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Determination of Stereochemical Compositions of Oligo- and Poly(α-methylstyrene)s by ^{1}H and ^{13}C NMR

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ABSTRACT: A set of oligo- and poly(α-methylstyrene) samples were prepared by anionic polymerization, giving particular attention to the polymerization temperature and the initial monomer concentration. The samples were characterized by ^{1}H and ^{13}C NMR spectroscopy and also by three kinds of two-dimensional NMR spectroscopy. It is shown that they have almost the same value 0.72 ± 0.01 of the fraction f_r of racemo diads independent of molecular weight, indicating that they are adequate for a study of dilute polymer solutions within the new framework of polymer solution science based on the helical wormlike chain model.

KEY WORDS Poly(α-methylstyrene) / α-Methylstyrene Oligomer / ^{1}H Nuclear Magnetic Resonance / ^{13}C Nuclear Magnetic Resonance / 2D Nuclear Magnetic Resonance / Gauge-Independent Atomic Orbital Method / Modified Neglect of Diatomic Overlap Method / Stereochemical Composition / Helical Wormlike Chain /

Since the late 1980s there have been made a series of experimental studies[1] of dilute solution behavior of some flexible polymers and their oligomers in the unperturbed Θ state on the basis of the helical wormlike (HW) chain model.[2,3] Concerning their chain stiffness and local chain conformations, very remarkable is the result that among the polymers studied so far, atactic poly(methyl methacrylate) (a-PMMA) with the fraction of racemo diads $f_r = 0.79$ has the largest chain stiffness and the strongest helical nature.[2,4] It turns out that the a-PMMA chain tends to retain rather large and clearly distinguishable helical portions in dilute solution. Such a remarkable feature of this chain may be regarded as arising from the inequality of the two successive skeletal bond angles in its main chain and the predominance of the *trans–trans* conformation for its racemo diads.[4,5]

Now poly(α-methylstyrene) (PαMS), which is a disubstituted asymmetric polymer, belongs to the same category as PMMA, and therefore the former chain with large f_r may be considered to be similar to the latter in dilute solution behavior. An analysis[6] of the data for the rotational isomeric state model[7] supports this expectation. On the other hand, there have been a number of experimental investigations of PαMS.[8—12] Unfortunately, however, all of them have used the samples with rather large molecular weight M ($\gtrsim 5 \times 10^4$) and the data obtained have been analyzed on the basis of the Gaussian chain model[13] or the Kratky–Porod wormlike chain model,[2,14] so that they do not give any information of interest to us about the local chain conformations of PαMS in dilute solution. In addition, there are some problems in the stereochemical compositions of the samples used, as mentioned below. Under these circumstances, it is desirable to pursue further an experimental study of dilute solution properties of PαMS in the same spirit as in the previous studies.[1] In this work as a first step, we prepare some PαMS samples suitable for the purpose above and determine their stereochemical compositions.

As often mentioned in the previous studies,[1] the dilute solution behavior of mono- and disubstituted asymmetric polymers, including PαMS, remarkably depends on the stereochemical composition as specified by f_r, so that the samples with fixed f_r should be used for such a study. Furthermore, it is suitable for the present purpose to prepare the samples whose f_r values are as large as possible. Then the regulation of f_r requires some remarks. Kato *et al.*[8] and Elgert and Seiler[15] found that f_r of a PαMS sample polymerized under a certain condition depends on M. This implies that the polymerization condition must be changed with M in order to prepare the samples with fixed f_r. Thus, by trial and error, we search a proper set of conditions on the basis of the data reported by Wicke and Elgert[16] for the dependence of f_r on the polymerization temperature and the initial monomer concentration.

In this connection, it is pertinent here to make further a remark in anticipation of the results. If the diad distribution in a polymer chain is Bernoullian, its stereochemical composition may be completely specified by f_r. This is the case with atactic polystyrene (a-PS)[17] and a- and isotactic (i-) PMMAs[18,19] previously studied but not with PαMS in the present work. For a complete specification of the stereochemical composition of PαMS, we must use the fractions of stereoisomeric sequences in the triad. However, we finally specify its composition only by f_r as before, for convenience.

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EXPERIMENTAL

Materials

All the PαMS samples were prepared by living anionic polymerization except the sample named 20538-2, which is a commercial one from Polymer Laboratories Ltd. The polymerization was carried out in tetrahydrofuran with *s*-butyllithium as an initiator. As mentioned in the Introduction, the polymerization conditions, *i.e.*, the polymerization temperature T_p and the initial monomer concentration $[M]_0$, required special attention. Elgert and Seiler[15] showed that f_r of a polymerized sample increases with decreasing M under the condition of constant T_p. Further, Wicke and Elgert[16] showed that f_r of a polymerized sample with a given M increases with increasing T_p and that it may also be somewhat dependent on $[M]_0$. Considering these facts, we changed T_p from -70 to -40℃ with increasing M so that f_r had a given constant value for all the polymerized samples. As for $[M]_0$, it was kept at *ca.* 0.6 mol L^{-1} in all cases.

The polymerization was terminated by adding methanol after the reaction proceeded for *ca.* 1 min for $M \lesssim 1\times10^3$, *ca.* 5 min for $1\times10^3 \lesssim M \lesssim 5\times10^4$, *ca.* 20 min for $5\times10^4 \lesssim M \lesssim 5\times10^5$, and *ca.* 2 h for $M \gtrsim 5\times10^5$. The initiating chain end of each original PαMS sample thus obtained is a *s*-butyl group and the other end is a hydrogen atom. We note that although the detailed information about the polymerization of the commercial sample could not be obtained, its initiating and terminating chain ends may be considered to be an *n*-butyl group and a hydrogen atom, respectively.

The original synthesized and commercial samples were separated into fractions by preparative GPC for the test samples with $M \lesssim 2\times10^3$ and by fractional precipitation using benzene as a solvent and methanol as a precipitant for those with $M \gtrsim 2\times10^3$.

