NOTES

Determination of Stereochemical Compositions of Oligostyrenes by ^{13}C NMR

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We have recently started an experimental study of various dilute solution properties of atactic α -hydro- ω -butylpolystyrenes (a-PS) over a wide range of molecular weight including the oligomer region.^{1,2} The motivation is to examine whether the helical worm-like chain³ can give a self-consistent explanation of experimental results for solution properties of flexible chains. As reported previously,¹ solution properties such as the mean-square radius of gyration $\langle S^2 \rangle$ and the mean-square optical anisotropy $\langle I^2 \rangle$ are affected by the stereochemical composition (expressed by the fraction P_r of racemic dyads) of a-PS. Thus it is desirable to determine P_r of the samples prior to measurements of their solution properties.

In order to determine P_r , we need the assignments of ^{13}C NMR spectra of the samples. Those for the trimer,^{4,5} tetramer,⁵ and polymers with sufficiently large degrees of polymerization⁶ have already been made experimentally, and we use them for these samples. However, for x -mers with $x \geq 5$, there is no available assignment, and therefore we must resort to another criterion. In this report, we make assignments of spectra of the pentamer with the help of calculated chemical shifts obtained by taking quantitative account of the γ effect, as done by Tonelli⁷ on the basis of the rotational isomeric state (RIS) model.⁸ The

adequacy of the calculated values is verified for the case of the tetramer for which the assignments were made.⁵ With these assignments, P_r of the tetramer and pentamer are determined from measured ^{13}C NMR spectra of these samples.

The α -hydro- ω -butyloligostyrene sample used was a commercial one supplied by the courtesy of the Tosoh Co., Ltd. The whole oligostyrene sample designated A-500 by the company was separated into pure x -mers by gel permeation chromatography. It was performed on two Tosoh G2000H₆ (600 $\times$ 50 mm) columns joined to each other, with chloroform as an eluent at a flow rate of 17 ml min⁻¹. The sample solutions of the tetramer and pentamer were prepared using as a solvent deuterated chloroform that contained tetramethylsilane (TMS) as an internal standard. The sample concentrations were approximately 0.6 g ml⁻¹.

The ^{13}C NMR spectra of aliphatic carbons of these samples were recorded on a JEOL JNM GX-400 spectrometer at 100.5 MHz and at 27°C. An rf pulse angle of 90° (20.5 μ s) was used with a pulse repetition time of 21 s, which is more than 5 times as long as the longest spin-lattice relaxation time T_1 of aliphatic carbon atoms under observation. The spectral width was 20000 Hz, and 32 K data tables were used. Gated proton decoupling was employed. Figure 1(a) shows the aliphatic carbon reso-

nances of the tetramer, and its chemical shifts δ obtained from these spectra are given in Table I. Their assignments were determined by the use of the results obtained by Ray *et al.*⁵

Although they did not make the assignments *mr* and *rm* (*m*=meso, *r*=racemic) of methylene carbons, we have made these assignments on the basis of the calculated chemical

Figure 1. ^{13}C NMR of aliphatic carbons of the tetramer (a) and the pentamer (b) of oligostyrenes. The peaks indicated by the asterisk are due to impurities.

Table I. Observed and calculated values of ^{13}C NMR chemical shifts and intensities of the tetramer
 $\text{CH}_2(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

Peak No.	Assignment	δ/ppm		Intensity/%		Peak No.	Assignment	δ/ppm		Intensity/%	
		Obsd	Calcd	Obsd	Calcd			Obsd	Calcd	Obsd	Calcd
1	C-4 <i>mr</i> ^{a,b}	45.33	45.19	5.69	6.00	16	C-5 <i>mm</i>	40.76	—	6.44	6.50
2	C-6 <i>rm</i> [*]	45.30	45.19			17	C-5 <i>rr</i>	40.72	—		
3	C-4 <i>rr</i> ^{**}	44.29	44.27	4.36	4.50	18	C-5 <i>mr</i> ^{†††}	40.42	—	6.04	6.00
4	C-6 <i>rr</i> ^{**}	43.99	44.27	4.16	4.50	19	C-5 <i>rm</i> ^{†††}	40.39	—		
5	C-4 <i>mm</i> ^{***}	43.78	44.02	1.98	2.00	20	C-2 <i>rm</i>	39.80	39.84	3.42	3.00
6	C-6 <i>mm</i> ^{***}	43.68	44.02	2.23	2.00	21	C-2 <i>rr</i>	39.08	39.48	4.60	4.50
7	C-3 <i>rr</i>	43.27	43.23	7.52	7.50	22	C-8 <i>mr</i>	37.92	38.09	2.62	3.00
8	C-3 <i>rm</i> ^{****}	43.21	43.23			23	C-2 <i>mr</i>	37.78	38.15	2.77	3.00
9	C-3 <i>mr</i> ^{****}	43.07	43.23	12.82	12.50	24	C-8 <i>rr</i>	37.33	37.73	4.31	4.50
	C-7 <i>rr</i>	43.07	43.13			25	C-2 <i>mm</i>	37.16	37.39	2.28	2.00
10	C-7 <i>mr</i> [†]	43.01	43.13	2.87	3.00	26	C-8 <i>rm</i>	36.17	36.40	3.22	3.00
11	C-3 <i>mm</i>	42.97	43.23			27	C-8 <i>mm</i>	35.75	35.63	2.13	2.00
12	C-7 <i>rm</i> [†]	42.64	43.13	7.92	8.00	28	C-1 <i>rm</i> ^{††††}	33.70	33.75	7.67	7.50
13	C-4 <i>rm</i> ^{††}	42.51	42.23			29	C-1 <i>rr</i>	33.65	33.75		
14	C-6 <i>mr</i> ^{††}	42.49	42.23	4.95	5.00	30	C-1 <i>mr</i> ^{††††}	33.42	33.75	4.95	5.00
15	C-7 <i>mm</i>	42.44	43.13			31	C-1 <i>mm</i>	33.36	33.75		

