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Model Studies of End Capping of Mono- and Biended Polystyrene Anions. Stereoisomerism at the Chain Ends

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ABSTRACT: Model studies of end capping of living polystyryl anions, with and without α-methylstyrene at the chain ends, with chlorotrimethylsilane and chloromethyl methyl ether were done. In ^{1}H NMR spectra multiple peaks for $Si(CH_3)_3$ and CH_2OCH_3 group protons were observed. However, $Si(CH_3)_3$ peak patterns for polymers with and without α-methylstyrene at the chain ends were quite different. Trimethylsilyl end-group protons and methine or methylene protons of the polystyrene chain were not coupled, as determined by decoupling experiments. Various parameters such as initiator, solvent, temperature, and molecular weights did not change the peak pattern. This study indicates that the multiple peaks are due to stereoisomerism at the chain ends. Due to steric factors, selective stereoisomer formation is indicated when α-methylstyrene is the terminal unit before end capping. Further, the chain-end tacticities correspond to bulk tacticities and statistical analyses of multiple peaks gave $P_r = 0.55$, which is consistent with the reported values for anionically prepared polystyrene. Thus, end-group spectroscopy provides a means of determining bulk tacticity.

Introduction

Polyrotaxanes are two component systems in which a linear backbone polymer is threaded through macrocycles. This association of linear and cyclic species may result in polymers with improved solution, thermal, and mechanical properties.[1–8] Our goals were to synthesize cyclic polystyrene (PS) of low molecular weights (ca. 1500–2500) so as to have 30–50 ring atoms in the macrocycles and to use these macrocycles for making polyrotaxanes.

The synthesis and characterization of cyclic polystyrene has been reported in the literature. A broad range of molecular weights for cyclic polystyrene has been synthesized.[4,9–14]

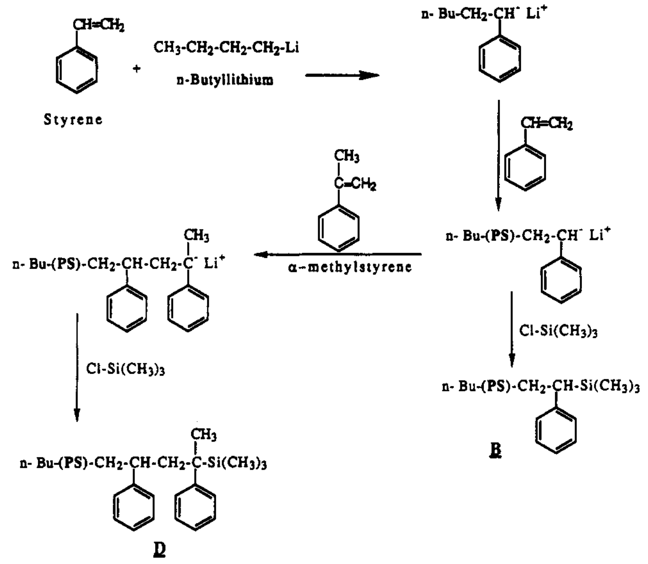
Our early efforts to synthesize cyclic polystyrene using sodium naphthalide as initiator and dichlorodimethylsilane (DCDMS) as cyclization agent (difunctional terminator) presented us with two problems: (i) multiple peaks for the dimethylsilyl group protons in the ^{1}H NMR spectrum and (ii) incorporation of very low amounts of the terminator. The latter problem was corrected by using better experimental and analytical techniques. However, the first problem of multiple peaks persisted.

DCDMS has been used for the synthesis of cyclic polymers;[10,12] however, there is no report on the characterization of the dimethylsilyl group incorporated into cyclic polymers. Further, multifunctional chlorosilanes have been extensively used for the synthesis of star-shaped polymers;[15] however, no detailed characterization of incorporated silanes has been done. Thus, the origin of the multiple peaks in our polymer was puzzling. Hence we decided to do model reactions by end capping living polystyryl anions (prepared by using *n*-butyllithium and sodium naphthalide as initiators) with chlorotrimethylsilane (CTMS) and chloromethyl methyl ether (CMME). The lower molecular weights of the model polymers enabled us to study the nature of the end groups by spectroscopic methods.

Experimental Section

THF was distilled once from sodium–benzophenone and then styrene and *n*-butyllithium were added to it; the solution was freeze–thawed on the vacuum line (ca. 10^{-5} Torr) five to six times, distilled on the vacuum line, and stored in the glovebox ($[H_2O] = 0.6$ ppm, $[O_2] = 1.0$ ppm).