The values of the weight-average molecular weight M_w and the ratio of M_w to the number-average molecular weight M_n determined for the test samples thus obtained are given in Table I along with those of T_p. From analytical GPC measurements, the oligomer samples OAMS2 through OAMS7 were found to be completely monodisperse. The samples OAMS2 and OAMS3 were confirmed to be the dimer and trimer, respectively, by ^{1}H and ^{13}C NMR spectroscopy (see the next section), and the samples OAMSx (x=4—7), to be the x-mer, respectively, by analytical GPC. The values of M_w for the samples OAMS8 through AMS320 were determined from light scattering (LS) measurements, and those of M_w/M_n for these samples except AMS320, from analytical GPC. The details of LS measurements will be reported in a forthcoming paper.[20] We note that the value of M_w/M_n for AMS320 could not be determined with high accuracy because of the lack of the GPC calibration curve in the necessary range. The three groups of the samples OAMS 2 through OAMS13, OAMS19 and OAMS25, and OAMS 33 and OAMS38 are the fractions from three original samples, respectively, and the sample AMS40 is a fraction from the commercial sample 20538-2. As seen from the values of M_w/M_n, all the samples except AMS320 are sufficiently narrow in molecular weight distribution.

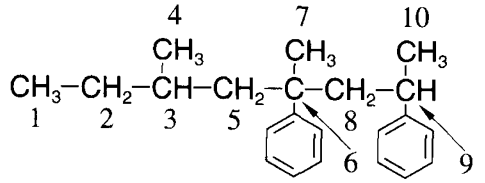

Figure 1. Chemical structure of the dimer with the numbering system.

Reversed-Phase HPLC

For an NMR analysis, small amounts of the dimer sample OAMS2 and the trimer sample OAMS3 were separated into their stereoisomers, respectively, by reversed-phase high-performance liquid chromatography (HPLC) using Develosil ODS-HG-5 (10 mm i.d.$\times$ 250 mm) as a stationary phase and a mixture of acetonitrile/dichloromethane/water (8/1/1, volume ratio) as a mobile phase at a flow rate of 3.5 ml min^{-1}.

^{1}H and ^{13}C NMR

The NMR spectra were recorded on a JEOL JMN GX-400 spectrometer in deuterated chloroform at 50℃. The relative chemical shifts δ_r of ^{1}H and ^{13}C signals of a test sample referred to the ^{1}H and ^{13}C signals, respectively, of chloroform were measured and then converted to the chemical shifts in the tetramethylsilane (TMS) scale $\delta = \delta_r + \Delta$ with Δ =7.24 and 77.00 ppm, respectively. The instrument was operated with frequencies of 399.8 MHz for ^{1}H and 100.5 MHz for ^{13}C. Measurements of the one-dimensional (1D) ^{1}H NMR spectra were made using an rf pulse angle of 90° with a pulse repetition time of 30 s for the samples with $M_w < 5\times10^3$ and of 15 s for the samples with $M_w > 5\times10^3$. The 1D ^{13}C NMR experiments, including the distortionless enhancement by polarization transfer (DEPT) experiments, were performed with a pulse repetition time of 9 s. For a quantitative analysis of ^{13}C in the 1D ^{13}C NMR experiments, the nuclear Overhauser effect was eliminated by the gated decoupling method. The spectral width was 4000 Hz for ^{1}H and 20000 Hz for ^{13}C.

In the ^{1}H two-dimensional correlation spectroscopy (COSY) experiments, we adopted a recycle time of 1.2 s with 32 transients collected for each value of the evolution period t_1. A total of 512 spectra, each consisting of 1024$\times$1024 data points, were accumulated with a spectral width of 3200 Hz in both the t_1 and t_2 dimensions, where t_2 is the detection period. Both in the ^{1}H-detected heteronuclear single quantum coherence (HSQC) experiments and in the ^{1}H-detected heteronuclear multiple bond coherence (HMBC) experiments, we adopted a recycle time of 1.3 s with 64 transients collected for each value of t_1. A total of 512 spectra, each consisting of 2048 $\times$1024 data points, were accumulated with a spectral width of 14000 and 3200 Hz in the t_1 and t_2 dimensions, respectively.

RESULTS AND DISCUSSION

Dimer

Figure 1 shows the chemical structure of the dimer with the numbering system for the hydrogen and carbon atoms in the main chain and the side methyl groups.

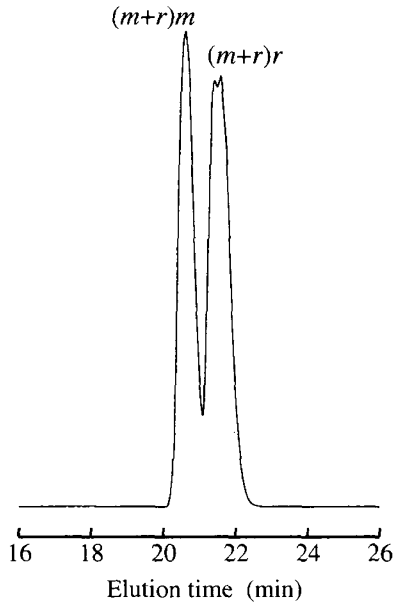

Figure 2. HPLC trace of the dimer sample OAMS2.

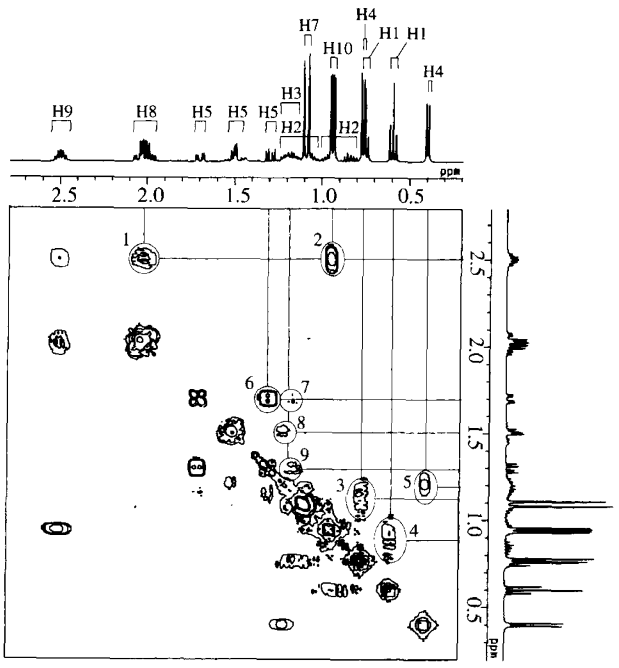

Figure 3. ^{1}H COSY and ^{1}H NMR spectra in the alkyl region for the first fraction of the dimer sample OAMS2.

