

MEASUREMENT OF NUMBER AVERAGE MOLECULAR WEIGHT OF STYRENE OLIGOMER BY ^{13}C -NMR METHOD*

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Abstract ^{13}C -NMR ^1H -decoupled spectra of styrene polymers were assigned by comparison with model compounds, then used in measurements of number average molecular weights. The higher limit of an exact determination of the end group signal is less than a molecular weight of 10^4 . For polymer samples with $M_n < 10^3$, the results obtained from ^{13}C -NMR spectra of saturated carbon region are in excellent agreement with the values determined by ^1H -NMR, SEC, and VPO methods, while the results from ^{13}C -NMR spectra of phenyl C-1 carbon region are somewhat higher than the values determined by other methods.

Keywords Molecular weight measurement, Styrene oligomer, ^{13}C -NMR spectra

INTRODUCTION

A quantitative analysis by ^{13}C -NMR spectra usually needs particular techniques, such as inverse gated decoupling, prolonging acquisition time and so on. These techniques either require long measuring times or are complicated in procedure. General ^{13}C -NMR measurements use the complete ^1H -decoupled method, in which the signal intensity of carbons is not exactly in proportion to the carbon numbers due to the interference of different relaxation times and Overhauser effects, so it is only usually used in qualitative analyses. This work will attempt to use ^{13}C -NMR ^1H -decoupled spectra for measuring the number average molecular weights of styrene oligomers. The results obtained were compared with those measured by ^1H -NMR, SEC, and VPO methods.

The ^{13}C -NMR spectra of styrene oligomers with the methyl and propyl end groups have been studied by Jasse et al.^[1] and Sato et al.^[2-5]. However, all of these studies were aimed at the assignment of ^{13}C -NMR spectra of polystyrene and the samples used had a molecular weight less than 610. The styrene oligomers used in this work were narrow MWD polystyrene standard samples with butyl and ethyl-phenyl end groups and known molecular weights from 460 to 2800.

EXPERIMENTAL

Materials

Styrene oligomers and polymers were prepared with *n*-butyllithium as an initiator and methanol as terminator in benzene in this laboratory. Characterization data of the samples by SEC are summarized in Table 1.

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Table 1. Characterization of Polystyrenes Determined by SEC*

Sample	M_n	M_w	M_w/M_n	Sample	M_n	M_w	M_w/M_n
A	460	570	1.25	D	21600	22400	1.04
B	750	860	1.15	E	267000	278000	1.04
C	2800	2900	1.04	F	1550000	1690000	1.09

* Determined in tetrahydrofuran at room temperature

Measurements

^{13}C -NMR and ^1H -NMR spectra were recorded on a Bruker AM-125 spectrometer at 60 °C at 15% by weight in 1, 2-dichlorobenzene. Tetramethylsilane was used as an internal standard for the measurement of chemical shifts. 90° pulse width and an acquisition time of 2 s were employed. The number of transients collected varied from 2000 to 7000. In addition, ^{13}C -NMR spectra were decoupled from protons. Resonance area measurements were made by spectral integration.

RESULTS AND DISCUSSION**Assignment of ^{13}C -NMR Spectra of Styrene Oligomer and Polymer**

Styrene oligomers and polymers studied in this work have the end methyl carbon A, the end methylene carbons B, C, D, E, I and J, the external methin carbon F, central methylene carbons G and central methin carbons H in the main chain, the phenyl carbons C-1, C-2, C-3 and C-4 of the external phenyl group (i), central phenyl group (ii), and the end phenyl group (iii) as the side chains.

