Stereoregular Oligomers of Methyl Methacrylate III.[†] ¹H and ¹³C NMR Spectra of the Pure-Isotactic and Pure-Syndiotactic Oligomers from Dimers to Octamers

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(Received June 23, 1989)

ABSTRACT: Pure-isotactic (*it*-) and pure-syndiotactic (*st*-) MMA oligomers from dimers to octamers were isolated from stereoregular living polymerization systems of MMA in toluene at -78°C with *t*-BuMgBr and *t*-BuLi/Et₃Al, respectively, and their ¹H and ¹³C NMR spectra were investigated in detail. The peak assignments for all the ¹H and ¹³C signals except for methoxy signals were unambiguously made by ¹H COSY and long-range ¹³C–¹H COSY (COLOC). NMR chemical shifts of protons and carbons in the monomeric units of the third and farther positions from the α - and ω -ends were nearly the same as those in the corresponding stereosequences of high molecular weight PMMA. Both the *it*- and *st*-oligomers were found to take the extended, all *trans* conformation in solution, from the observed patterns of the ⁴J_{HH} long-range correlation peaks in the ¹H COSY spectra. The ¹³C-*T*₁ values of the *it*-hexamer were larger than those of the *st*-hexamer for any carbon in any monomeric unit, indicating differences in segmental mobility.

KEY WORDS MMA / Anionic Living Polymerization / Stereoregular Polymerization / Oligomer / ¹H NMR / ¹³C NMR / 2D NMR / Conformation / Spin-Lattice Relaxation Time / Stereocomplex /

The stereochemistry associated with the early stage of chain growth reaction has been of special concern in anionic polymerization of methacrylates.^{1–6} Recent developments in NMR spectroscopy and X-ray crystallographic determination permitted the unambiguous identification of the stereoisomers of oligomers,^{1–20} with the aid of increasingly improved separation and purification techniques such as high performance liquid chromatography (HPLC). In the last two years, several laboratories reported the stereochemical analysis using NMR spectroscopy of the MMA oligomer series (from mono-adducts to tetra-adducts) prepared by the radical polymerization with tetraphenylethane initiators,¹⁵ by

the radical telomerization with thiophenol,¹⁶ and by group transfer polymerization.¹⁷ The above polymerization systems are not stereospecific (rather syndiotactic) and thus the resultant MMA oligomers consist of comparable amount of some stereoisomers. Prior to these publications, Cacioli and his coworkers¹¹ investigated the preferred conformations of the MMA oligomers by ¹H COSY experiments; the synthesis and separation of the diastereomers of the penta-adducts (three of four possible isomers) were described in their paper. Volpe *et al.*⁶ prepared the “symmetric” oligomer of MMA by the initiation with lithio- and sodiomethyl isobutyrate enolate in THF followed by termination with methyl iodide,

[†] References 2 and 3 are Parts I and II of the series “Stereoregular Oligomers of Methyl Methacrylate,” respectively.

and demonstrated the ^{13}C NMR spectrum of the mixture of three isomers out of six possible stereoisomers of hexamer.

As reported previously,²¹⁻²⁴ we found the living and highly-stereospecific polymerizations of MMA. The polymerization of MMA initiated with *t*-BuMgBr in toluene at -78°C gives highly isotactic (*it*-) PMMA (*mm* > 97%) with narrow molecular weight distribution (MWD),^{21,22} while the polymerization with *t*-BuLi-trialkylaluminum complex in toluene at -78°C affords highly syndiotactic (*st*-) PMMA (*rr* > 90%) with narrow

MWD.^{23,24} The pure-isotactic and pure-syndiotactic MMA oligomers composed exclusively of *meso* (*m*) dyads and exclusively of *racemo* (*r*) dyads, respectively, can be prepared and isolated effectively¹⁻³ through these polymerization systems by the aid of HPLC technique.⁴ Even the octamers for which 128 diastereomers are theoretically possible, are isolated stereochemically pure. It should be noted that these polymerization systems provide polymers and oligomers carrying the same terminal groups. The MMA oligomers are

denoted by the sequential arrangement of *m* and *r* dyads preceded with the degree of polymerization (*n*) (e.g. 3*mm*, 4*rrr*). Although the propagation step is highly stereospecific, the termination reaction with methanol exhibits low stereospecificity in both polymerization systems. Therefore, two series of *it*-oligomers 2*m*, 3*mm*, 4*mmm*, 5*mmmm*, ... (**Mm**) and 2*r*, 3*mr*, 4*mmr*, 5*mmmr*, ... (**Mr**), and two series of *st*-oligomers 2*m*, 3*rm*, 4*rrm*, 5*rrrm*, ... (**Rm**) and 2*r*, 3*rr*, 4*rrr*, 5*rrrr*, ... (**Rr**) are produced in the polymerization systems.

In this work, ^1H and ^{13}C NMR spectra of the pure diastereomers isolated from these oligomer mixtures were investigated in detail. These oligomers are considered to be good model compounds of stereoregular polymers.