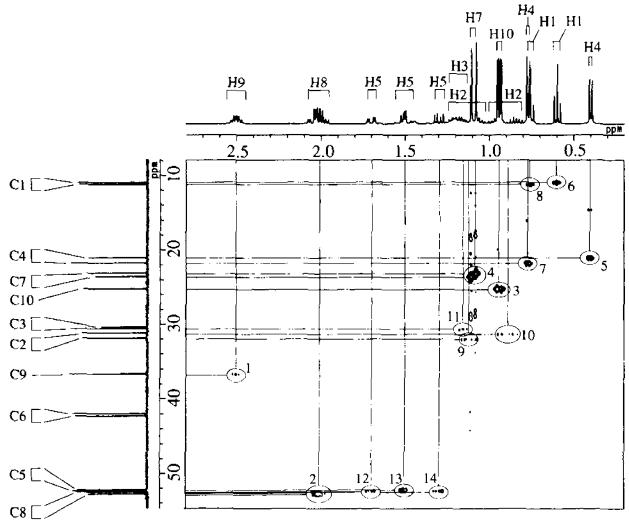

Figure 4. HSQC and ^{13}C NMR spectra in the alkyl region for the first fraction of the dimer sample OAMS2.

The xth carbon atom is designated by Cx, and the hydrogen atom(s) bonded to it, by Hx ($x=1, \cdots, 9$). Since the dimer has the three asymmetric carbons C3, C6, and C9, the dimer sample OAMS2 may be considered to be composed of the four stereoisomers denoted by *rr*, *rm*, *mr*, and *mm*, where *r* and *m* denote the racemo and meso diads, respectively, and the first and second letters (*r* or *m*) indicate the stereoisomeric states of the C3–C5–C6 and C6–C8–C9 diads, respectively. For convenience, the stereoisomeric state of the C3–C5–C6 diad is assumed to be *m* if both C4 and C7 are on the same side of the backbone in the planar *trans* conformation, and *r* otherwise.

In order to reduce the complexity of NMR spectra for the dimer sample OAMS2, a mixture of the four stereoisomers, we separated its small amount into two fractions by reversed-phase HPLC, its trace being shown in Figure 2. They are referred to as the first and second fractions, respectively, in order of elution time. In what follows, we first assign the signals in the ^{1}H and ^{13}C NMR spectra to Hx and Cx, respectively, for the first and second fractions, and then determine their assignments to the stereoisomers by a comparison of the observed chemical shifts with the quantum-chemical theoretical values. In anticipation of the results, we note that the first fraction is composed of the two stereoisomers *mm* and *rm*, which we abbreviate to (*m*+*r*)*m*, and that the second is composed of *mr* and *rr*, which we abbreviate to (*m*+*r*)*r*.

In Figures 3 and 4 are shown the ^{1}H COSY and ^{1}H NMR spectra and the HSQC and ^{13}C NMR spectra, respectively, all in the alkyl region, for the first fraction. Since the signal from the benzyl proton (H9) must appear in the lowest field among those from the aliphatic protons under consideration, the multiplet located at 2.45 to 2.53 ppm in the ^{1}H NMR spectrum may be assigned to H9. From the correlation peaks 1 and 2 in the ^{1}H COSY spectrum and from the fact that the signal from the methylene protons appears in the field lower than that from the methyl protons, the two signals in the ^{1}H NMR spectrum at 1.95 to 2.07 ppm and at 0.93 to 0.95 may be assigned to H8 and H10, respectively. From the correlation peaks 1, 2, and 3 in the HSQC spectrum, the three signals in the ^{13}C NMR spectrum at 36.68 and 36.74 ppm, at 52.57 and 52.87 ppm, and at 25.28 and 25.29 ppm may be assigned to C9, C8, and C10, respectively, these assignments being consistent with the result from the DEPT spectrum that the first and third signals are due to the methyl and/or methine carbons, and the second, to the methylene ones. (The DEPT spectrum is not explicitly shown here.) Since the quaternary ^{13}C (C6) and the protons (H7) in the methyl group bonded to it have no correlation peak in the HSQC and ^{1}H COSY spectra, respectively, the signal in the ^{13}C NMR spectrum at 42.02 and 42.33 ppm and that in the ^{1}H NMR spectrum at 1.08 and 1.10 ppm may be as-

signed to C6 and H7, respectively. From the correlation peak 4 in the HSQC spectrum, the signal in the ^{13}C NMR spectrum at 23.12 and 23.62 ppm may then be assigned to C7.

From the assignments above in the ^{13}C NMR spectrum, it is seen that each of the signals from C6, C7, and C8 consists of two peaks clearly distinguishable from each other, while this is not the case with those from C9 and C10. It may then be concluded that the first fraction is composed of two stereoisomers which have the different stereoisomeric states for the C3–C5–C6 diad but have the same one for the C6–C8–C9 diad; that is, the first fraction is $(m+r)m$ or $(m+r)r$ and the second is the counterpart.

The signals from the methyl protons (H1, H4) in the *s*-butyl group may be expected to appear in the highest field among those from the aliphatic protons under consideration. Thus the doublet at 0.39 and 0.41 ppm and the triplet at 0.57 to 0.61 ppm in the ^1H NMR spectrum may be assigned to H4 and H1, respectively, from their multiplicities. From the correlation peaks 5 and 6 in the HSQC spectrum, the signals in the ^{13}C NMR spectrum at 21.10 and 10.97 ppm may be assigned to C4 and C1, respectively. The peak at 21.79 ppm just adjacent to the one at 21.10 ppm may be considered to be also the signal from C4 in the other stereoisomer, and therefore the doublet in the ^1H NMR spectrum at 0.76 and 0.78 ppm may be assigned to H4 from the correlation peak 7 in the HSQC spectrum. Similarly, the peak in the ^{13}C NMR spectrum at 11.24 ppm may be assigned to C1, and then the triplet in the ^1H NMR spectrum at 0.74 to 0.77 ppm may be assigned to H1 from the correlation peak 8 in the HSQC spectrum. It has been found from the long-range heteronuclear correlation peaks in the HMBC spectrum, although not shown here, that the H1 triplet at 0.57 to 0.61 ppm, the H4 doublet at 0.76 and 0.78 ppm, the C1 peak at 10.97 ppm, and the C4 peak at 21.79 ppm belong to one stereoisomer, and the H1 triplet at 0.74 to 0.77 ppm, the H4 doublet at 0.39 and 0.41 ppm, the C1 peak at 11.24 ppm, and the C4 peak at 21.10 ppm, to the other.