Scheme I
Model Reactions Using *n*-Butyllithium as Initiator



Poly(styryl)lithium solutions in cyclohexane and benzene were freeze–thawed five to six times and distilled on the vacuum line, and the pure solvents were stored in the glovebox.

CMME and CTMS were distilled under nitrogen and the middle fractions were freeze–thawed five to six times, distilled on the vacuum line, and stored in the glovebox.

Styrene was passed through alumina and titrated against dibutylmagnesium until light yellow and distilled under a vacuum of 38 Torr (N_2) at 57 °C. The middle fraction was freeze–thawed five to six times on the vacuum line and distilled freshly before use.

Sodium naphthalide was prepared in 30 mL of THF by mixing 1.0 g of sodium and 10.0 g of naphthalene. It was allowed to stir for 1 day at 25 °C in the glovebox and titrated against 0.5 N HCl before use.

Styrene was polymerized and then end capped with CTMS or CMME in the glovebox. Styrene (4.0 mL) polymerization in THF–benzene (55:45 v/v, 110.0 mL) was initiated by using *n*-butyllithium or sodium naphthalide. Polymerizations were done at 10–15 °C for 30 min. Living polymers were end capped with 2–3 equiv (relative to the initiator) of the end-capping agents. In some cases, 1.1–2.0 equiv of α-methylstyrene were added to the living polystyrene and after 15 min the resulting living polymer

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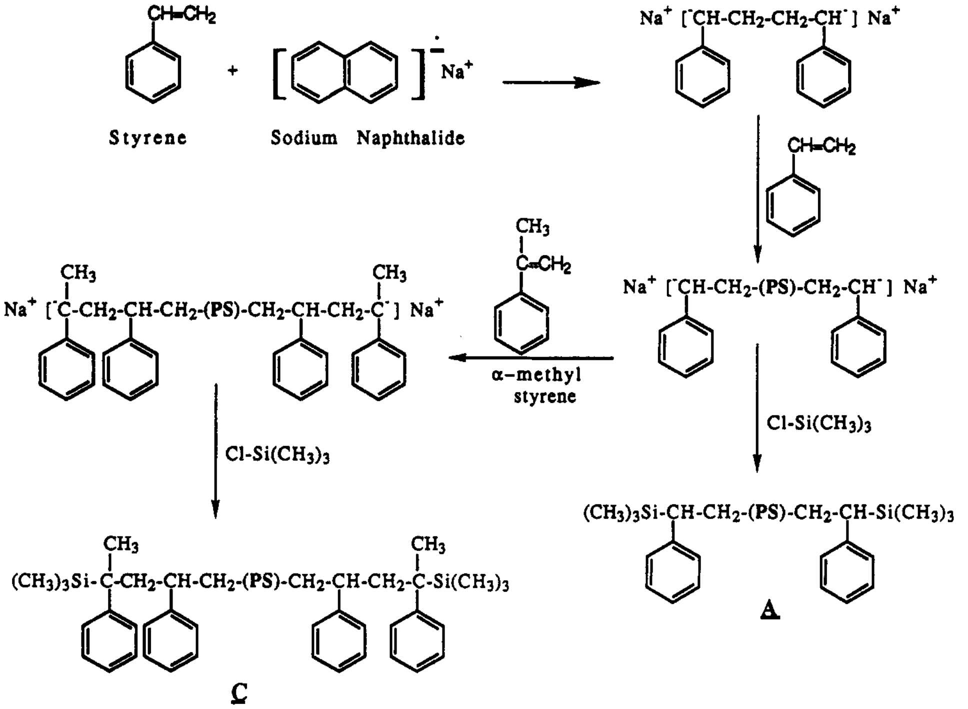
Scheme II
Model Reactions Using Sodium Naphthalide as Initiator



was end capped with DCDMS. Polymers were precipitated into methanol and washed with ethanol to remove naphthalene.

GPC analyses of the polymers were done at 30 °C in THF using a Waters system (RI and UV detectors) after calibration with PS standards. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were obtained on a Varian Unity 400-MHz spectrometer. Deconvolution of the proton NMR peaks was accomplished by assuming pure Lorentzian peak shapes using built-in software of the spectrometer. Routine proton NMR and integrations of the signals for each model polymer synthesized were done on Brucker WP 270 spectrometer.