^a *m*=meso; *r*=racemic.

^b Assignments indicated by the same superscript can be interchanged.

shifts (see below). We have interchanged their assignments of C-6 and C-6' in Table II of ref 5, considering the fact that the internal-methine carbons of the polymers resonate around $\delta=41$.⁹

The values of the chemical shifts δ of the x -mer may be estimated by the use of the known values of δ of the $(x-1)$ -mer as follows. The difference $\Delta\delta$ in δ between a given aliphatic carbon of a stereoisomer of the x -mer in a given conformation and that in the *trans* planer conformation can be calculated, fol-

lowing Tonelli⁷ with his value of -5.3 ppm for the magnitude of the γ effect. Since other effects such as the phenyl ring currents are small in magnitude compared to the γ effect, we do not take account of them, for simplicity. The observed δ of the aliphatic carbon of the stereoisomer may be regarded as a sum of the chemical shift δ^* in the *trans* planer conformation and an averaged difference $\langle\Delta\delta\rangle$, which may be estimated on the basis of the RIS model regarding the x -mer as a methylene-styrene diblock copolymer. The

Table II. Observed and calculated values of ^{13}C NMR chemical shifts and intensities of the pentamer

$\overset{1}{\text{CH}_2}(\text{C}_6\text{H}_5)\overset{2}{\text{CH}_2}\overset{3}{\text{CH}}(\text{C}_6\text{H}_5)\overset{4}{\text{CH}_2}\overset{5}{\text{CH}}(\text{C}_6\text{H}_5)\overset{6}{\text{CH}_2}\overset{7}{\text{CH}}(\text{C}_6\text{H}_5)\overset{8}{\text{CH}_2}\overset{9}{\text{CH}}(\text{C}_6\text{H}_5)\overset{10}{\text{CH}_2}\overset{11}{\text{CH}_2}\overset{13}{\text{CH}_2}\overset{14}{\text{CH}_3}$											
Peak No.	Assignment	δ/ppm		Intensity/%		Peak No.	Assignment	δ/ppm		Intensity/%	
		Obsd	Calcd	Obsd	Calcd			Obsd	Calcd	Obsd	Calcd
1	C-6 <i>rmr</i> ^a	46.43	46.43	1.26	1.41	12	C-9 <i>mmm</i>	42.79			
2	C-4 <i>mrm</i>	45.35	45.36	3.93	4.00		C-9 <i>mrm</i>	42.44	42.79	5.09	4.83
3	C-8 <i>mrm</i>	45.27	45.25				C-9 <i>rrm</i>	?	42.79		
4	C-6 <i>rrr</i>	45.18	45.80				C-4 <i>rrm</i>	42.29	41.77		
5	C-4 <i>mrr</i>	44.93	45.15	1.41	1.41		C-8 <i>mmr</i>		41.67		
6	C-8 <i>rrm</i>	44.81	45.04	1.30	1.41	13	C-6 <i>mrm</i>	41.44	41.74	0.97	1.02
7	C-6 <i>mmr</i> ^{*b}	44.57	45.05	1.08	1.02			40.70			
8	C-6 <i>rrm</i> [*]	44.33	45.05	2.38	2.44	14	C-5, 7	?	40.57	20.02	20.00
	C-4 <i>rrm</i>		44.59					40.31			
9	C-8 <i>mrr</i>	44.20	44.48	1.37	1.41	15	C-2 <i>rrm</i>	39.74	39.67	1.15	1.02
10	C-4 <i>mmr</i>		44.28	29.58	29.62	16	C-2 <i>rmr</i>	39.62	39.53	1.48	1.41
	C-6 <i>mmm</i>		44.21			17	C-2 <i>rrr</i>	39.06	39.25	3.79	3.36
	C-8 <i>rrm</i>		44.17			18	C-2 <i>rrm</i>	39.00	39.17		
	C-4 <i>rrr</i>		44.13			19	C-10 <i>mmr</i>	37.87	38.01	4.26	4.48
	C-8 <i>rrr</i>		44.02			20	C-2 <i>mrm</i>	37.81	37.97		
	C-6 <i>mrr</i>		43.83				C-10 <i>rmr</i>		37.86		
	C-6 <i>rrm</i>		43.83			21	C-2 <i>mmr</i>	37.70	37.26		
		43.67				22	C-2 <i>mrr</i>	37.45	37.83	1.37	1.41
	C-4 <i>mmm</i>	?	43.70			23	C-10 <i>rrr</i>	37.31	37.59	4.04	4.11
		42.92									
	C-8 <i>mmm</i>		43.59			24	C-2 <i>mmm</i>	37.24	36.88		
	C-3		43.13			25	C-10 <i>mrr</i>	37.17	37.51		
	C-9 <i>mmr</i>		42.79			26	C-10 <i>mrm</i>	36.24	36.30	1.01	1.02
	C-9 <i>mrr</i>		42.79			27	C-10 <i>rrm</i>	36.19	35.60	1.01	1.02
	C-9 <i>rmr</i>		42.79			28	C-10 <i>rrm</i>	35.86	36.17	1.37	1.41
	C-9 <i>rrr</i>		42.79			29	C-10 <i>mmm</i>	35.76	35.22	0.65	0.74
	C-4 <i>rmr</i>		42.58					33.68			
	C-8 <i>rmr</i>		42.47			30	C-1	?	33.53	10.14	10.00
11	C-9 <i>rrm</i>	42.59	42.79	1.34	1.41			33.22			