As for the other signals for the first fraction, we have successfully assigned them to H2, H3, H5, C2, C3, and C5 from the correlation peaks 3 through 9 in the ^1H COSY spectrum and those 9 through 14 in the HSQC spectrum with the use of the DEPT spectrum, these assignments being shown in Figures 3 and 4. For convenience, we omit the detailed procedure for these assignments. As in the case of H1, H4, C1, and C4 above, we have been able to group the signals from H2, H5, C2, C3, and C5 and also from C6, C7, and C8 from the long-range heteronuclear correlation peaks in the HMBC spectrum for each of the stereoisomers. Although we have not been able to group the signals from H3, H7 through H10, C9, and C10 directly from the HMBC spectrum, those from C9 and C10 have been able to be grouped from the difference between the values 0.48 and 0.52 of the fractions of the two stereoisomers.

Then we proceed to make assignments of the signals for the second fraction. In Figure 5 are shown the ^1H COSY and ^1H NMR spectra in the alkyl region for this fraction. As a whole, all the spectra, including the HSQC and ^{13}C NMR spectra, which are not explicitly

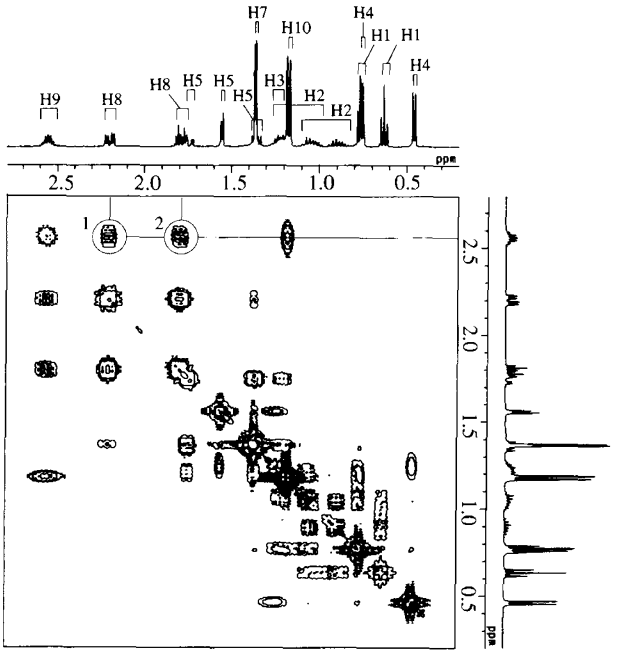

Figure 5. ^1H COSY and ^1H NMR spectra in the alkyl region for the second fraction of the dimer sample OAMS2.

shown here, are the same as those for the first fraction except for the signals from H8. Starting from the H9 multiplet located at 2.51 to 2.59 ppm in the ^1H NMR spectrum, both the two multiplets at 1.76 to 1.83 ppm and at 2.18 to 2.23 ppm may be assigned to H8 from the correlation peaks 1 and 2 in the ^1H COSY spectrum. The other signals have been able to be assigned to Hx and Cx in a manner similar to that in the case of the first fraction. The assignments for all Hx for the second fraction are shown in Figure 5. Further, the signals from Hx and Cx except those from H3 and H7 through H10 have been able to be grouped for each of the stereoisomers. The difference in the signal from H8 between the first and second fractions indicates that the magnetic environments for the two methylene protons H8 are similar to each other for the first fraction but not for the second.

The problem that remains is a determination of the stereoisomeric states of the C6–C8–C9 diad for the two fractions and also those of the C3–C5–C6 diad in the two unidentified groups for each fraction by a comparison of the observed chemical shifts of H1, H4, and H8 with the corresponding quantum-chemical theoretical values calculated by the Gauge-Independent Atomic Orbital (GIAO) method at the restricted Hartree–Fock 6-31G* level of theory and STO-3G optimized geometries of the four stereoisomers. Since the degree of freedom of the dimer under consideration is rather large, we have generated its initial geometry necessary for input parameters for the GIAO method by the use of the Modified Neglect of Diatomic Overlap (MNDO) method. All the MNDO calculations have been performed by the use of MOPAC suite of programs,[21] and all the GIAO calculations, by the use of GAUSSIAN 98 suite of programs.[22] We note that the optimized geometries for each stereoisomer are consistent with the structures expected from the ^3J coupling constants between H8 and H10 and between H3 and H5 through the vicinal Karplus correlation.[23] The

Table I. Values of M_w, M_w/M_n, and the polymerization temperature T_p for oligo- and poly(α-methylstyrene)s

Sample	M_w	M_w/M_n	T_p / ℃
OAMS2	2.94×10^2	1	−70
OAMS3	4.12×10^2	1	−70
OAMS4	5.30×10^2	1	−70
OAMS5	6.48×10^2	1	−70
OAMS6	7.66×10^2	1	−70
OAMS7	8.84×10^2	1	−70
OAMS8	1.04×10^3	1.01	−70
OAMS10	1.27×10^3	1.01	−70
OAMS13	1.60×10^3	1.02	−70
OAMS19	2.27×10^3	1.07	−68
OAMS25	2.96×10^3	1.06	−68
OAMS33	3.95×10^3	1.04	−65
OAMS38	4.57×10^3	1.07	−65
OAMS67	7.97×10^3	1.04	−60
AMS1	1.30×10^4	1.02	−52
AMS2	2.48×10^4	1.02	−48
AMS5	5.22×10^4	1.02	−44
AMS6	6.46×10^4	1.03	−44
AMS11	1.15×10^5	1.04	−40
AMS15	1.46×10^5	1.02	−40
AMS24	2.38×10^5	1.05	−40
AMS40 [a]	4.07×10^5	1.02	—
AMS80	8.50×10^5	1.05	−40
AMS200	2.06×10^6	1.05	−40
AMS320	3.22×10^6	—	−40

[a] Separated from the commercial sample 20538-2.