EXPERIMENTAL

Preparation

The *it*-oligomers were prepared by the living

polymerization of MMA with *t*-BuMgBr in toluene at -78°C ($[\text{MMA}]/[t\text{-Bu}] = 50 \text{ mol/mol}$).¹⁻³ The reaction was terminated 15 min after initiation by adding a small amount of methanol to the polymerization mixture. The solvent and unreacted monomer were removed by distillation, and the inorganic salts were removed by centrifugation (yield 8.4%). The *st*-oligomers were prepared by the oligomerization of MMA with *t*-BuLi/Et₃Al in toluene at -78°C for 3 h ($[\text{Li}]/[\text{Al}] = 1/2 \text{ mol/mol}$, $[\text{MMA}]/[t\text{-Bu}] = 1/5 \text{ mol/mol}$, yield 93%).^{3,23,24}

Separation

The oligomer mixture was fractionated by HPLC on a column (0.72 × 50 cm) packed with silica gel using the butyl chloride and acetonitrile mixtures as an eluent (*n*-BuCl/CH₃CN = 96/4—80/20).⁴ A Shodex SE-11 RI-detector was used.

NMR Measurements

^1H and ^{13}C NMR spectra were measured in CDCl_3 at 55°C using a JEOL JNM-GX500 spectrometer. Spin-lattice relaxation times (T_1) were determined by the inversion recovery method in toluene- d_8 or in N,N -dimethylformamide- d_7 at 35°C using a sealed NMR sample tube under nitrogen atmosphere. Double-quantum filtered (DQF) ^1H COSY²⁵ and long-range ^{13}C - ^1H COSY with ^1H broadband decoupling (COLOC; correlation spectroscopy via long range couplings)²⁶ were performed by using the pulse sequences included in a JEOL PLEXUS (ver. 1.5) software package. The typical conditions for two-dimensional measurements are as follows. The DQF-COSY experiments employed a recycle time of 2.5 s, with 16 transients being collected for each t_1 value. A total of 512 spectra, each consisting of 1024 data points, were accumulated within a frequency range of 1600 Hz in both dimensions. The COLOC experiments employed a recycle time of 1.5 s, with 256

transients being collected for each t_1 value. A total of 128 spectra, each consisting of 8192 data points, were accumulated, covering 1600 Hz in F_1 dimension and 21000 Hz in F_2 dimension. The data matrix was zero-filled to 256×8192 points before the double Fourier transformation.

RESULTS AND DISCUSSION

^1H NMR Spectra and the Stereostructures of the Dimers to Octamers

Figure 1 shows HPLC traces of the *it*-oligomer (A) prepared with *t*-BuMgBr, and of the *st*-oligomer (B) prepared with *t*-BuLi/Et₃Al (trimer and tetramer fraction). Both oligomers consisted of two series of diastereomers **Mm**+**Mr**, and **Rm**+**Rr**. Each isomer was collected separately, and the stereostructure was determined by ^1H NMR spectroscopy. Figure 2 demonstrates the ^1H DQF-COSY of the *it*-hexamer **6mmmmm** measured in CDCl_3 . The assignment of the methyl

Figure 1. HPLC traces of the MMA trimers and tetramers obtained from polymerization by *t*-BuMgBr in toluene at -78°C (A) and by *t*-BuLi/Et₃Al in toluene at -78°C (B). Eluent, *n*-BuCl/CH₃CN = 96/4; column, Develosil 100-5, 0.46 (i.d.) $\times$ 25 cm; detector, RI.

Figure 2. 500 MHz ^1H DQF-COSY spectrum of the pure-isotactic hexamer of MMA ($6mmmmmm$) prepared with $t\text{-BuMgBr}$ in toluene at -78°C (CDCl_3 , 35°C).

and methylene proton signals can be made by the use of the network of correlation peaks beginning with the strong singlet at 0.85 ppm due to the t -butyl group and ending with the multiplet at 2.45 ppm due to the ω -end methine proton (H_ω). The *meso*/*racemo* assignment was based on the fact that the chemical shift between the nonequivalent methylene protons in an *in-chain* monomeric unit is larger for *meso* sequences than for *racemo* sequences

while that in the ω -end unit is larger for *racemo* sequences than for *meso* sequences.^{*1} This was confirmed by the X-ray crystallographic analysis of the *it*-trimer $3mm$.³ The assignment of the ^1H NMR signals and the determination of stereostructures for other oligomers were carried out in similar manners.

The chemical shifts of methylene protons of the *it*-oligomers **Mm** from dimer to octamer are displayed in simplified bar graphs in Figure

*¹ The *meso*/*racemo* assignment made by Fujishige^{7,8} and by Bessiere *et al.*¹⁶ is different from the present assignment with regard to the ω -end dyads.

3, together with those of highly isotactic PMMA. The monomeric units in the MMA

oligomers (6mmmmm for example) are numbered as follows.

Figure 3. ^1H NMR chemical shifts of the methylene protons in *it*-oligomers of MMA and in *it*-PMMA (CDCl_3 , 55°C).

Figure 4. ^1H NMR chemical shift of the methylene protons in *st*-oligomers of MMA and in *st*-PMMA (CDCl_3 , 55°C).

