

New Stereochemical Assignments of ^{13}C NMR Signals for Predominantly Syndiotactic Polystyrene

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We recently published our results regarding the syndiospecificity of the living anionic styrene polymerization with heteroleptic benzylcalcium compounds.¹ Difficulties arose when determining the exact tacticity of our polymers by ^{13}C NMR spectroscopy: a variety of different J -ade assignments have been reported.^{2–9} The J -ade assignments for atactic polystyrene are based partially on Bernoullian³ and partially on Markovian statistics.⁴ Other studies concerning J -ade assignments make use of either oligomeric model systems⁵ or polystyrenes with increased isotactic⁶ or syndiotactic⁷ parts.

Hitherto, the assignments used for tacticity determination in the polystyrene chain¹⁰ have all been made on a pentad/hexad level.^{2–9} During the course of our studies on anionic syndiotactic styrene polymerization, we became aware that most of the reported pentads should actually be assigned on a heptad level. Here we describe new assignments of the hexads and heptads for predominantly syndiotactic polystyrene.

We recently showed that styrene polymerization with heteroleptic benzylcalcium initiators yields polymers enriched in syndiotactic parts.¹ The syndiotacticity strongly increases with monomer concentration and decreasing temperature^{1a} (polymer **A** at 20 °C and 50% styrene, polymer **B** at 20 °C and 100% styrene, and polymer **C** at –20 °C and 100% styrene). Analogous to titanium half-sandwich catalysts, benzylcalcium initiators behave like single-site catalysts, and the stereochemistry of monomer insertion is chain end controlled.¹ Solitary errors (i.e., m -diads) should be distributed statistically throughout the polymer chains.

In general, ^{13}C NMR signals of the phenyl *ipso*-carbons and the methylene carbons are used for determination of the tacticity of polystyrene. The methylene signals show a good resolution over a 5 ppm range, whereas those of the *ipso*-carbons are spread over a range of only 2 ppm. However, the advantage of a determination according to the *ipso*-carbon is that, going from low to high field, its signals can be assigned to sequences that increase in r -diads. The methylene signals show no simple order. A rough determination of tacticity is therefore easier to realize according to analyses of the *ipso*-carbon signals.

Our predominantly syndiotactic polystyrenes, in order of increasing syndiotacticity: polymers **A**, **B**, and **C**, show only four distinct ^{13}C signals in the *ipso*-carbon region (solvent: tetrachloroethane- d_2 ; Figure 1a). The main signal corresponds with that of highly syndiotactic polystyrene obtained by titanocene catalyses.⁹ The remaining three signals of roughly equal intensity decrease uniformly with the syndiotacticity of the polymer, while retaining their approximate 1/1/1 ratio.

On the pentad level the main signal can be assigned to the $rrrrr$ pentad. According to Bernoullian statistics,