Results and Discussion

n-Butyllithium (Scheme I) and sodium naphthalide (Scheme II) were used to initiate the polymerization of styrene to obtain mono- and biended living polystyrene anions followed by end capping with CTMS (with and without incorporation of α-methylstyrene at the chain ends). The reactivity ratios of styrene and α-methylstyrene in anionic copolymerizations are 35.0 and 0.003, respectively,[16] because the methyl groups hinder the addition of the α-methylstyrene unit to the α-methylstyryl anion. This permits incorporation of essentially only one α-methylstyrene unit at the chain end, thus allowing selective changes in the resulting living anion.

Typical target molecular weights for model polymers were in the range 1600–2500. Molecular weights obtained were within 10% of the target molecular weights. The molecular weight distributions were between 1.05 and 1.20. Integration values in ^{1}H NMR spectra of phenyl ring protons vs end-group protons and GPC molecular weights were used to calculate percent end capping for the model polymers. The end capping yields were found to be between 92 and 96%. The estimated error was ±8%.

The ^{1}H, ^{13}C, and ^{29}Si NMR spectra of $Si(Me)_3$ end groups of model polymers initiated with sodium naphthalide, with and without a terminal α-methylstyrene unit, are shown in Figure 1. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra of $Si(Me)_3$ end groups of model polymers initiated with *n*-butyllithium, with and without a terminal α-methylstyrene unit, are shown in Figure 2.

The multiple peaks observed in the ^{1}H NMR spectra of difunctionally (A) and monofunctionally (B) terminated samples were investigated further. The peaks are identical except that peaks for polymer B are shifted to lower field by 0.1 ppm. Four major peaks are seen in the region from −0.05 to −0.30 ppm, which are split further, resulting in eight distinguishable peaks. The $Si(CH_3)_3$ group protons of the corresponding α-methylstyrene-terminated polymer C and D are identical; however, compared to A and B they are very different. A broad peak ranging from −0.05 to −0.26 ppm shows three additional peaks embedded in it as they appear as shoulders on the main peak. Thus, it has four different peaks. Again, the peaks for polymer B are shifted downfield by ~0.1 ppm. Similar behavior was observed in ^{13}C and ^{29}Si NMR spectra for $Si(CH_3)_3$ groups of model polymers. For model polymers A and B, in both ^{13}C and ^{29}Si NMR spectra there were two major peaks, which were further split. In ^{13}C and ^{29}Si NMR spectra of C and D, one major peak is seen and another peak of one-fourth the size appears downfield. Further, in ^{29}Si NMR spectra, peaks for model polymers C and D have shifted downfield by 5.8 ppm relative to those of A and B.

The above results are surprising considering that $Si(CH_3)_3$ group protons, carbons, and silicons are equivalent and should appear as singlets in the respective NMR spectra. In a recent study[17] it was shown that $Si(CH_3)_3$ group protons of 4-(trimethylsilyl)methylstyrene and 4-bis(trimethylsilyl)methylstyrene do not exhibit any coupling with α-methylene or methine protons and the carbon and proton nuclei produce singlets in respective NMR spectra. To ascertain that these results are not artifacts and to understand the origin of multiple peaks, various parameters such as polymerization conditions, molecular weight, and NMR parameters were studied.[18]

Initiators. In this study two initiators were used, namely, sodium naphthalide and *n*-butyllithium. The ^{1}H NMR peak patterns for $Si(CH_3)_3$ groups did not change with initiators. This also indicates that the peak pattern is not dependent on counterions, e.g., Na^+ and Li^+.

Polymerization Conditions. Typically, a benzene–THF (45:55) mixture was employed for polymerization at 10–15 °C for 30 min. Changing polymerization times from 15 min to 1 h or polymerizations temperature to 0–5 °C had no effect on the peak patterns observed. Changing