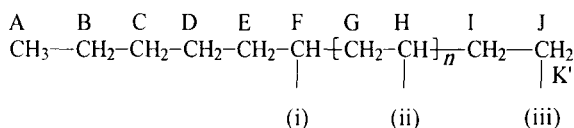


Figure 1 shows ^{13}C -NMR spectra of polystyrenes with molecular weights from 10^2 to 10^6 . The

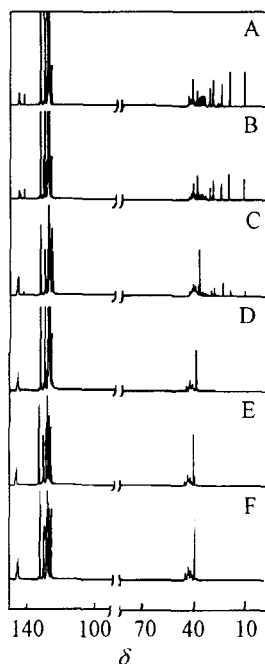


Fig. 1 ^{13}C -NMR spectra of styrene oligomers and polymers with molecular weights (A) 460, (B) 750, (C) 2800, (D) 21600, (E) 267000, (F) 1550000, measured in 1, 2-dichlorobenzene at 60 °C

spectra were assigned by comparing with the Sadtler standard spectra of polystyrene^[6]. Resonances in the range of $\delta = 40 \sim 47$ are attributed to the central methylene carbon G and methin carbon H, resonances in the range of $\delta = 125 \sim 129$ are attributed to central phenyl C-4, C-3 and C-2 carbons, resonances between $\delta = 144$ and $\delta = 147$ are assigned to the central phenyl C-1 carbon. It should be noted that there are several peaks at $\delta < 40$ as well as in the range of $\delta = 142 \sim 143$ in spectra of samples with molecular weights less than 10^4 , but they were not observed in spectra of higher molecular weight samples, so these peaks must be attributed to the signals of the end groups. Table 2 shows a comparison of chemical shifts of styrene oligomers with the corresponding carbons of model compounds^[2, 6]. From this comparison the assignment of end carbons could be made. Resonances at about $\delta = 14.1$, 22.6, 27.1, 32.0, 33.9, and in the range of $\delta = 37 \sim 40$ can be attributed to the end methyl carbon A, and end methylene carbons B, D, C, J, I and E, respectively. The resonance at around $\delta = 43$, attributed to the external methin carbon F, overlapped with those of the central methylene carbon G. Resonances in the range of $\delta = 142 \sim 143$ is attributed to the end phenyl C-1 carbon K'. The assignment results of spectra were illustrated in Fig. 2. It shows that the end group signals were clearly visible in either the saturated carbon or the phenyl C-1 carbon regions. This means that there were two different ways to measure molecular weights by the ^{13}C -NMR method.

Table 2. Assignment of end carbon signal by comparing with model compounds

Sample	Assignment											Ref.
	Saturated carbon						Phenyl C-1					
	A	B	C	D	E	F	G	H	I	J		
PS	CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH-[CH ₂ -CH] _n -CH ₂ -CH ₂ — Ph(iii)											This work
Chemical shift	14.1	22.6	32.0	27.1	38~40	43.0	42~47	41.0	37~40	33.8	142~143	
Model compound I	ABCD CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ Ph(i)Ph(ii)											6
Chemical shift	14.222.831.629.2 EFGH											
Model compound II	CH₃CH₂CH₂CH-[CH₂-CH]₃CH₂CHCHCH3H7 Ph(i)Ph(ii)Ph(i)											2
Chemical shift	384342~4741											
Model compound III	IJ CH ₃ CHCH ₂ CHCH ₂ -CH ₂ — Ph(iii) PhPh											6
Chemical shift	37.633.8142~143											

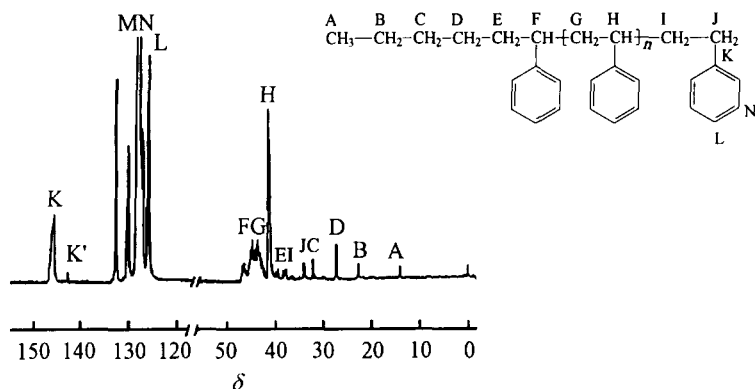


Fig. 2 Assignment of ^{13}C -NMR spectra of styrene oligomers with $M_w = 2800$, measured in 1,2-dichlorobenzene at 60°C