The proton signals due to α_1 - and ω_1 -units are observed apart from the other signals. On the other hand, the methyl and methylene protons in the monomeric units of the third and farther positions from the α - and ω -ends*² resonate at nearly the same positions with those of *it*-PMMA. A similar tendency was found in the *st*-oligomers **Rr** (Figure 4). Methylene protons of **Rr** are nonequivalent in the α_1 -, α_2 -, ω_1 - and ω_2 -units, while the nonequivalency almost disappeared in the third and farther monomeric units from the α - and ω -ends. The chemical shifts of the α_4 -CH₂ protons agreed with those of the methylene protons in highly syndiotactic PMMA (*rrr*-tetrad). These results indicate

that the magnetic environments in the third and farther monomeric units from the terminal groups are very similar to those in the polymer chain. Therefore, the pentamers and the higher oligomers should provide fairly good models in the NMR studies of stereoregular PMMA.

Determination of the Stereostructure of the ω -End Triad

The chemical shift of H_ω in the four diastereomer series **Mm**, **Mr**, **Rm**, and **Rr** does not depend on the degree of polymerization over the tetramers (Figure 5), and the chemical shift values for the **Mm**-, **Mr**-, **Rm**-, and **Rr**-hexamers are 2.445, 2.477, 2.359, and

*² The beginning of chain (the *t*-Bu group side) and the terminating end (the H_ω side) are designated as the α -end and the ω -end, respectively.

Table I. The range of chemical shifts between nonequivalent methylene protons (H_A and H_B) and the range of $^3J_{HH}$ coupling constants between the ω -end methine (H_ω) and methylene (H_a and H_b) protons in the MMA oligomers from the trimer to octamer^a

Stereostructure	$\alpha_2 \sim \omega_2$ units		ω -End unit	
	$\delta(H_A) - \delta(H_B)$	$\delta(H_a) - \delta(H_b)$	$^3J(H_a - H_\omega)$	$^3J(H_b - H_\omega)$
	ppm	ppm	Hz	Hz
$mm \cdots mm$ (Mm)	0.48 ~ 0.64	0.20 ~ 0.27	8.5 ~ 8.6	2.8 ~ 3.0
$mm \cdots mr$ (Mr)		0.42 ~ 0.48	8.2 ~ 8.4	3.4
$rr \cdots rr$ (Rr)	0.00 ~ 0.17	0.86 ~ 0.88	8.4 ~ 8.6	3.4
$rr \cdots rm$ (Rm)		1.00 ~ 1.03	8.0 ~ 8.2	3.7 ~ 3.9

^a In $CDCl_3$ at 35.0°C.

Figure 5. 1H NMR chemical shift of the ω_1 -CH protons in the MMA oligomers ($CDCl_3$, 55°C).

2.481 ppm, respectively. It is thus possible to determine the stereostructure of the ω -end triads by the chemical shift value of H_ω . The ω -end stereosequence can also be determined from the chemical shift between the nonequivalent ω_1 -CH₂ protons (Table I). The extent of nonequivalency is largest in the **Rm** series, and decreases discontinuously in the order of **Rr**, **Mr**, and **Mm**.

These rules should be applicable to any other oligomers and polymers of MMA which have a methine hydrogen at the ω -end of chain; such oligomers and polymers should be formed for example by disproportionation or chain transfer reaction in radical polymerization, or by living anionic polymerization terminated with acidic hydrogen.

Conformation of the MMA Oligomers in Solution

1H NMR spectroscopy provides significant informations regarding not only the configuration but also the conformation of the MMA oligomers. Schilling and his coworkers²⁷ observed in the 1H COSY spectrum of the *it*-PMMA a cross peak between the *mmmm* methyl resonance and the *mmm erythro* methylene resonance but not the *threo* resonance and interpreted the peak to arise from weak $^4J_{HH}$ -couplings (1–2 Hz) through a “W”-shaped four-bond path. Similar $^4J_{HH}$ -connectivities were reported by Cacioli *et al.*¹¹ and by Johns *et al.*¹² for the telomers of MMA [I] ($n=2-4$) prepared by radical polymerization with cobalt(II) tetraphenylporphyrin as chain transfer reagent.

In a similar manner, inspection of long-range $^4J_{HH}$ connectivities observed in 1H DQF-COSY (see Figure 2 for example) indicated the all-extended conformaiton of the *it*-oligomers (*tt* $\cdots$ *tt* form along the skeletal sequence *t*-Bu-(C-C)_n-CH₃). Among the two nonequivalent methylene protons in each monomeric unit, only one of them showed correlation peaks with the protons of the two neighboring

methyl groups due to $^4J_{\text{HH}}$ coupling. For instance, the $^4J_{\text{HH}}$ correlation was observed between CH_3 and H_A (one of the nonequivalent methylene protons resonating at the higher frequency) but not between CH_3 and H_B (the other one) in the ^1H DQF-COSY spectrum of *6mmmmmm* (Figure 2). This indicates the four-bond planar "W" arrangement between the respective protons in a highly preferred conformation of the MMA units.^{3,11,12,27}

The "W" arrangement in all the $\text{CH}_2\text{--C--CH}_3$ groups in a chain requires that one of the methylene protons and the methyl carbon should be in the *trans* state, that is, that the main chain backbone be in the repeated *tt* conformation. In the repeated *tt* conforma-

tion, H_A is flanked by carbonyl groups and H_B by methyl groups, which results in the larger chemical shift values of H_A than H_B .

