 (3)	C21–C20–C22–O3	88.4 (3)				
O1–C17–O2–C18	2.6 (3)	O3–C22–O4–C23	–2.1 (3)				

^a Estimated standard deviations in the least significant digits are in parentheses.

lar formula = $C_{23}H_{26}O_4$, molecular weight = 366.46, *orthorhombic*, space group $P2_12_12_1$, $a = 12.296$ Å, $b = 26.077$ Å, $c = 6.277$ Å, $V = 1996.7$ Å³, $Z = 4$, $D_c = 1.219$ g cm^{–3}. A total of 3604 reflections with $2\theta < 125^\circ$ was collected by a Rigaku automated four-circle diffractometer (Rigaku AFC-5R) using Cu- K_α radiation ($\lambda = 1.5418$ Å). The structure was solved by direct methods (MULTAN 78),¹⁰ and refined by the full-matrix least-squares procedure (FMLS)¹¹ with anisotropic thermal parameters for nonhydrogen atoms and isotropic ones for hydrogen atoms to the final $R = 0.032$ and $R_w = 0.036$ for 348 variables and 1836 independent reflections with $|Fo| > 3\sigma(|Fo|)$. HPLC analysis of the crystalline dimer showed the crystal to consist entirely of one antipode of enantiomers, which is consistent with the non-centro-symmetric structure.

¹H NMR spectra were measured in CDCl₃ at 35°C with a JEOL JNM-GX500 spectrometer (500 MHz).

Figure 1 shows the ORTEP diagram¹² of the crystalline dimer, which indicates the diastereomer to be the so-called *meso* isomer (the smallest configurational sequence of an isotactic polymer chain). The configuration of the asymmetric centers (C15 and C20) was (*S,S*) or (*R,R*). The bond lengths, bond angles,

Figure 1. ORTEP diagram of *meso* MMA-dimer having a 9-fluorenyl group at the α -end.

and torsional angles are summarized in Table I. The conformation of the main chain (fluorenyl–C14–C15–C19–C20–H23 bond) was tg^-g^+ as the (*R,R*) isomer. It has been shown that the main chain of the *meso-meso* (*R,S,R*) MMA-trimer with a *t*-butyl group at the α -end has ttg^+tg^+ conformation.⁶ The conformation (g^+tg^+) of the terminal two monomeric units of the trimer is different from tg^-g^+ of the dimer. The conformations seem to depend on the preceding group.

Figure 2 shows the ¹H NMR spectra of two diastereomers of the MMA-dimer. Differences in the chemical shifts and coupling constants are summarized in Table II. Difference in the

Figure 2. ^1H NMR spectra of MMA-dimer; *meso* (A) and *racemo* (B).

Table II. The difference of chemical shifts of methylene protons and the coupling constants between methine proton and methylene protons of the ω -end^a

	<i>meso</i>	<i>racemo</i>
$\delta(H_A) - \delta(H_B)/\text{ppm}$	0.35	0.36
$\delta(H_a) - \delta(H_b)/\text{ppm}$	0.23	0.92
$^3J(H_a - H_\omega)/\text{Hz}$	5.3	5.3
$^3J(H_b - H_\omega)/\text{Hz}$	3.7	3.2

^a In CDCl_3 at 35°C .

chemical shifts of the methylene protons (ω end) of the *racemo* isomer exceeds that of the *meso* isomer. Since this agrees with the results for methylene protons of the ω -end of the MMA-trimer which has a *t*-butyl group at the α -end,⁶ this assignment of the stereostructure of the ω -

end by the nonequivalency of the methylene protons clarified here may be applicable to the MMA-trimer and higher MMA-oligomers with a 9-fluorenyl group at the α -end.

The previous assignment of the stereoisomers of the dimer and the trimer having a 9-fluorenyl group at the α -end² should thus be revised as shown in Figure 3 [*cf.*, Figure 2 in ref 2)] and Table III. In ref 2, the *R,S*-notation was used to represent the structures of the optical isomers of the dimer, based on the correlation between the absolute configuration and optical activity of several model compounds. However, since the absolute configuration of the dimer has not yet been determined, the *D,L*-notation was used here to represent the structure of the dimer. If the

Figure 3. Chromatograms of separation of diastereomers of MMA-dimer and -trimer (A) and optical resolution of MMA-dimer (B) derived from TrMA-dimer and -trimer with revised assignments. Previous assignments appear in parentheses.

Table III. Revisal of assignments for the trimer

Previous assignment	Revised assignment
<i>RRS</i>	<i>LLL</i>
<i>SSR</i>	<i>DDD</i>
<i>RSR</i>	<i>LDD</i>
<i>SRS</i>	<i>DLL</i>
<i>RSS</i>	<i>LDL</i>
<i>SRR</i>	<i>DLD</i>
<i>SSS</i>	<i>DDL</i>
<i>RRR</i>	<i>LLD</i>

previous assumption was applicable, the DD isomer should have the *RR* configuration.

In spite of revisal of the assignments, the essence of the conclusion on the mechanism for asymmetric polymerization of TrMA re-

ported in ref 2 is still valid because the stereostructure of the ω -end of the oligo(MMA) is determined in the process of protonation of the terminal anion with methanol and has no correlation with the polymerization reaction.

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Supplementary Material Available. Tables of observed and calculated structure factors (9 page), fractional atomic coordinates and equivalent isotropic thermal parameters (1

page), and anisotropic thermal parameters (1 page). On request, these materials are available from the authors or editorial office of The Society of Polymer Science, Japan.

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