Molecular Weight Measurement by ¹³C-NMR Spectra of Saturated Carbon Region

In spectra of the saturated carbon region the end methylene carbon B, C, D and E were used as known molecular weight standard. The signal intensity of various groups was measured by spectral integration and are given in Table 3. The results show that the intensity ratio of the central methylene carbon G to the central methin carbon H decreases as molecular weight increases. The reason is that the signals of carbon G ($\delta = 42 \sim 47$) overlap with the external methin carbon F (ca. $\delta = 43$), while the signal intensity of the external groups decreases as molecular weight increases. For higher molecular weight samples, the intensity ratio of the carbon G to H is about 1. This means that the intensity of the carbon G can be approximately expressed by one-half intensity of both carbons G and H. Thus, the following equation can be used to determine the degree of polymerization:

$$P_n = [\frac{S_g + S_h}{(S_b + S_c + S_d + S_e)/4} - 1]/2 + 2 \tag{1}$$

where P_n is the degree of polymerization, S_b, S_c, S_d, S_e, S_g and S_h are the resonance area of carbon B, C, D, E, G and H, respectively, $(S_b + S_c + S_d + S_e)/4$ is the average intensity for carbon B, C, D and E, “-1” means to substrate the area of the external methin carbon F from the total area of the central methylene carbon G and the central methin carbon H ($S_g + S_h$), “+2” means to add the contribution of both end repeat units to P_n that is the contribution of the external methylene carbon E and end methylene carbon I. The number average molecular weight is given by:

$$\overline{M}_n = P_n \times 104 + 57 \tag{2}$$

where 104 and 57 are the molecular weight of the repeat unit and end butyl group. From Eqs. (1) and (2) the average molecular weights of 480, 700 and 3260 are obtained for sample A, B and C, respectively.

Table 3. Relative resonance areas of saturated carbon of ¹³C-NMR spectra*

Sample	CH ₂ (B)	CH ₂ (C)	CH ₂ (D)	CH ₂ (E)	CH ₂ (G)	CH(H)	CH ₂ (G)/CH(H)
A	258	278	266	265	1010	380	2.66
B	185	196	193	194	1130	657	1.71
C	10	39	15	25	655	650	1.01
D	-	-	-	-	788	788	1.00
E	-	-	-	-	681	699	0.97
F	-	-	-	-	1010	1040	0.97

* Measured in 1, 2-dichlorobenzene at 60°C

Molecular Weight Measurement by ¹³C-NMR Spectra of Phenyl C-1 Carbon Region

In ¹³C-NMR spectra of phenyl C-1 carbon region, the C-1 carbon K' of the end phenyl group Ph(iii) was used as the known molecular weight standard. The signal intensity of various phenyl groups are given in Table 4 and the average molecular weights can be calculated as follows:

$$\overline{M}_n = \frac{\text{Total phenyl C-1 carbon intensity}}{\text{Single phenyl C-1 carbon intensity}} \times 104 + 57 \tag{3}$$

where the total and single carbon intensity are given by:

$$\text{Total phenyl C-1 carbon intensity} = S_{\text{Ph(i)}} + S_{\text{Ph(ii)}} + S_{\text{Ph(iii)}} \tag{4}$$

$$\text{Single phenyl C-1 carbon intensity} = S_{\text{Ph(iii)}} \tag{5}$$

where $S_{\text{Ph(i)}}, S_{\text{Ph(ii)}}$ and $S_{\text{Ph(iii)}}$ are resonance areas of the phenyl C-1 carbon from Ph(i), Ph(ii) and Ph(iii) groups, respectively. Using Eqs. (1) ~ (3), the average molecular weights are 550, 920, 2970 for sample A, B and C.