The ^1H DQF-COSY of the *st*-oligomers also showed $^4J_{\text{HH}}$ connectivities between the methyl and methylene protons; the methylene protons in the monomeric units at the α_1 to α_3 and ω_1 to ω_3 -positions are nonequivalent even in the *st*-oligomers as mentioned before. In contrast to the *it*-oligomer, both the nonequivalent methylene protons in a monomeric unit of the *st*-oligomer showed $^4J_{\text{HH}}$ connectivity to only one of the two neighboring methyl groups. For example, H_A (one of the nonequivalent methylene protons resonating at the higher frequency) in the α_2 unit of the pure-syndiotactic pentamer *5rrrr* showed a correlation peak only with $\alpha_1\text{--CH}_3$, while H_B (the other one) in the same unit showed it only with $\alpha_2\text{--CH}_3$ (Figure 6). In the same way, H_A in the ω_2 -unit showed connectivity only to $\omega_2\text{--CH}_3$ whereas H_B to $\alpha_3\text{--CH}_3$. These observations are explained if we assume the all-extended conformation [III].

Preference of near *trans* conformation was also suggested by the conformational statistics on *it*- and *st*-PMMA.^{28,29}

The preferred conformation of the ω -end $\text{C--CH}_2\text{--C--H}_\omega$ arrays can be determined from the $^3J_{\text{HH}}$ vicinal coupling constants between H_ω and the $\omega_1\text{--CH}_2$ protons (Table I). The coupling constant between H_ω and H_a (the methylene proton resonates at the higher frequency) is about 8.4 Hz regardless of the stereostructure of the oligomers, which indicates that these two vicinal protons are nearly in *trans* (*t*) state. $^3J_{\text{HH}}$ between H_ω and H_b (the other methylene proton) of about 3.4 Hz indicates the *gauche* (*g*) arrangement of

the protons. Therefore the preferred conformation of the ω -end is the *trans* form along $\text{C--CH}_2\text{--C--CH}_3$ [IV] irrespective of the stereostructure of the ω -end dyad.

The *trans* form along the skeletal sequence $\text{C--CH}_2\text{--C--CO}_2\text{CH}_3$ [V] also accounts for the vicinal couplings mentioned above but is re-

Figure 6. ^1H DQF-COSY spectrum (methyl and methylene proton region) of the pure syndiotactic pentamer (5rrrr) prepared with *t*-BuLi/ Et_3Al in toluene at -78°C (CDCl_3 , 35°C , 500 MHz). The missing $^4J_{\text{HH}}$ connectivities are enclosed by dashed line(s).

jected for the following reasons: (1) both H_a and H_b should be in the *gauche* state with respect to $\omega_1\text{-CH}_3$ since $^4J_{\text{HH}}$ -connectivity was not detected between the methylene and methyl resonances, (2) conformational energy calculations on the *meso* and *racemo* dimers¹⁴ and X-ray crystallographic determination on 3mm^3 showed the conformation of [IV], (3) the chemical shifts of H_a and H_b can be reasonably explained if the ω -end conformation of [IV] is assumed.³ Fujishige⁷ reported similar values of the *vicinal* coupling constants for the MMA-dimers and trimers prepared with CH_3OLi ; however, the proposed ω -end conformation is different from ours.

^{13}C NMR Chemical Shifts of the MMA Oligomers

The complete assignment of the ^1H NMR signals permitted unambiguous assignment of

the ^{13}C NMR signals of the stereoregular oligomers by measuring the long-range ^{13}C - ^1H COSY (COLOC). In Figure 7 are shown the COLOC spectrum of 6mmmm as a typical example. Carbonyl carbons and quaternary carbons showed correlation peaks with methyl protons through $^3J_{\text{CH}}$ and $^2J_{\text{CH}}$ couplings, respectively. Methylene carbons showed $^3J_{\text{CH}}$ connectivity to the two neighboring methyl groups. Correlation peaks due to $^1J_{\text{CH}}$ coupling were also observed between the methyl carbons and protons. Thus, the signal assignment of all but methoxy carbons was achieved.

Figure 8 shows the ^{13}C NMR signals of all MMA oligomers studied. The signals attributable to the carbons in the α_1 - and ω_1 -units are apart from those in the other monomeric units, and their chemical shifts reached nearly constant values over trimer. The chemical shifts of the carbons in the monomeric units up to

¹H and ¹³C NMR Spectra of the MMA Oligomers

Figure 7. 125 MHz long-range ¹³C-¹H COSY (COLOC) spectrum of the pure-isotactic hexamer (6mmmm) (CDCl₃, 55°C).