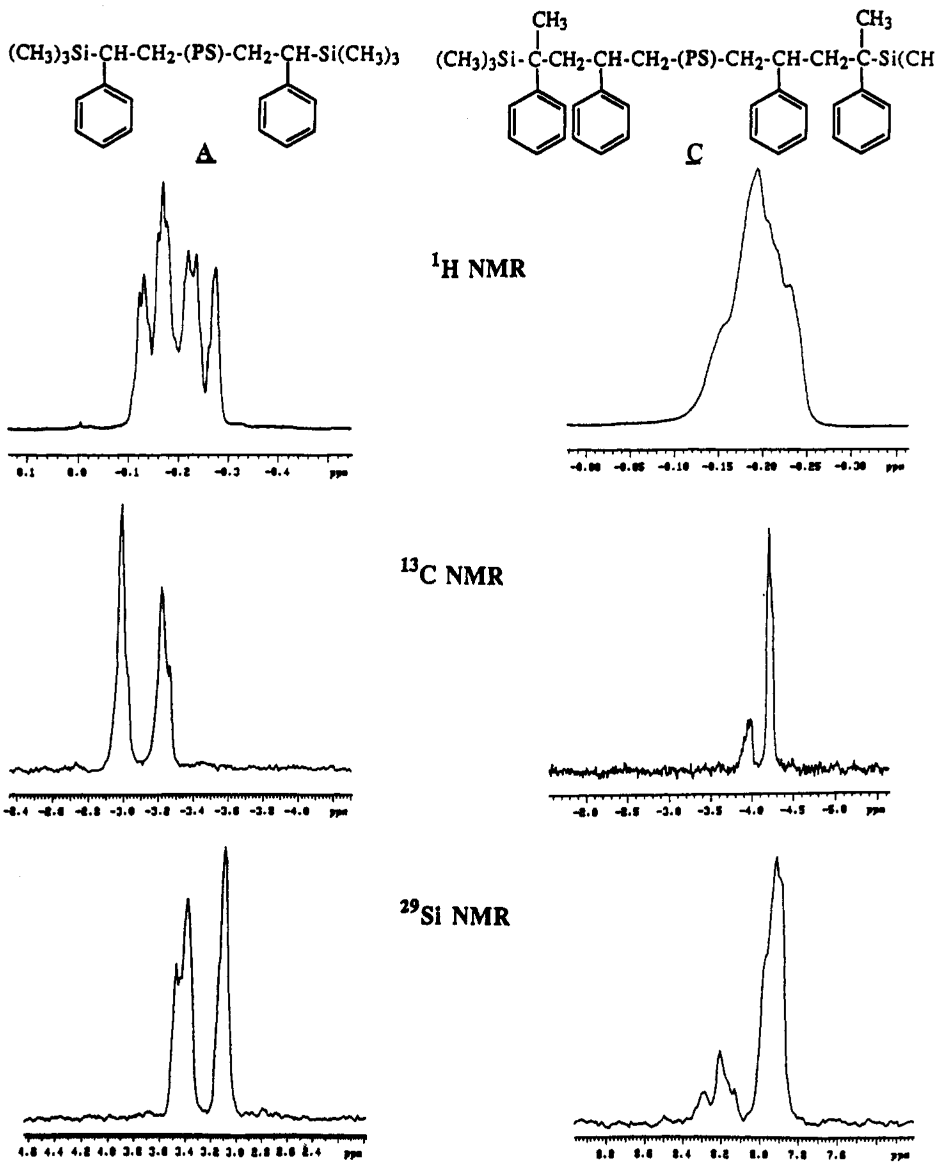


Figure 1. ^{1}H, ^{13}C, and ^{29}Si NMR spectra of $Si(CH_3)_3$ groups of model polymers A (M_n = 2200, M_w/M_n = 1.15) and C (M_n = 2300, M_w/M_n = 1.15).

the polymerization solvent to THF (10–15 °C, 30 min) had no effect on the peak pattern; however, a broader molecular weight distribution was obtained.

Molecular Weight. Model polymers of molecular weight 1000–50000 were studied to determine if longer or shorter chains had any effect on the peak patterns, but this was found not to be the case.

End-Capping Agent. Three different batches of CTMS were used to see if any impurity may be responsible, but there was no change.

NMR Parameters. No changes were observed in the proton NMR peak pattern when the relaxation delay was varied between 2 and 16 s. To determine if the multiple peaks are the due to long-range coupling of CH_2 and CH protons of the polystyrene chain with the protons of the $Si(CH_3)_3$ end group, decoupling experiments in proton NMR were performed; no such coupling was found.

Incorporation of α-methylstyrene units at the chain ends changes the NMR peak pattern for model polymers; the only difference is that the methine proton on the last styrene repeat unit is replaced by a methyl group. The results indicate that $Si(CH_3)_3$ groups are exposed to more than one environment at the chain ends. This led us to conclude that the eight peaks observed for polymers A and B in proton NMR spectra are due to stereoisomerism (tacticity) at the chain ends and that tetrad structures are seen. In principle, eight possible tetrad structures are possible at the chain ends, and in principle $Si(CH_3)_3$ groups attached to each tetrad structure should have different chemical shifts. In fact, we have been able to resolve these peaks in proton NMR spectra.