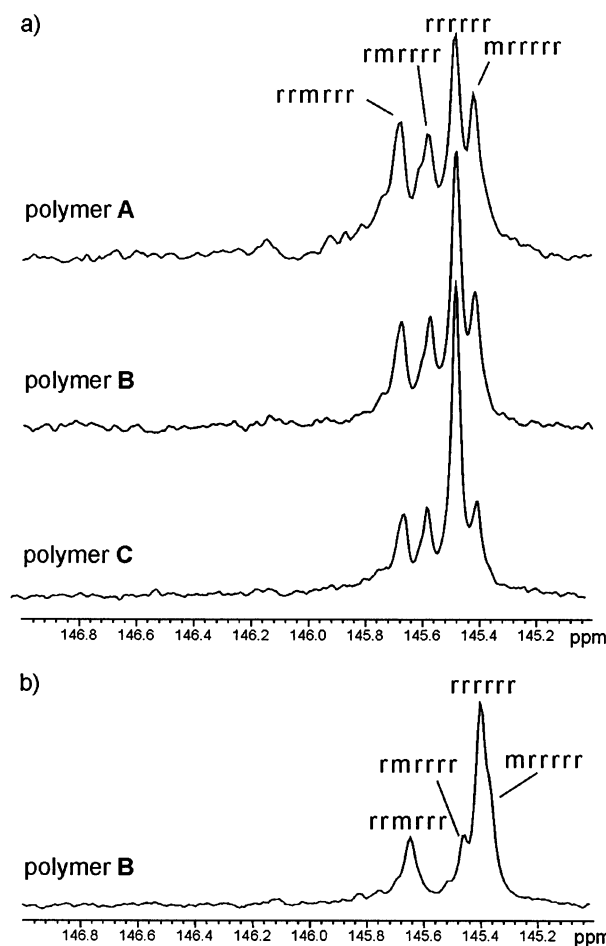


Figure 1. ^{13}C NMR assignments of the most probable heptads in the phenyl *ipso*-carbon region: (a) polymers **A**, **B**, and **C** in tetrachloroethane- d_2 , $T = 100$ °C; (b) polymer **B** in *o*-dichlorobenzene- d_4 , $T = 100$ °C.

the two next probable single- m pentads ($mrrr$ and $rmrr$) should appear with same intensities. The probability for double- m pentads in predominantly syndiotactic polystyrene is much lower. It is therefore not possible to assign the remaining three signals observed in our spectra on a pentad level. However, if the main signal (145.5 ppm) is assigned to the $rrrrr$ heptad, the next probable heptads are $mrrrr$, $rmrrr$, and $rrmrr$. These three heptads should appear with equal intensities as in the case of our polymers. For polymers with high syndiotacticity other heptads are statistically negligible (Table 1). The signal at 145.7 ppm, which lies in the range usually assigned to the mr triad, corresponds to the $rrmrr$ heptad. The signal at 145.4 ppm lies in the range usually assigned to the $rrrr$ pentad and therefore belongs to the $mrrrr$ heptad. The remaining signal at 145.6 ppm is located between the $rmrrr$ and the $rrmrr$ heptads and should be assigned to the $rmrrr$ heptad.

It should be mentioned that the shift sensitivity for the *ipso*-carbon is much lower in *o*-dichlorobenzene- d_4 , the solvent most commonly used for polystyrene analyses, than in tetrachloroethane- d_2 . In *o*-dichlorobenzene- d_4 the $rmrrr$ heptad is hardly separated from the $rrrrr$ heptad, while the $mrrrr$ heptad appears only as a weak shoulder of the $rrrrr$ heptad (Figure 1b). Therefore, in *o*-dichlorobenzene- d_4 a J -ade resolution close to the

Table 1. Calculated Values of All Diads, Triads, and Tetrads and the Most Probable Pentads, Heptads, and Hexads According to Bernoullian Statistics for Polymers B and C

assignment		calculated proportions	
		polymer B	polymer C
diads	<i>m</i>	0.118	0.078
	<i>r</i>	0.882	0.922
triads	<i>mm</i>	0.014	0.006
	<i>mr</i>	0.208	0.144
	<i>rr</i>	0.778	0.850
tetrads	<i>mmm</i>	0.002	0.001
	<i>mmr</i>	0.024	0.011
	<i>mrmm</i>	0.012	0.006
	<i>rmr</i>	0.092	0.066
	<i>mrr</i>	0.183	0.132
	<i>rrr</i>	0.686	0.784
	<i>rrrr</i>	0.162	0.122
pentads	<i>mmrr</i>	0.162	0.122
	<i>rmrr</i>	0.162	0.122
	<i>rrrr</i>	0.605	0.723
	all others	<0.022	<0.010
hexads	<i>mmrrr</i>	0.143	0.113
	<i>rmrrr</i>	0.143	0.113
	<i>rrmrr</i>	0.071	0.056
	<i>rrrrr</i>	0.534	0.667
	all others	<0.019	<0.009
heptads	<i>mmrrrr</i>	0.126	0.104
	<i>rmrrrr</i>	0.126	0.104
	<i>rrmrrr</i>	0.126	0.104
	<i>rrrrrr</i>	0.471	0.615
	all others	<0.017	<0.009

pentad level is observed.

The here proposed assignment on the heptad level is validated by ^{13}C NMR spectra of atactic polystyrene: the *ipso*-carbon regions in our spectra show more signals than can be expected with a resolution on the pentad level (10 possible pentads).