Table II. Parameters for the calculation of ¹³C NMR chemical shifts (δ_{calc}) of the isotactic and syndiotactic MMA-oligomers^a

Carbon	Shift parameters R , $P_x(i)$, $P_\omega(j)$ /ppm								
	R	$P_x(1)$	$P_x(2)$	$P_x(3)$	$P_x(\geq 4)$	$P_\omega(\geq 4)$	$P_\omega(3)$	$P_\omega(2)$	$P_\omega(1)$
Isotactic (<i>mm...m</i>)									
C=O	176.51	1.08	0.13	0.03	0.00	0.00	0.22	0.53	1.18
CH ₂	52.26	2.77	1.54	-0.14	0.00	0.00	0.47	-0.76	-9.43
Quat.	45.77	0.28	0.00	0.03	0.00	0.00	-0.16	-0.32	-9.17 ^b
CH ₃	22.18	-0.16	0.12	-0.11	0.00	0.00	-0.72	0.33	-2.29
Syndiotactic (<i>rr...r</i>)									
C=O	177.71	0.51	0.51	0.30	0.00	0.00	0.09	-0.82	-0.97
CH ₂	54.29	1.94	0.01	0.21	0.00	0.00	0.47	-2.92	-7.61
Quat.	44.89	0.53	-0.12	0.01	0.00	0.00	0.01	0.01	-9.52 ^b
CH ₃	17.10	2.97	0.12	-0.28	0.00	0.00	-0.33	1.35	2.33

^a The chemical shift (δ_{calc} , in CDCl₃ at 55°C) of the carbon in the monomeric unit at the i -th position from the α -end and the j -th position from the ω -end is calculated by $\delta_{\text{calc}} = R + P_x(i) + P_\omega(j)$.

^b Parameter for the ω -end methine carbon.

the third monomeric units from the terminal groups seemed to be influenced by the structures of the end groups. The signals due to the

α_4 - and ω_4 -units roughly agreed with those of PMMAs.

According to the above considerations, we

Figure 8. 125 MHz ^{13}C NMR spectra of the MMA oligomers from dimer to octamer and of the *it*- and *st*-PMMA (CDCl₃, 55°C).

Table III-1. ¹³C chemical shifts (δ_{obs}) and the difference between calculated (δ_{calc}) and observed values for the MMA oligomers (carbonyl carbons)

Oligomer	$\delta_{\text{obs}} (\delta_{\text{calc}} - \delta_{\text{obs}}) / \text{ppm}$							
	α_1	α_2	α_3	α_4	ω_4	ω_3	ω_2	ω_1
2m	177.88 (+0.24)							177.60 (+0.22)
3mm	177.79 (+0.02)	177.21 (-0.04)						177.83 (-0.11)
4mmm	177.54 (+0.05)	176.80 (+0.06)					177.10 (-0.03)	177.71 (-0.02)
5mmmm	177.56 (+0.03)	176.78 (-0.14)	176.61 (+0.15)				177.04 (0.00)	177.67 (+0.02)
6mmmmm	177.54 (+0.05)	176.60 (+0.04)	176.57 (-0.03)			176.71 (+0.02)	176.99 (+0.05)	177.63 (+0.06)
7mmmmmm	177.54 (+0.05)	176.64 (0.00)	176.52 (+0.02)	176.59 (-0.08)		176.69 (+0.04)	176.99 (+0.05)	177.64 (+0.05)
8mmmmmmm	177.59 (0.00)	176.64 (0.00)	176.54 (0.00)	176.59 (-0.08)	176.66 (-0.15)	176.73 (0.00)	177.04 (0.00)	177.69 (0.00)
2r	177.60 (-0.20)							177.17 (+0.08)
3rr	177.35 (+0.96)	178.47 (-1.07)						176.87 (+0.17)
4rrr	178.21 (+0.01)	178.45 (-0.14)					176.91 (+0.28)	176.74 (0.00)
5rrrr	178.22 (0.00)	178.23 (-0.01)	178.03 (+0.07)				176.92 (-0.03)	176.74 (0.00)
6rrrrr	178.21 (+0.01)	178.23 (-0.01)	178.03 (-0.02)			177.80 (0.00)	176.88 (+0.01)	176.73 (+0.01)
7rrrrrr	178.21 (+0.01)	178.21 (+0.01)	178.01 (0.00)	177.81 (-0.10)		177.80 (0.00)	176.88 (+0.01)	176.73 (+0.01)
8rrrrrrr	178.22 (0.00)	178.22 (0.00)	178.01 (0.00)	177.82 (-0.11)	177.78 (-0.07)	177.80 (0.00)	176.89 (0.00)	176.74 (0.00)

calculated the ¹³C chemical shifts of the oligomers by the following equations:

$$\delta_{\text{calc}} = R + P_{\alpha}(i) + P_{\omega}(j)$$

where R is the standard value (ppm) for the carbon of interest, and $P_{\alpha}(i)$ and $P_{\omega}(j)$ are the shift parameters for the monomeric unit to which the carbon belongs (Table II). The chemical shifts for the *it*- and *st*-PMMA (tetrad and pentads) were employed as R values for the corresponding oligomer series (**Mm**, and **Rr**). $P_{\alpha}(\geq 4)$ and $P_{\omega}(\geq 4)$ were set at zero since the chemical shifts of the carbons in the fourth and farther monomeric unit were considered to be unaffected by the end-groups. $P_{\alpha}(i)$ for the monomeric unit at the i -th po-