Four peaks are observed in proton NMR of model polymers (C and D) with terminal α-methylstyrene units. This suggests that the bulkier methyl group favors selective stereoisomer formation due to the steric factors, thus limiting the number of stereoisomers possible, and that triad structures are seen. Further, ^{13}C and ^{29}Si spectra of these polymers show one major peak. This also supports the above conclusion that multiple peaks are due to tacticity at the chain ends. In a similar study, multiple peaks due to $^{13}CH_3$ end groups on poly(2-vinylpyridine) have been attributed to stereoisomerism at the chain ends.[19]

Living polystyrene end capped with chloromethyl methyl ether (E) was analyzed by ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H and ^{13}C NMR spectra of CH_2OCH_3 end groups of model polymers initiated with sodium naphthalide are shown in Figure 3. In proton NMR the OCH_3 groups appear as multiple peaks (at least eight) from 3.1 to 3.2 ppm while OCH_2 peaks appear as diffuse multiplets from 3.2 to 3.4 ppm. There is some overlapping of these signals; however, tacticity at the chain ends is evident. The ^{13}C NMR spectrum in DMF shows two sharp peaks

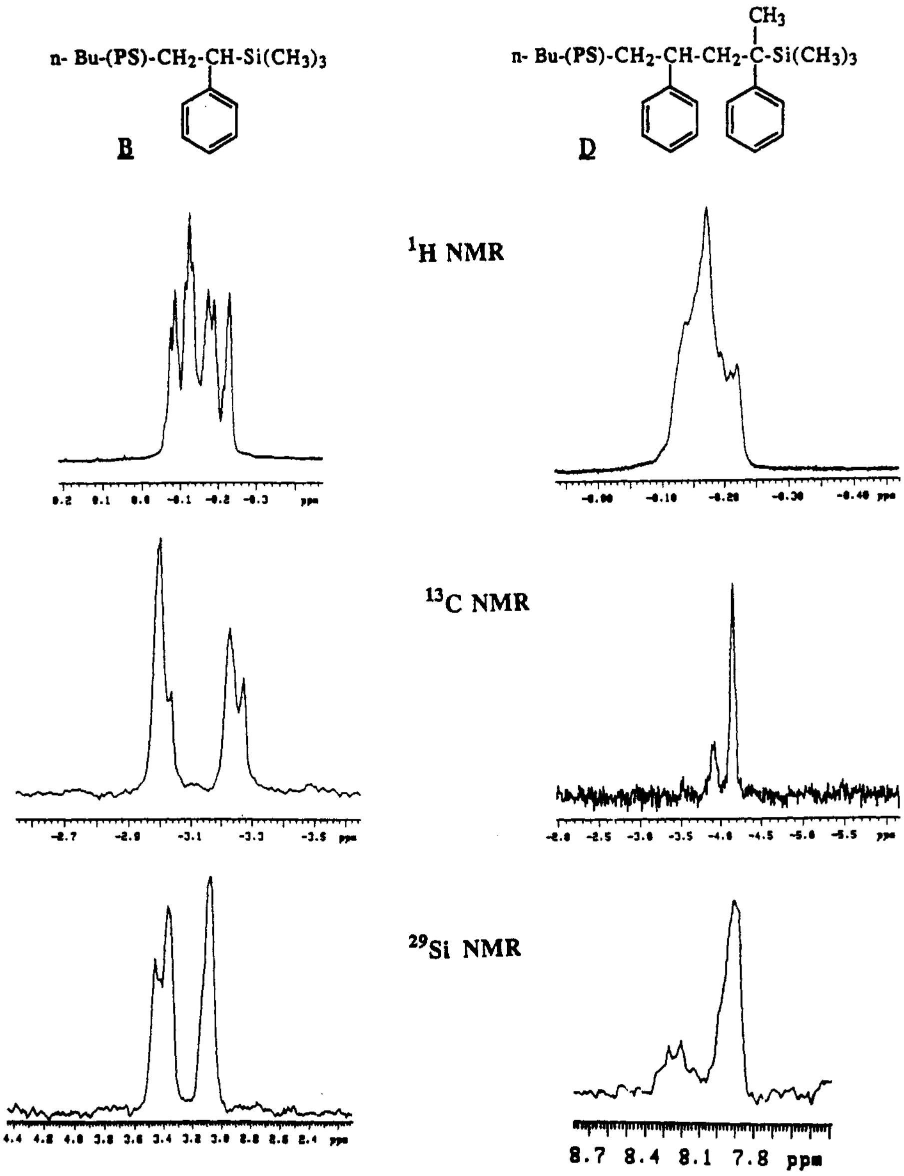


Figure 2. ^1H, ^{13}C, and ^{29}Si NMR spectra of $Si(CH_3)_3$ groups of model polymers B (M_n = 1800, M_w/M_n = 1.10) and D (M_n = 2500, M_w/M_n = 1.09).