To confirm our heptad assignment, we also examined the methylene carbon region in the ^{13}C NMR spectra of our polymers (Figure 2a). Four distinct signals are present here. The main signal (44.4 ppm) can be assigned to the *rrrrr* hexad. Bernoullian statistics predicts that the next probable signals should be the *mrrrr*, *rmrrr*, and the *rrmrr* hexads in an expected ratio of 2/2/1. Because of its intensity, the signal at 45.9 ppm can be assigned to the *rrmrr* hexad. The remaining two signals with same intensity (each twice the intensity of the *rrmrr* hexad) can be assigned to the *mrrrr* (45.0 ppm) and the *rmrrr* hexad (43.2 ppm). The signal separation of the methylene carbon in tetrachloroethane- d_2 and *o*-dichlorobenzene- d_4 is similar (Figure 2b).

For highly syndiotactic polystyrene, like polymer C, other hexads are negligible and only appear just above the noise level. These signals grow with decreasing syndiotacticity of the polymer and are well-visible in the spectrum for polymer A. They can be assigned to the six different double-*m* hexads (relative ratio in parentheses): *mmrrr* (2), *mrmmr* (2), *mrrmr* (2), *mrrrm* (1), *rrmmr* (2), and *rrmrr* (1). No conclusive assignment of these signals can be given here due to low intensity and partial overlap.

Our hexad assignment corresponds best with that reported by Suparno et al.³ (based on Bernoullian statistical calculations); however, it does not agree with that according to Xu et al. (based on studies of predominantly syndiotactic polystyrene).⁷ The latter assign a low field shoulder of the *rrrrr* peak as the *mrrrr* hexad. We also observe this shoulder in the spectra of our polymers but believe it to originate from the beginning of octad splitting (Figure 2).

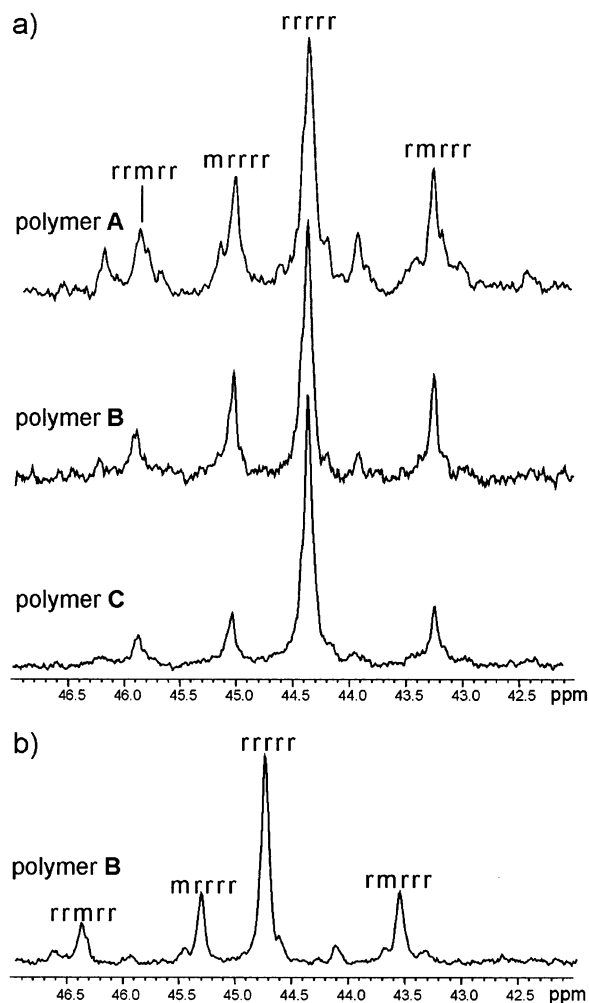


Figure 2. ^{13}C NMR assignments of the most probable hexads in the methylene carbon region: (a) polymers A, B, and C in tetrachloroethane- d_2 , $T = 100\text{ }^\circ\text{C}$; (b) polymer B in *o*-dichlorobenzene- d_4 , $T = 100\text{ }^\circ\text{C}$.