^a *m* = meso; *r* = racemic.

^b Assignments indicated by the same superscript can be interchanged.

value of δ^* for the carbon of the x -mer under consideration may be estimated by the use of the observed values of δ and the calculated values of $\langle\Delta\delta\rangle$ for a similar carbon of the $(x-1)$ -mer, assuming that δ^* is independent of the stereochemical sequence. In practice, the difference $\langle\Delta\delta\rangle$ may be calculated by the use of the statistical weight for the first- and second-order interactions determined by Flory and coworkers^{10,11} for the methylene and styrene blocks. Reasonable values have been chosen for the second-order statistical weights for the pairs of interacting groups separated by the junction point of the two blocks and also for those associated with the end group of the styrene block.

The chemical shifts of the tetramer thus calculated are given in Table I. In obtaining these values, we have made the aliphatic carbons C-1, C-2, C-3, C-4, C-6, C-7, and C-8 of the tetramer correspond to C-1, C-2, C-3, C-4, C-4, C-5, and C-6 of the trimer, respectively, and used the values of δ for these carbons of the trimer determined by Ray *et al.*⁵ (The number system employed for the aliphatic carbons of the trimer is similar to that for those of the tetramer.) Note that we cannot obtain δ of C-5 (internal methine carbon) of the tetramer from δ of the trimer. There is in general good agreement between the observed and calculated ¹³C NMR chemical shifts.

Assuming the intensity distribution to be Bernoullian, we have determined the fraction P_r of racemic dyads so that the root-mean-square deviation of calculated intensities from observed ones is a minimum. The value of P_r obtained for the tetramer is 0.60. The observed and calculated intensities are also given in Table I.

Figure 1(b) shows the aliphatic carbon resonances of the pentamer, and its measured and calculated chemical shifts and intensities

are given in Table II. The calculated chemical shifts have been obtained, making C-1, C-2, C-3, C-4, C-5, C-7, C-8, C-9, and C-10 of the pentamer correspond to C-1, C-2, C-3, C-4, C-5, C-5, C-6, C-7, and C-8 of the tetramer, respectively, and using the observed δ given in Table I. In this case, we cannot obtain δ of C-6 (internal methylene carbon) of the pentamer from δ of the tetramer, so that we have assigned C-6 *rmr* to the peak 1 at $\delta=46.43$. In order to make assignments, the intensities of the peaks have also been considered, assuming that $P_r>0.5$. Thus the calculated chemical shifts do not necessarily correspond to the observed ones in numerical order. The value of P_r obtained for the pentamer is 0.58. The result is believed to be reasonable.

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