Table II. Chemical shifts of ^{1}H in the stereoisomers of the dimer

^{1}H	δ / ppm			
	mm	*rm*	*mr*	*rr*
H1	0.57—0.61	0.74—0.77	0.61—0.65	0.75—0.79
H2	0.80—1.00	1.04—1.24	0.84—1.12	0.99—1.28
H3	1.12—1.24		1.21—1.28	
H4	0.76, 0.78	0.39, 0.41	0.76, 0.77	0.45, 0.47
H5	1.27—1.32 1.68—1.72	1.45—1.56	1.33—1.39 1.72—1.77	1.55—1.56
H7	1.10, 1.08		1.37, 1.36	
H8	1.95—2.07		1.76—1.83 2.18—2.23	
H9	2.45—2.53		2.51—2.59	
H10	0.93—0.95		1.17—1.19	

chemical shifts have been determined by a comparison of the isotropic absolute shielding constants calculated for these protons with those for protons in TMS.

The theoretical values of the chemical shifts so obtained for H8 are 2.12 and 2.18 ppm for both the stereoisomers *mm* and *rm*, while those are 1.95 and 2.38 ppm for both *mr* and *rr*, indicating that the difference in chemical shift, *i.e.*, in magnetic environment, between the two methylene protons H8 is appreciably larger for $(m+r)r$ than for $(m+r)m$. From a comparison of these values with the corresponding values 1.95—2.07 ppm observed for H8 for the first fraction and those 1.76—1.83 and 2.18—2.23 ppm for H8 for the second, it may be concluded that the stereoisomers in the first and second fractions are $(m+r)m$ and $(m+r)r$, respectively. This conclusion is consistent with the previous result for the stereoisomeric states of the diad at the terminating end for MMA oligomers.[24,25] For the chemical shifts of H1 and H4, the theoretical values have been calculated to be 0.80 and 1.03 ppm for *mm*, 1.00 and 0.79 ppm for *rm*, 0.80 and 1.14 ppm for *mr*, and 1.08 and 0.77 ppm for *rr*, respectively. From a comparison between the observed and theoretical chemical shifts of H1 and H4 with respect to the order of their magnitude, we have been able to determine the stereoisomeric states of the C3–C5–C6 diad in the two groups for each fraction. The values of the chemical shifts of all Hx and Cx are summarized in Tables II and III, respectively.

Table III. Chemical shifts of ^{13}C in the stereoisomers of the dimer

^{13}C	δ / ppm			
	mm	*rm*	*mr*	*rr*
C 1	10.97	11.24	10.99	11.26
C 2	31.22	31.92	31.32	31.86
C 3	30.42	30.65	30.54	30.75
C 4	21.79	21.10	21.68	21.10
C 5	52.43	52.27	51.07	51.03
C 6	42.33	42.02	42.38	42.10
C 7	23.62	23.12	24.64	24.10
C 8	52.57	52.87	52.99	53.28
C 9	36.74	36.68	36.46	36.42
C 10	25.28	25.29	25.33	25.24

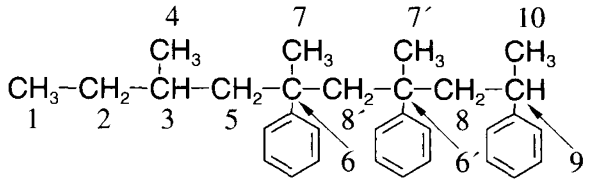

Figure 6. Chemical structure of the trimer with the numbering system.

Finally, the fractions of the four stereoisomers in the dimer sample OAMS2 determined from the peak intensities in the ^{13}C NMR spectrum are $mm : rm : mr : rr = 0.21 : 0.23 : 0.27 : 0.29$. Then the value of f_r of the dimer sample is calculated to be 0.56 (=0.27+0.29) without consideration of the C3–C5–C6 diad at the initiating end.

Trimer

Figure 6 shows the chemical structure of the trimer with the numbering system for the aliphatic hydrogen and carbon atoms, which are designated by Hx and Cx, respectively, as in the case of the dimer. The trimer has the four asymmetric carbons C3, C6, C6′, and C9, and therefore the trimer sample OAMS3 may be considered to be composed of the eight stereoisomers denoted by *rrr*, *rrm*, *rmr*, *mrr*, *rmm*, *mrm*, *mmr*, and *mmm*, where the first, second, and third letters indicate the stereoisomeric states of the C3–C5–C6, C6–C8′–C6′, and C6′–C8–C9 diads, respectively. The assumption of the stereoisomeric state of the C3–C5–C6 diad is the same as in the case of the dimer.

We separated a small amount of the trimer sample OAMS3 into three fractions by reversed-phase HPLC as before, as shown in Figure 7. They are referred to as the first, second, and third fractions, respectively, in order of elution time. Starting from the assignment of the ^{1}H

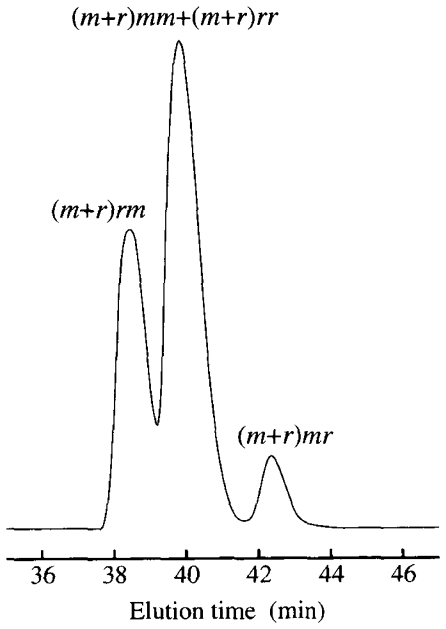

Figure 7. HPLC trace of the trimer sample OAMS3.

multiplet in the lowest field to the benzyl proton (H 9), we have assigned all the signals in the ^{1}H and ^{13}C NMR spectra to Hx and Cx, respectively, for each fraction with the use of correlation peaks in the ^{1}H COSY and HSQC spectra and of the information about the kind of carbon from the DEPT spectra. Having regard to the splits of the signals from Cx with $x=6$—10, we may conclude that both the first and third fractions are composed of two stereoisomers which have the same stereoisomeric states for the C6–C8′–C6′ and C6′–C8–C9 diads but not for the C3–C5–C6 one, and therefore that the second fraction is composed of the remaining four stereoisomers. We note that the second fraction is almost composed of two stereoisomers which have the same stereoisomeric states for the C6–C8′–C6′ and C6′–C8–C9 diads but not for the C3–C5–C6 one. From this conclusion along with that for the dimer sample, it may be said that the oligomer samples cannot be separated with respect to the stereoisomeric state of the C3–C5–C6 diad by reversed-phase HPLC.