sition from the α -end and $P_{\omega}(j)$ for the monomeric unit at the j -th position from the ω -end were evaluated from chemical shifts of the octamers. For instance, $P_{\alpha}(2)$ for the carbonyl carbon of **Mm** series (0.13 ppm) was defined as the difference in chemical shift values of the carbonyl carbon in the *mmmm* pentad of *it*-PMMA (176.51 ppm) and that in the α_2 -unit of *8mmmmmmmm* (176.64 ppm). $P_{\omega}(3)$ for the carbonyl carbon of **Mm** series (0.22 ppm) was defined likewise based on the shift value of the ω_3 -unit of *8mmmmmmmm* (176.73 ppm). The chemical shift value for the α_2 -carbonyl carbon of the *it*-tetramer *4mmm*, for example, is thus given by the sum of these three parameters:

Table III-2. ^{13}C chemical shifts (δ_{obs}) and the difference between calculated (δ_{calc}) and observed values for the MMA oligomers (methylene carbons)

Oligomer	$\delta_{\text{obs}} (\delta_{\text{calc}} - \delta_{\text{obs}}) / \text{ppm}$							
	α_1	α_2	α_3	α_4	ω_4	ω_3	ω_2	ω_1
2m	53.62 (+0.65)							45.90 (-1.53)
3mm	55.25 (+0.25)	53.09 (-0.05)						42.42 (+0.27)
4mmm	54.99 (+0.04)	53.68 (+0.59)					51.30 (+0.06)	42.66 (+0.17)
5mmmm	54.96 (+0.07)	53.81 (-0.01)	52.51 (+0.08)				51.30 (+0.20)	42.87 (-0.04)
6mmmmm	55.01 (+0.02)	53.72 (+0.08)	52.12 (0.00)			52.57 (+0.16)	51.40 (+0.10)	42.85 (-0.02)
7mmmmmm	55.02 (+0.01)	53.77 (+0.03)	52.17 (-0.05)	52.03 (+0.23)		52.70 (+0.03)	51.40 (+0.10)	42.82 (+0.01)
8mmmmmm	55.03 (0.00)	53.80 (0.00)	52.12 (0.00)	52.10 (+0.16)	52.10 (+0.16)	52.73 (0.00)	51.50 (0.00)	42.83 (0.00)
2r	52.67 (+0.64)							46.18 (+0.51)
3rr	56.21 (+0.49)	50.67 (+0.71)						46.83 (+0.06)
4rrr	56.21 (+0.02)	54.21 (+0.56)					51.33 (+0.25)	46.68 (0.00)
5rrrr	56.23 (0.00)	54.25 (+0.05)	54.68 (+0.29)				51.36 (+0.01)	46.68 (0.00)
6rrrrr	56.21 (+0.02)	54.30 (0.00)	54.40 (+0.10)			54.71 (+0.05)	51.36 (+0.01)	46.67 (+0.01)
7rrrrrr	56.22 (+0.01)	54.29 (+0.01)	54.44 (+0.06)	54.44 (-0.15)		54.76 (0.00)	51.37 (0.00)	46.68 (0.00)
8rrrrrrr	56.23 (0.00)	54.30 (0.00)	54.50 (0.00)	54.50 (-0.21)	54.50 (-0.21)	54.76 (0.00)	51.37 (0.00)	46.68 (0.00)

Table III-3. ¹³C chemical shifts (δ_{obs}) and the difference between calculated (δ_{calc}) and observed values for the MMA oligomers (quaternary carbons)

Oligomer	$\delta_{\text{obs}} (\delta_{\text{calc}} - \delta_{\text{obs}}) / \text{ppm}$							
	α_1	α_2	α_3	α_4	ω_4	ω_3	ω_2	ω_1^a
2m	45.90 (-0.17)							36.26 (+0.34)
3mm	45.63 (+0.26)	45.58 (-0.13)						36.69 (-0.06)
4mmm	45.97 (+0.08)	45.63 (-0.02)					45.41 (+0.07)	36.62 (-0.02)
5mmmm	46.01 (+0.04)	45.75 (+0.02)	45.59 (+0.05)				45.42 (+0.03)	36.57 (+0.03)
6mmmmm	46.01 (+0.04)	45.76 (+0.01)	45.73 (+0.07)			45.57 (+0.04)	45.42 (+0.03)	36.56 (+0.04)
7mmmmm	46.02 (+0.03)	45.76 (+0.01)	45.76 (+0.04)	45.70 (+0.07)		45.57 (+0.04)	45.42 (+0.03)	36.56 (+0.04)
8mmmmmm	46.05 (0.00)	45.77 (0.00)	45.80 (0.00)	45.80 (-0.03)	45.80 (-0.03)	45.61 (0.00)	45.45 (0.00)	36.60 (0.00)
2r	45.62 (-0.19)							35.66 (-0.41)
3rr	45.37 (+0.06)	44.93 (-0.15)						35.42 (-0.04)
4rrr	45.45 (-0.03)	44.84 (-0.06)					44.91 (0.00)	35.37 (0.00)
5rrrr	45.42 (0.00)	44.79 (-0.02)	44.88 (+0.03)				44.87 (+0.03)	35.37 (0.00)
6rrrrr	45.42 (0.00)	44.77 (0.00)	44.90 (0.00)			44.90 (0.00)	44.90 (0.00)	35.36 (+0.01)
7rrrrrr	45.42 (0.00)	44.77 (0.00)	44.90 (0.00)	44.90 (-0.01)		44.90 (0.00)	44.90 (0.00)	35.36 (+0.01)
8rrrrrrr	45.42 (0.00)	44.77 (0.00)	44.90 (0.00)	44.90 (-0.01)	44.90 (-0.01)	44.90 (0.00)	44.90 (0.00)	35.37 (0.00)