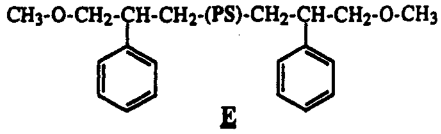
at 58.40 and 58.64 ppm corresponding to OCH_3 carbons while OCH_2 carbons appear as multiple peaks from 76.7 to 78.6 ppm. The assignment of these peaks to OCH_3 and OCH_2 carbons was confirmed by DEPT ^{13}C NMR.

As indicated above, the peak pattern did not change with molecular weights from 1000 to 50 000. This suggests that stereoisomerism seen at the chain ends of model polymers A and B is related to the bulk tacticity of the polymer. Thus, it is possible to obtain information on bulk tacticity of these anionically prepared polymers by analyses of multiple peaks for $Si(CH_3)_3$ in ^1H NMR.

Various attempts have been made to determine bulk tacticity of polystyrene prepared by anionic, cationic, and free-radical polymerization using ^{13}C NMR spectroscopy.[20-33] Methylene and C(1) phenyl carbons have been probed to determine the probability of racemic diad content (P_r). P_r values ranging from 0.5 to 0.79 had been reported for anionically prepared polystyrene. However, assignments of methylene or C(1) phenyl carbon peaks to tetrads and higher -ads were questionable.[20,25,27,32,33] Sato et al.[29-33] prepared oligomeric polystyrene anionically and isolated various triads, tetrads, and pentads. These were analyzed by ^{13}C and ^1H NMR spectroscopy to correctly assign methylene and C(1) phenyl carbon peaks to various meso and racemic *n*-ads. On the basis of these results and Bernoullian statistics, they found the value for P_r to be 0.56 for anionically prepared polystyrene. Other authors[25] have then correctly assigned the respective peaks, achieving the same values for P_r (0.50–0.54) within the experimental error.

The $Si(CH_3)_3$ peaks of polymer A were computer resolved into 16 peaks through deconvolution, and relative peak areas were determined by using pure Lorentzian peak shapes. Figure 4 shows the actual spectrum (top), the deconvoluted peaks (bottom), and the full fit (center). The resonance frequencies and intensity data of the deconvoluted peaks are shown in Table I. Estimated error is ±3%.

^{13}C NMR data cannot be used reliably for interpreting ^1H NMR peaks since the resonating order of various *n*-ads, even among the carbons of methylene and C(1) phenyl groups, were diffenent.[33] Thus, assignments of these peaks to tetrad structures are based on ^1H NMR studies of PS oligomeric triads[29] and comparative study of syndiotactic, isotactic, and atactic polystyrene by ^1H NMR.[34] The methine protons of the mm triad of oligomeric PS appears downfield (2.21 ppm), as much as 0.3 ppm relative to the rr triad (2.54 ppm). In the ^1H NMR spectrum of syndiotactic polymer, the methine protons appear 0.3 ppm upfield compared to isotactic polystyrene, while methyl-



$CH_3\text{-}O\text{-}CH_2\text{-}\underset{C_6H_5}{CH}\text{-}CH_2\text{-}(PS)\text{-}CH_2\text{-}\underset{C_6H_5}{CH}\text{-}CH_2\text{-}O\text{-}CH_3$