We then proceed to assign the signals from Hx and Cx to the stereoisomers for the three fractions. The assignments for the C3–C5–C6 and C6′–C8–C9 diads may be reasonably determined by considering the fact that the situation is the same as that for the C3–C5–C6 and C6–C8–C9 diads in the dimer, *i.e.*, that the chemical shift of H1 is smaller than that of H4 if the C3–C5–C6 diad is *m* and is larger otherwise, and the two signals from the H8 methylene protons overlap with each other if C6–C8–C9 diad is *m* and split otherwise. As for the middle C6–C8′–C6′ diad, we assume that the situation is the same as that for an *in-chain* diad in the long enough chain, so that the two signals from the methylene protons (H8′) in the *m* diad split farther from each other than in the *r* diad as in the case of PMMA[24–27] and PS.[28] It may therefore be concluded that the first fraction is composed of *mrm* and *rrm*, which we abbreviate to (*m*+*r*)*rm*, the third, of *mmr* and *rmr*, which we abbreviate to (*m*+*r*)*mr*, and almost all the part of the second, of *mrr* and *rrr*,

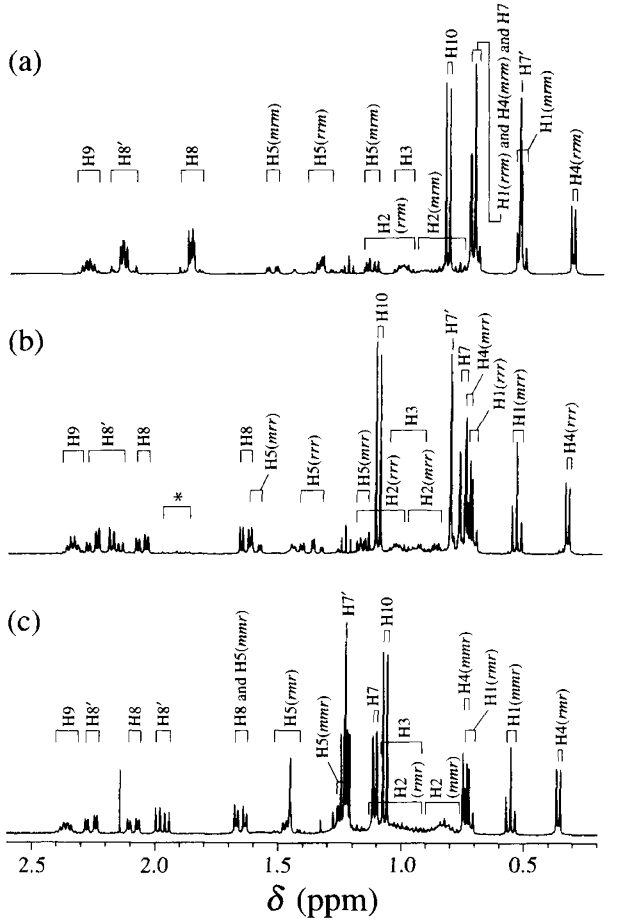

Figure 8. ^{1}H NMR spectra in the alkyl region for the trimer sample OAMS3 : (a) first fraction ; (b) second fraction ; (c) third fraction. The signals from (*m*+*r*)*mm* appear in the range indicated by the asterisk in (b).

which we abbreviate to (*m*+*r*)*rr*, indicating that the remaining part of the second fraction is composed of *mmm* and *rmm*, which we abbreviate to (*m*+*r*)*mm*, as shown in Figure 7.

In Figure 8 are shown the ^{1}H NMR spectra in the alkyl region for the first (a), second (b), and third (c) fractions along with the assignments. The signals from (*m*+*r*)*mm* in the second fraction appearing in the range indicated by the asterisk are very weak, and those in the other range are hidden by the signals from (*m*+*r*)*rr*, so that we have not made their assignments. In Figure 9 is shown the ^{13}C NMR spectrum in the alkyl region for the (whole) trimer sample OAMS3 along with the assignments. The intensities of the ^{13}C signals from the stereoisomers (*m*+*r*)*mr* and (*m*+*r*)*mm* are not large enough for a quantitative analysis, so that we have not made their assignments. The values of the chemical shifts of ^{1}H and ^{13}C are given in Tables IV and V, respectively. For the trimer, we have not recorded the HMBC spectrum for each fraction, and therefore have not been able to group the signals from Hx and Cx except those from C1 through C4 and from H1, H2, H4, and H5, which have been grouped by referring to the values of the chemical shifts of the corresponding signals for the dimer sample OAMS2.

From the peak intensities in Figure 9, the weight frac-

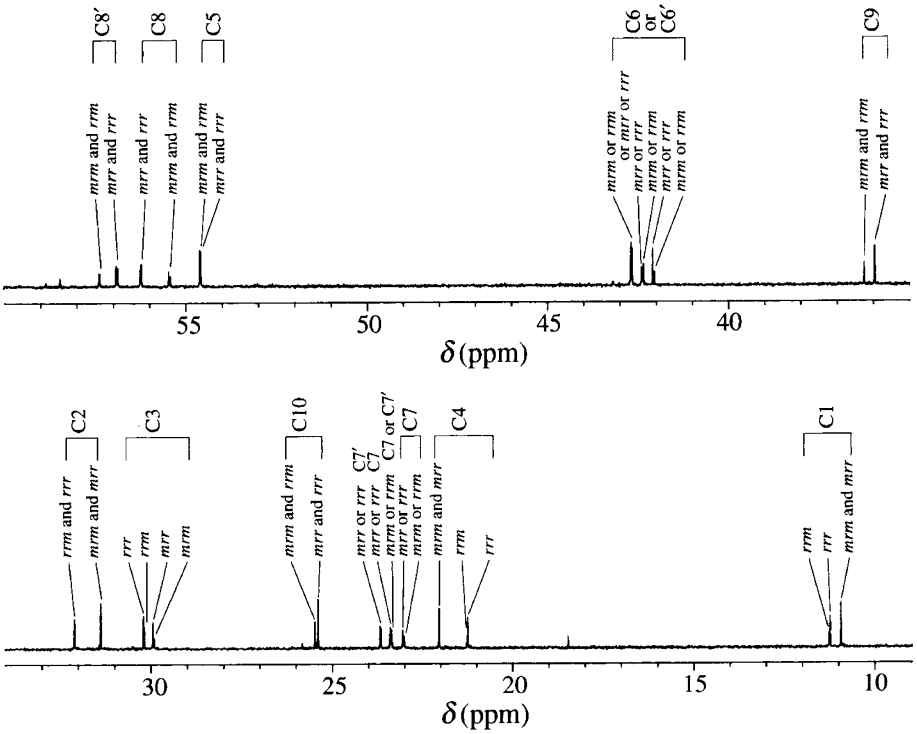

Figure 9. ^{13}C NMR spectrum in the alkyl region for the trimer sample OAMS3.