Table 4. Relative resonance areas of phenyl C-1 carbon of ¹³C-NMR spectra*

Sample	Ph _(i) + Ph _(ii)	Ph _(iii)
A	415	112
B	360	49
C	324	12

* Measured in 1,2-dichlorobenzene at 60°C

Molecular Weight Measurement by ¹H-NMR Spectra

¹H-NMR spectra of samples A and B are shown in Fig. 3. Resonances in the range of δ =0.76 ~ 0.68 were attributed to methyl protons, which were used as the internal standard for estimating molecular weight. Resonances between δ =7.30 and δ =6.65 were attributed to phenyl protons^[6, 7]. The signal intensities of protons for samples A and B are listed in Table 5. The average molecular weights are calculated according to the following equation:

$$\overline{M}_n = \frac{\text{Number of repeat units}}{\text{Number of end units}} \times 104 + 57$$

(6)

Number of repeat units = Resonance area of phenyl group /5

(7)

Number of end units = Resonance area of methyl group /3

(8)

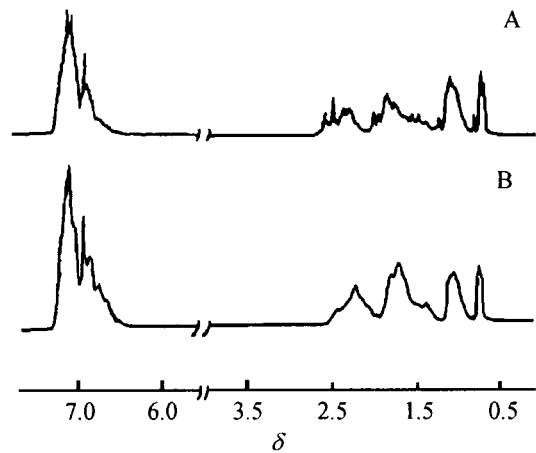


Fig. 3 ¹H-NMR spectra of sample A and B measured in 1,2-dichloro-benzene at 60°C

Table 5. Relative resonance areas of protons from ¹H-NMR spectra*

Sample	Phenyl	Methyl
A	70	10
B	48	4

*Measured in 1,2-dichlorobenzene at 60°C

Comparison of Molecular Weights Determined by Different Methods

Table 6 shows a comparison of the average molecular weights of styrene oligomers determined by different methods.

For sample A and B, the values obtained from ¹³C-NMR spectra of saturated carbon region are in excellent agreement with those obtained by ¹H-NMR, SEC and VPO^[8] methods, while the results from spectra of phenyl C-1 carbon region are somewhat higher than the values determined by other methods. The reason must be that in the case of saturated carbon regions, the signal intensity of the end group, which was used as the internal standard, is an average value of intensities of carbon B, C, D and E, and the resonance areas of these carbons are almost the same (Table 3). This means that relaxation time and Overhauser effects can be omitted, but in the phenyl

C-1 carbon region, the end phenyl carbon K' is bound to the methylene carbon J and the central phenyl C-1 carbon binds to the methin carbon H. These different chemical circumstances probably led to the difference in the relaxation time and signal intensity between the end and central C-1 carbons.

Table 6. Comparison of number average molecular weight of styrene oligomers determined by ^{13}C -NMR, ^1H -NMR, SEC and VPO^[8] methods

Sample	^{13}C -NMR	^{13}C -NMR	^1H -NMR	SEC	VPO
	phenyl carbon	saturated carbon			
A	550	480	490	460	490
B	920	700	680	750	790
C	2970	3270	-	2800	2000

It should also be noted that it is a different case for sample C compared with samples A and B in spectra of saturated carbon regions. The difference in resonance areas of the end saturated carbon B, C, D and E is remarkable (Table 3), so the molecular weight of sample C determined by this method is only an approximate value. Table 6 shows that the average molecular weights of sample C determined by both ^{13}C -NMR measurements are higher than those by SEC, VPO methods.

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