E

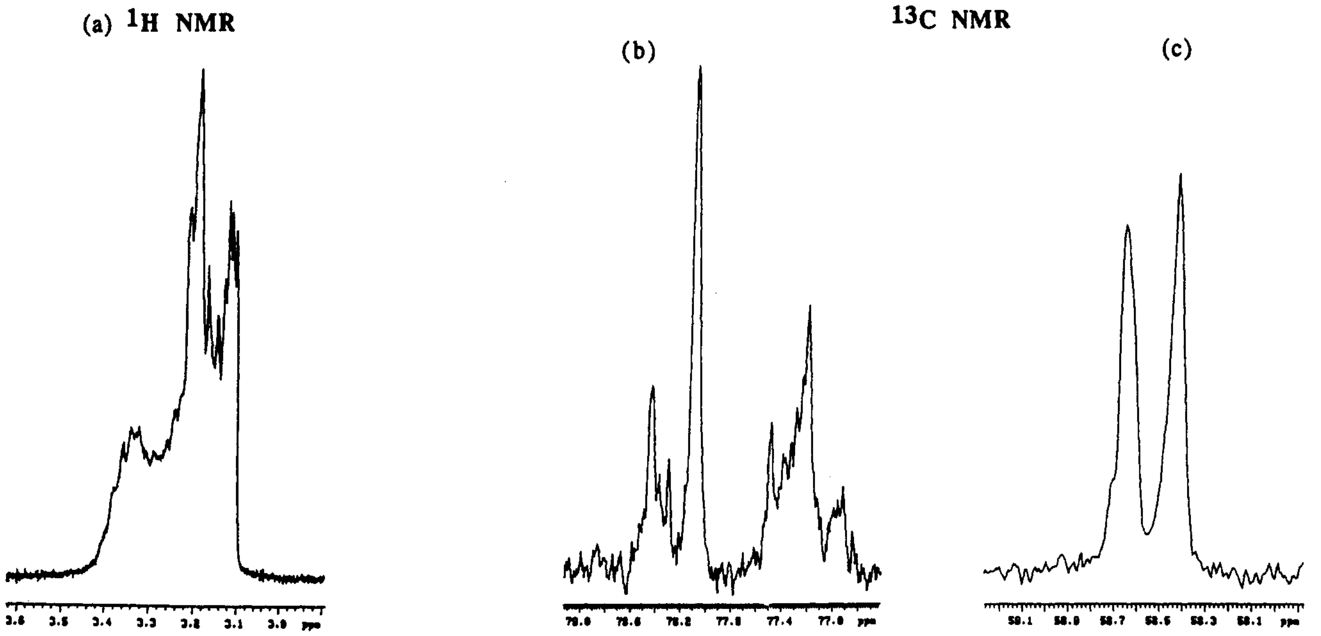
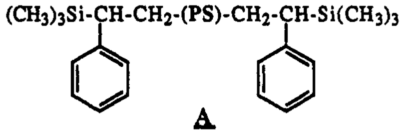


Figure 3. NMR spectra of CH_2OCH_3 groups of model polymer E (M_n = 1800, M_w/M_n = 1.12). (a) ^1H NMR and (b) ^{13}C NMR CH_2O groups; (c) ^{13}C NMR OCH_3 groups.



$(CH_3)_3Si\text{-}\underset{C_6H_5}{CH}\text{-}CH_2\text{-}(PS)\text{-}CH_2\text{-}\underset{C_6H_5}{CH}\text{-}Si(CH_3)_3$