Table IV. Chemical shifts of ^{1}H in the stereoisomers of the trimer

^{1}H	δ / ppm					
	mrm	*rrm*	*mrr*	*rrr*	*mmr*	*rmr*
H1	0.50—0.54	0.69—0.73	0.52—0.55	0.71—0.73	0.53—0.57	0.70—0.74
H2	0.76—0.95	0.97—1.16	0.72—0.98	1.01—1.20	0.77—0.92	0.94—1.15
H3	0.97—1.04		0.91—1.07		0.94—1.09	
H4	0.69, 0.73	0.30, 0.32	0.72, 0.74	0.32, 0.34	0.73, 0.75	0.35, 0.37
H5	1.11—1.16 1.52—1.56	1.29—1.39	1.14—1.20 1.58—1.62	1.33—1.45	1.22—1.26 1.63—1.67	1.41—1.51
H7	0.69—0.73		0.74, 0.77		1.10, 1.11	
H7′	0.53		0.80		1.23	
H8	1.82—1.91		1.61—1.66 2.03—2.08		1.63—1.67 2.06—2.11	
H8′	2.09—2.19		2.14—2.28		1.94—2.00 2.23—2.28	
H9	2.24—2.31		2.30—2.38		2.34—2.38	
H10	0.81—0.83		1.09—1.11		1.06—1.07	

tions of the four stereoisomers *mrm*, *mrr*, *rrm*, and *rrr* have been determined to be 0.19, 0.30, 0.20, and 0.31, respectively, but those of the other stereoisomers have failed to be accurately determined because of the weak signals. Fortunately, however, the necessary weight fractions of the four pairs of the stereoisomers $(m+r)mm$, $(m+r)mr$, $(m+r)rm$, and $(m+r)rr$ have been determined to be 0.07, 0.08, 0.33, and 0.52, respectively, by the use of the weight fractions of the three sets of the stereoisomers $(m+r)rm : (m+r)mm+(m+r)rr : (m+r)mr = 0.33 : 0.59 : 0.08$ evaluated from the respective peak intensities in the HPLC trace (in Figure 7). With the above values of these fractions, the fractions of the stereoisomers with the *r* C6–C8′–C6′ diad and of those with the *r* C6′–C8–C9 diad, both in the whole trimer sample OAMS3, are calculated to be 0.85 and 0.60, respectively. The difference between the two values may be regarded as arising from that in reaction mechanism, *i.e.*, the propagation reaction for the former and the termination reaction with methanol for the latter. Then the value of f_r of the trimer sample is calculated to be 0.73 (as an average of the above two values) without consideration of the C3–C5–C6 diad at the initiating end.

Other Oligomer and Polymer Samples

In Figure 10 are shown the ^{1}H NMR spectra of the α-methyl protons except those at the terminating end for the samples OAMS13 (a), OAMS67 (b), and AMS320 (c), respectively. Following the procedure proposed by Brownstein *et al.*[29] for the assignments of the signals from the protons under consideration to the stereoisomeric sequences in the triad, *i.e.*, *mm* (isotactic), *mr*

Table V. Chemical shifts of ^{13}C in the stereoisomers of the trimer

^{13}C	δ / ppm					
	mrm	*rrm*	*mrr*	*rrr*	*mmr*	*rmr*
C1	10.92	11.24	10.92	11.22	10.87	11.24
C2	31.38	32.10	31.38	32.10	31.43	32.02
C3	29.91	30.18	29.94	30.20	30.19	30.48
C4	22.03	21.25	22.03	21.23	21.86	21.16
C5	54.59		54.58		53.02†	
C6	42.04*		42.08***		42.33††	
	42.34*		42.38***		42.70††	
C6′	42.65*		42.65***		43.17††	
	42.68*		42.68***		43.20††	
C7	23.00		23.04		23.97	
	23.34**		23.38		24.56	
C7′	23.34		23.65		26.04	
	23.37**		23.66		26.11	
C8	55.42		56.21		53.07†	
	55.46		56.23		53.11†	
C8′	57.36		56.87		58.84	
	57.38		56.91			
C9	36.24		35.96		36.37	
C10	25.47		25.37		25.80	

Assignments indicated by the same superscript can be interchanged.

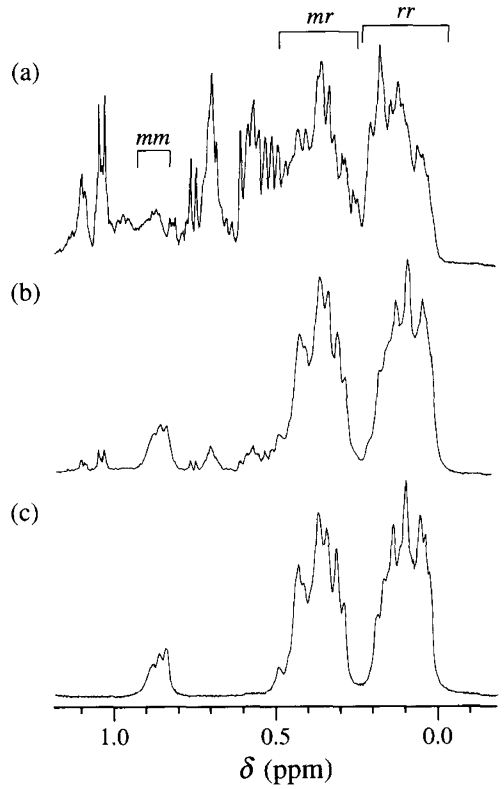

Figure 10. ^{1}H NMR spectra of the α-methyl protons for the samples OAMS13 (a), OAMS67 (b), and AMS320 (c).