^a Chemical shift of the ω -end methine carbon.

$$R + P_x(2) + P_\omega(3) = 176.51 + 0.13 + 0.22 \\ = 176.86 \text{ (ppm).}$$

The observed value (δ_{obs}) was 176.80 ppm. This scheme was applied to all carbons of the oligomers and the results are shown in Table III. The agreement between the observed and calculated values should be considered fairly well since the standard deviation of ¹³C chemical shift measurements for oligomers was evaluated as 0.02–0.04 ppm.³⁰ Particularly, the agreement over the pentamer was excellent for all the carbons.

The shift parameters may be widely used for the assignment of the ¹³C NMR signals due to the “terminal units” in PMMA, although the

Figure 9. ¹³C- T_1 values for the pure-isotactic and pure-syndiotactic hexamers of MMA (6mmmmm and 6rrrrr) and for the *it*- and *st*-PMMA measured in toluene- d_8 at 35°C (125 MHz).

Table III-4. ^{13}C chemical shifts (δ_{obs}) and the difference between calculated (δ_{calc}) and observed values for the MMA oligomers (α -methyl carbons)

Oligomer	$\delta_{\text{obs}} (\delta_{\text{calc}} - \delta_{\text{obs}})/\text{ppm}$							
	α_1	α_2	α_3	α_4	ω_4	ω_3	ω_2	ω_1
2m	21.67 (+0.68)							19.51 (+0.50)
3mm	22.69 (-1.39)	21.19 (+1.44)						19.85 (-0.07)
4mmm	21.95 (+0.07)	21.57 (+0.01)					22.59 (-0.19)	19.89 (0.00)
5mmmm	22.07 (-0.05)	22.14 (+0.16)	21.57 (-0.22)				22.49 (+0.02)	19.87 (+0.02)
6mmmmm	22.04 (-0.02)	22.35 (-0.05)	22.11 (-0.04)			21.47 (-0.01)	22.47 (+0.04)	19.86 (+0.03)
7mmmmmm	22.03 (-0.01)	22.34 (-0.04)	22.04 (+0.03)	22.31 (-0.13)		21.44 (+0.02)	22.48 (+0.03)	19.86 (+0.03)
8mmmmmmmm	22.02 (0.00)	22.30 (0.00)	22.07 (0.00)	22.30 (-0.12)	22.30 (-0.12)	21.46 (0.00)	22.51 (0.00)	19.89 (0.00)
2r	22.07 (-0.65)							20.14 (-0.59)
3rr	20.11 (-0.37)	18.39 (+0.18)						19.89 (-0.74)
4rrr	20.06 (+0.01)	17.29 (-0.40)					18.52 (-0.35)	19.46 (-0.03)
5rrrr	20.07 (0.00)	17.23 (-0.01)	16.85 (-0.36)				18.44 (+0.01)	19.42 (+0.01)
6rrrrr	20.07 (0.00)	17.22 (0.00)	16.82 (0.00)			16.79 (-0.02)	18.45 (0.00)	19.42 (+0.01)
7rrrrrr	20.07 (0.00)	17.22 (0.00)	16.83 (-0.01)	16.80 (+0.30)		16.77 (0.00)	18.45 (0.00)	19.42 (+0.01)
8rrrrrrr	20.07 (0.00)	17.22 (0.00)	16.82 (0.00)	16.80 (+0.30)	16.80 (+0.30)	16.77 (0.00)	18.45 (0.00)	19.43 (0.00)

terminal group at the α -end depends on the initiating species employed in the polymerization.

The ^{13}C Spin-Lattice Relaxation Times (T_1) of the Oligomers

The ^{13}C - T_1 values for the *it*-hexamer (6mmmm) and *st*-hexamer (6rrrrr) were measured in toluene- d_8 at 35°C (125 MHz). The results are shown in Figure 9. The T_1 s of the carbonyl, methylene, quaternary and methyl carbons decreased gradually as the monomeric units came apart from the terminal groups. However, the T_1 values were much longer than those for PMMA, even in the α_3 or ω_3 monomeric unit in the hexamers. The T_1 values for

the *st*-hexamer were smaller than those for the *it*-hexamer as to the corresponding carbon of the corresponding monomeric unit. This suggests lower segmental mobility of the *st*-oligomers than that of the *it*-oligomers.