A

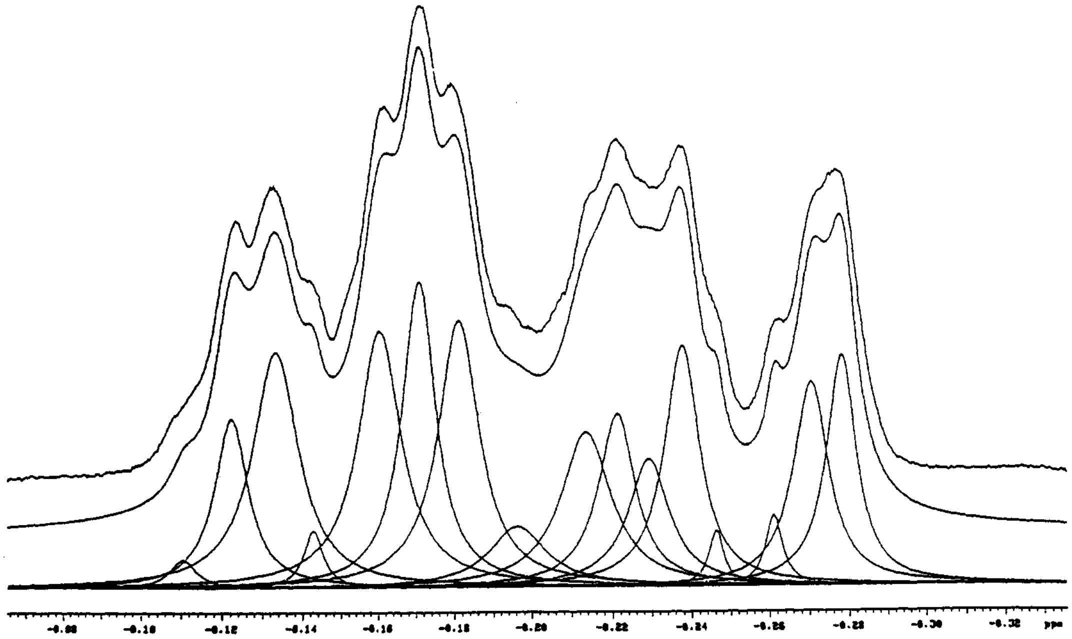


Figure 4. Deconvolution of the ^1H NMR spectrum of $Si(CH_3)_3$ groups of the model polymer A. The actual spectrum (top), the deconvoluted peaks (bottom), and the full fit (center) are shown.

ene protons appear 0.2 ppm upfield. Further, in atactic PS the respective methine and methylene proton chemical shifts are between those of syndiotactic and isotactic polystyrene.

The deconvoluted peaks 13–16 were assigned to rrr tetrads since they appear upfield, while peaks 1, 2, and 4 at low field were assigned to mmm tetrads. A P_r value of 0.55 was calculated from rrr tetrad probabilities, which agrees well with the reported P_r value of 0.56 for anionic polymerization.[29-33]

From Bernoullian statistics, using P_r = 0.55, probabilities for other tetrads (rmm, mmr, rrm, mrr rmr, mrm) were calculated and assigned. These are shown in Table II; assignments with marks # and * may be interchanged.

Table I
Frequencies and Integral Values of Deconvoluted Peaks

line	frequency, Hz	height[a]	line width, Hz	integral[a]
1	-44.048	5.29	3.15	16.68
2	-44.811	31.70	4.04	128.19
3	-53.177	43.97	5.56	244.57
4	-57.065	10.69	2.38	25.43
5	-64.020	47.88	5.55	265.88
6	-68.250	57.02	4.20	239.70
7	-72.264	49.77	5.11	254.49
8	-78.443	11.33	7.06	79.98
9	-85.323	28.92	5.99	173.25
10	-88.350	32.27	4.41	142.25
11	-91.577	23.87	5.06	120.84
12	-94.961	44.80	4.27	191.19
13	-98.370	10.38	1.88	19.52
14	-104.315	13.27	2.04	27.06
15	-108.062	37.98	4.23	160.59
16	-111.007	42.88	3.66	157.06

[a] Arbitrary units.

Table II
Statistical Analyses of Deconvoluted Multiple Peaks

		intensity, %	
assignments[b]	peaks	obsd	$P_r = 0.55$[a]
mmm	1, 2, 3	7.6	9.1
rmm and mrm#	4, 5	22.7	22.3
mmr# and rmr*	6, 7, 8	25.6	24.8
mrr and rrm*	9, 10, 11, 12	27.9	27.3
rrr	13, 14, 15, 16	16.2	16.6

[a] Calculated from Bernoullian statistics. [b] Assignments marked # and * may be interchanged.

More than one peak has been assigned to the various tetrads observed because tetrad structures usually show splitting up to pentads and hexads; however, it is difficult to assign all these peaks to higher -ads than tetrads without having oligomeric model compounds.

The above results support the claim that chain-end tacticities in these systems are related to the bulk tacticities. By use of a similar method it would be possible to analyze the multiple peaks observed for CH_2OCH_3 end groups to obtain information on bulk tacticity. This offers a new method, by incorporating specific groups at the chain ends, to determine bulk tacticity just by ^1H NMR spectroscopy without resorting to time-consuming ^{13}C NMR methods. Further, polymers of low molecular weights can also be analyzed as reliable models for higher molecular weight polymers where solubility in common NMR solvents is a problem.

Conclusions

Model polymers of low molecular weights enabled us to study the nature of the $Si(CH_3)_3$ and CH_2OCH_3 end groups by NMR spectroscopy. Various parameters were studied and the results indicate that multiple peaks are due to chain-end tacticity. Selective stereoisomer formation is indicated when α-methylstyrene is the terminal unit before the polymer is end capped. The tacticity at the chain ends had no dependence on the molecular weight and hence provides a facile way to determine the bulk polymer tacticity. Devoncolution of the multiple peaks and statistical analyses indicated the probability of racemic diad content, P_r, to be 0.55. This result is consistent with reported literature values.

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