(or *rm*) (heterotactic), and *rr* (syndiotactic), we have determined the fractions of the sequences, which we denote by f_{mm}, f_{mr}, and f_{rr}, respectively, for the samples OAMS13 through AMS320. Here we must make some remarks on the assignments by Brownstein *et al.*, *i.e.*, those of the signals in the ranges from 0.80 to 0.93 ppm, from 0.25 to 0.51 ppm, and from -0.04 to 0.25 ppm to *mm*, *mr*, and *rr*, respectively. In contradiction to these assignments, Sakurada *et al.*[30] claimed that these signals must be assigned to *rr*, *mr*, and *mm*, respectively. Subsequently, Ramey *et al.*[31] re-reassigned them to *mr*, *mm*, and *rr*, respectively. Recently, however, Berger *et al.*[32] have given strong support to the assignments by Brownstein *et al.* on the basis of a precise analysis of the HMBC spectra, and therefore we have adopted them. We note that the same assignments have been made in the investigations by Kato *et al.*,[8] Tsunashima,[10] and Elgert and co-workers.[15,16]

Table VI. Values of the fractions of stereoisomeric sequences in the triad and of racemo diads

Sample	f_{mm}	f_{mr}	f_{rr}	f_r
OAMS13	0.07	0.45	0.48	0.71
OAMS19	0.06	0.44	0.50	0.72
OAMS25	0.06	0.45	0.49	0.72
OAMS33	0.06	0.44	0.50	0.72
OAMS38	0.06	0.45	0.49	0.72
OAMS67	0.05	0.45	0.50	0.72
AMS1	0.05	0.44	0.51	0.73
AMS2	0.05	0.44	0.51	0.73
AMS5	0.05	0.44	0.51	0.73
AMS6	0.06	0.45	0.49	0.72
AMS11	0.05	0.44	0.51	0.73
AMS15	0.05	0.44	0.51	0.73
AMS24	0.05	0.44	0.51	0.73
AMS40	0.05	0.44	0.51	0.73
AMS80	0.05	0.45	0.50	0.72
AMS200	0.06	0.44	0.50	0.72
AMS320	0.05	0.43	0.52	0.73

As seen from Figure 10, as the degree of polymerization is decreased in the oligomer region, the ^{1}H NMR spectrum of a sample becomes complicated, so that the reliability of the resultant values of f_{mm}, f_{mr}, and f_{rr} is diminished. Thus we have not evaluated their values for the samples OAMS4 through OAMS10. The values thus determined for the samples OAMS13 through AMS320, including AMS40 separated from the commercial sample, are given in the second, third, and fourth columns, respectively, of Table VI.

In the last column of Table VI are given the values of f_r, which are the final desired results, calculated from the equation,

$$f_r = f_{rr} + \frac{f_{mr}}{2} \tag{1}$$

with the values of f_{mr} and f_{rr} given in the third and fourth columns, respectively. It is seen from the table that all the present samples have almost the same value 0.72 ± 0.01 of f_r independent of M_w.

Figure 11 shows plots of f_r against log M_w for PαMS. The unfilled circles represent the values for the samples prepared in this work and the horizontal straight line represents their average value 0.72. The figure also includes the values for the samples prepared by Elgert and Seiler[15] (filled circles), by Kato *et al.*[8] (triangle), and by Tsunashima[10] (square) along with those for the commercial samples from Polymer Laboratories Ltd. (diamond). It is reconfirmed from the figure that we have successfully prepared a set of the desired test samples. The samples prepared by Kato *et al.* and also those by Tsunashima may be used for a study of polymer solutions in the restricted range of $M_w \gtrsim 2 \times 10^5$ if the values of f_r for them meet its purposes. However, the samples with larger f_r as above are required for our study men-

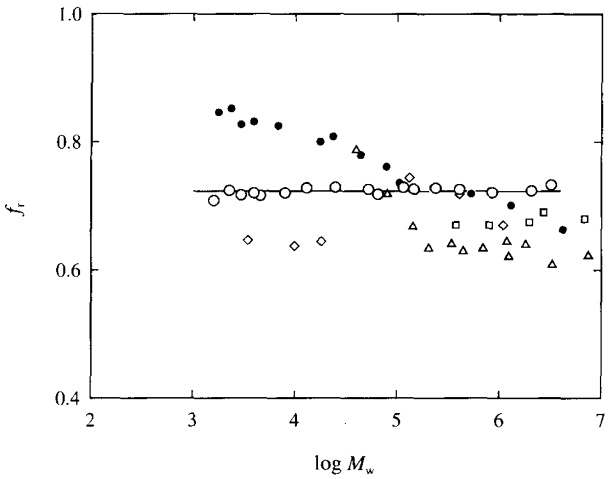

Figure 11. Plots of f_r against the logarithm of M_w for PαMS : (○) the present samples ; (●) those prepared by Elgert and Seiler ;[15] (△) those prepared by Kato *et al.* ;[8] (□) those prepared by Tsunashima ;[10] (◇) commercial ones (Polymer Laboratory Ltd.).

tioned in the Introduction. Indeed, we have succeeded in the preparation by setting the polymerization temperature at −40℃ higher than −78℃ (dry ice–methanol mixture) adopted by the above groups. Neither the samples prepared by Elgert and Seiler nor those from Polymer Laboratories Ltd. are adequate for a study of polymer solutions.

Finally, we make a remark on f_r values for the samples OAMS4 through OAMS10. As mentioned in the Experimental section, the samples OAMS2 through OAMS13 were separated from the same original sample. All those samples may therefore be regarded as having almost the same value ($\sim$ 0.71) of f_r as OAMS13. (Recall that f_r of OAMS3 is 0.73.)

CONCLUSION

Giving particular attention to the polymerization temperature and also to the initial monomer concentration, we have successfully prepared PαMS samples with the fixed stereochemical composition $f_r = 0.72 \pm 0.01$ in the range of M_w from 4.12×10^2 (trimer) to 3.22×10^6. These test samples thus obtained are adequate for our later study of dilute solution properties of PαMS within the new framework of polymer solution science based on the HW chain model.

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