Our heptad and hexad assignments are confirmed by tacticity determination of our polymers: calculations based on either hexad or heptad assignments give the same results (B: *m* 11.8%; *r* 88.2%; C: *m* 7.8%; *r* 92.2%). A statistical calculation of all possible heptads and hexads with these starting values show the big gap between the probabilities for single-*m* and higher-*m* *J*-ades (Table 1). The signals of lower intensity correspond to higher-*m* *J*-ades, for which no definite assignment can be presented here.

In summary, ^{13}C NMR signals in the *ipso*-carbon region should not be assigned on a pentad but on a heptad level. This means that the syndiotacticities of polystyrenes earlier reported by us¹ and others¹⁰ are significantly higher.

Polymer Analyses. All polymers are characterized by GPC and show M_n values varying from 4.8×10^4 to 9.0×10^4 g/mol. Fractionation of the polymers with ethyl methyl ketone gives a separation according to molecular weight rather than tacticity. ^{13}C NMR spectra were recorded on a Bruker DRX600 (600 MHz) machine at $100\text{ }^\circ\text{C}$ (ca. 1000 scans). Each sample contained 65 mg of polymer dissolved in either 0.5 mL of tetrachloroethane- d_2 (internal reference: 74.1 ppm) or *o*-dichlorobenzene- d_4 (127.7, 130.5, and 132.6 ppm).

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References and Notes

- (1) Harder, S.; Feil, F.; Knoll, K. *Angew. Chem.* **2001**, *113*, 4391; *Angew. Chem., Int. Ed.* **2001**, *40*, 4261. (b) Harder, S.; Feil, F. *Organometallics* **2002**, *21*, 2268.
- (2) Johnson, L. F.; Heatley, F.; Bovey, F. A. *Macromolecules* **1970**, *3*, 175. (b) Randall, J. C. *J. Polym. Sci., Phys. Ed.* **1975**, *13*, 889.
- (3) Suparno, S.; Lacoste, J.; Raynal, S.; Regnier, J. F.; Schué, F.; Sempere, R.; Sledz, J. *Polym. J.* **1980**, *12*, 861.
- (4) Inoue, Y.; Nishioka, A.; Chûjô *Makromol. Chem.* **1972**, *156*, 207.
- (5) Jasse, B.; Lauprêtre, F.; Monnerie, L. *Makromol. Chem.* **1977**, *178*, 1987. (b) Sato, H.; Tanaka, Y.; Hatada, K. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 1667. (c) Sato, H.; Tanaka, Y. *ACS Symp. Ser.* **1984**, *247*, 181.
- (6) Matsuzaki, K.; Uryu, T.; Osada, K.; Kawamura, T. *Macromolecules* **1972**, *5*, 816. (b) Uryu, T.; Seki, T.; Kawamura, T.; Funamoto, A.; Matsuzaki, K. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 3035. (c) Kawamura, T.; Toshima, N.; Matsuzaki, K. *Macromol. Rapid Commun.* **1994**, *15*, 479.
- (7) Xu, J.; Ouyang, J.; Fan, Z.; Chen, D.; Feng, L.; Yang, Y. *Polym. J.* **1998**, *30*, 720.
- (8) Natta, G.; Pino, P.; Corradini, P.; Danusso, F.; Mantica, E.; Mazzanti, G.; Moraglio, G. *J. Am. Chem. Soc.* **1955**, *77*, 1708.
- (9) Ishihara, N.; Seimiya, T.; Kuramoto, M.; Uoi, M. *Macromolecules* **1986**, *19*, 2464.
- (10) For example: (a) Po, R.; Cardi, N.; Abis, L. *Polymer* **1998**, *39*, 959. (b) Zhang, Y.; Hou, Z.; Wakatsuki, Y. *Macromolecules* **1999**, *32*, 939. (c) Baudry-Barbier, D.; Camus, E.; Dormond, A.; Visseaux, M. *Appl. Organomet. Chem.* **1999**, *13*, 813. (d) Kaminsky, W.; Arrowsmith, D.; Strübel, C. *J. Polym. Sci., Part A: Polym. Chem. Ed.* **1999**, *37*, 2959. (e) Hultsch, K. C.; Voth, P.; Beckerle, K.; Spaniol, T. P.; Okuda, J. *Organometallics* **2000**, *19*, 228.

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