^{13}C - T_1 measurements were also carried out on a 1:1 mixture of 6mmmm and 6rrrrr in toluene- d_8 or in *N,N*-dimethylformamide- d_7 at 35°C. However, the T_1 values for the respective carbons (including methoxy carbons; $T_1 = 2.1$ —2.8 s for 6mmmm and 1.5—2.8 s for 6rrrrr) showed little difference from those measured in the solutions of individual *it*- or *st*-hexamer, indicating no appreciable interaction between the *it*- and *st*-hexamers (stereo-complex formation) under these conditions.

Further studies are now under way on this problem.

Acknowledgments. A part of this work was supported by a Grant-in-Aid for Scientific Research (No. 61430022) from the Ministry of Education, Science, and Culture of Japan.

REFERENCES

1. K. Hatada, K. Ute, K. Tanaka, M. Imanari, and N. Fujii, *Polym. J.*, **19**, 425 (1987).
2. K. Hatada, K. Ute, K. Tanaka, and T. Kitayama, *Polym. J.*, **19**, 1325 (1987).
3. K. Ute, T. Nishimura, Y. Matsuura, and K. Hatada, *Polym. J.*, **21**, 231 (1989).
4. Y. Okamoto, E. Yashima, T. Nakano, and K. Hatada, *Chem. Lett.*, 759 (1987).
5. G. Wulff, R. Szczepan, and A. Steigel, *Tetrahedron Lett.*, **27**, 1991 (1986).
6. R. A. Volpe, T. E. Hogen-Esch, A. H. E. Müller, and F. Gores, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **28**(2), 423 (1987).
7. S. Fujishige, *Makromol. Chem.*, **177**, 375 (1976).
8. S. Fujishige, *Makromol. Chem.*, **179**, 2251 (1978).
9. A. Kimura, T. Kodaira, and M. Hamashima, *Polym. J.*, **15**, 293 (1983).
10. A. Kimura, and M. Hamashima, *Polym. J.*, **18**, 21 (1986).
11. P. Cacioli, D. G. Hawthorne, S. R. Johns, D. H. Solomon, E. Rizzardo, and R. I. Willing, *J. Chem. Soc., Chem. Commun.*, 1355 (1985).
12. S. R. Johns, R. I. Willing, and D. A. Winkler, *Makromol. Chem., Rapid Commun.*, **8**, 17 (1987).
13. G. D. Fallon, M. L. Felsbourg, K. A. Holland, and I. D. Rae, *Aust. J. Chem.*, **40**, 501 (1987).
14. K. Ute, T. Nishimura, K. Hatada, Y. Matsuura, and K. Sakaguchi, *Polym. Prepr. Jpn.*, **37**, 2480 E432 (1988).
15. A. Bledzki, H. Balard, and D. Braun, *Makromol. Chem.*, **189**, 2807 (1988).
16. J.-M. Bessiere, B. Boutevin, and L. Sarraf, *J. Polym. Sci., A*, **26**, 3275 (1988).
17. T. Konishi, Y. Tamai, M. Fujii, Y. Einaga, and H. Yamakawa, *Polym., J.*, **21**, 329 (1989).
18. M. A. Buese, and T. E. Hogen-Esch, *Macromolecules*, **17**, 119 (1984).
19. O. Vogl, K. Ute, T. Nishimura, F. Xi, F. Vass, and K. Hatada, *Macromolecules*, in press.
20. K. Ute, T. Nishimura, K. Hatada, F. Xi, F. Vass, and O. Vogl, *Makromol. Chem.*, in press.
21. K. Hatada, K. Ute, K. Tanaka, T. Kitayama, and Y. Okamoto, *Polym. J.*, **17**, 977 (1985).
22. K. Hatada, K. Ute, K. Tanaka, Y. Okamoto, and T. Kitayama, *Polym. J.*, **18**, 1037 (1986).
23. T. Kitayama, T. Shinozaki, E. Masuda, M. Yamamoto, and K. Hatada, *Polym. Bull.*, **20**, 505 (1988).
24. T. Kitayama, T. Shinozaki, E. Masuda, M. Yamamoto, and K. Hatada, *Makromol. Chem. Suppl.*, **15**, 167 (1989).
25. U. Piantini, O. W. Sørensen, and R. R. Ernst, *J. Am. Chem. Soc.*, **104**, 6800 (1982).
26. H. Kessler, C. Crisinger, J. Zarbock, and H. R. Loosli, *J. Magn. Reson.*, **50**, 331 (1984).
27. F. C. Schilling, F. A. Bovey, M. D. Bruch, S. A. Kozłowski, *Macromolecules*, **18**, 1418 (1985).
28. M. Vacatello, and P. J. Flory, *Macromolecules*, **19**, 405 (1986).
29. P. R. Sundararajan, *Macromolecules*, **19**, 415 (1986).
30. R. Chûjô, K. Hatada, R. Kitamaru, T. Kitayama, H. Sato, and Y. Tanaka, *Polym. J.*, **19**, 413 (1987).