Macromolecules 1987, *20*, 2035-2037

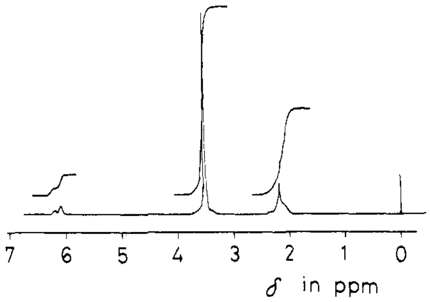


Figure 1. ^{1}H NMR spectrum of poly(1).

Table I
Anionic Polymerization of 1 in THF at -78 °C

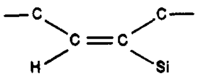
1 mmol	K-Naph, mmol	α-MeSt, mmol	$\bar{M}_n \times 10^{-4}$ calcd[a]	$\bar{M}_n \times 10^{-4}$ obsd[b]	$\bar{M}_w/\bar{M}_n$
3.95	0.205	0.358	0.71	0.79	1.09
12.10	0.300	0.576	1.4	1.4	1.10
13.00	0.112	0.280	4.1	4.6	1.14

[a] $\bar{M}_n$(calcd): calculated from the monomer to initiator ratio. [b] $\bar{M}_n$(obsd): calculated by vapor pressure osmometry in benzene.

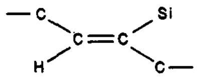
Table II
^{1}H and ^{13}C Chemical Shifts of Olefinic Proton and Carbons of 4-(Trimethoxysilyl)-4-octene and Poly(1)[a]

		model compounds		poly(1)	
		E form	*Z* form	*E* form	*Z* form
^{1}H	=CH	6.09	6.15	6.14	6.21
^{13}C	=CSi	131.6	127.4	131.1	127.8
	=CH	146.4	148.3	146.4	148.5

[a] Solvent $CDCl_3$; ppm from internal tetramethylsilane.



E form



Z form

can be seen, the olefinic proton of the *Z* isomer resonates at lower field than that of the *E* isomer. A similar tendency was also reported for trialkylsilyl-substituted olefins.[7] Accordingly, the olefinic proton signals centered at 6.14 and 6.21 ppm in Figure 1 can be assigned to *E* and *Z* forms of monomer units incorporated in the polymer, respectively. The estimated *E*:*Z* ratio was about 70:30.

Further information about the microstructure of poly(1) was provided by ^{13}C NMR analysis. Figure 2 shows olefinic region of the proton-decoupled ^{13}C NMR spectrum of the resulting polymer, where two pairs of olefinic carbons are observed. Detail assignments of the signals were carried out by comparing the chemical shifts with those of the corresponding model compounds. They are summarized in Table II. Two major peaks at 146.4 and 131.1 ppm in Figure 2 can be assigned to carbons of 1,4-*E* configuration, and the other minor peaks at 148.5 and 127.8 ppm are attributable to those of 1,4-*Z* form. Based on the assumption that nuclear Overhauser enhancement is equally effective to both carbons of isomeric forms, the *E*:*Z* ratio of monomer units in the polymer chain is estimated to be 67:23 from relative intensities of the signals at 146.4 and 148.5 ppm, which agrees with the result of the ^{1}H NMR study. It should be noted that no other peaks which can be assigned to 1,2- or 3,4-structure were observed within the detection limits of our ^{13}C NMR spectrometer. This is in contrast to the anionic polymerizations of butadiene and isoprene[8,9] where dangling vinyl structures were main components under the conditions employed here. Detail study of polymerization of this monomer and its derivatives will be published in the near future.

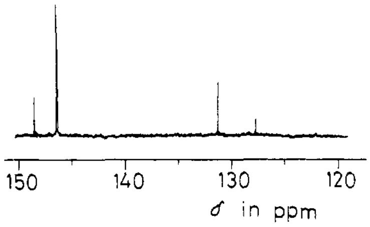


Figure 2. Olefinic region of proton-decoupled ^{13}C NMR spectrum of poly(1).

Registry No. 1, 104955-47-7; $H_3C(CH_2)_2C(Si(OCH_3)_3)=CH(CH_2)_2CH_3$, 109432-67-9.

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β-Hydrogen Abstraction and Regiospecific Insertion in Syndiotactic Polymerization of Styrene

In this paper are reported some results concerning the mechanism of polymerization of styrene to a highly syndiotactic polymer.[1,2] In particular the insertion of the monomer into the active bonds of the catalytic complexes is investigated, both in the initiation and the chain propagation steps.

In a previous paper[3] it was reported that a sharp methylene resonance at 18.4 ppm is observed in the ^{13}C NMR spectrum of highly syndiotactic polystyrene prepared in the presence of the homogeneous catalytic system tetrabenzyltitanium (TBT)/methylalumoxane (MAO)/triethylaluminum 70% enriched with ^{13}C on the methylene carbon (^{13}TEA). The resonance considered was assigned to the presence of [4-^{13}C]-2-phenylpentyl end groups arising from secondary insertion of styrene on active metal-^{13}C enriched ethyl bonds (chain initiation step) formed either via exchange between the catalytic complexes and ^{13}TEA or via chain transfer with ^{13}TEA:

$$M{-}^{13}CH_2CH_3 + C_8H_8 \rightarrow M{-}CH(C_6H_5)CH_2{}^{13}CH_2CH_3$$

where M = metal of the catalytic complex. According to ref 3, in the considered chain initiation step, secondary insertion occurs exclusively since no methylene resonance

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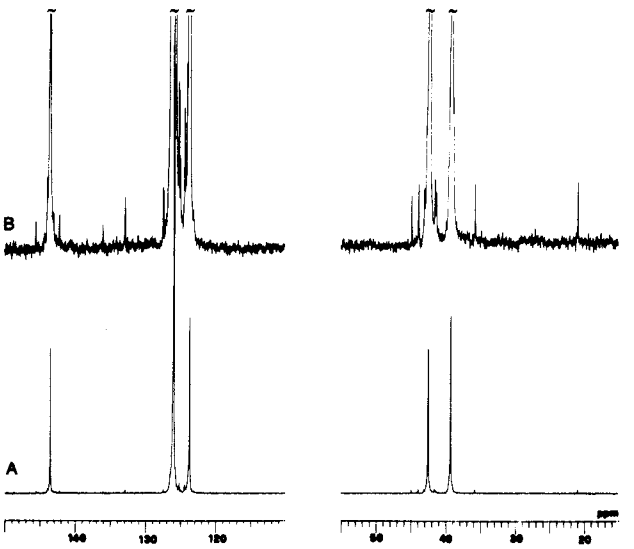


Figure 1. (A) ^{1}H-decoupled ^{13}C NMR spectrum of sample 1 (HMDS scale); (B) 16–fold vertical expansion of the same spectrum. The high stereoregularity of the sample can be appreciated, according to ref. 1, from the presence of only one sharp resonance for the methylene (42.4 ppm) and for the quaternary aromatic carbon (143.5 ppm).

is observed at 29 ppm as expected for initiation steps involving primary insertion:

$$\text{M}-{}^{13}\text{CH}_2\text{CH}_3 + \text{C}_8\text{H}_8 \rightarrow \text{M}-\text{CH}_2\text{CH}(\text{C}_6\text{H}_5){}^{13}\text{CH}_2\text{CH}_3$$

Of course, due to the composition of the catalytic system, it is expected that chain propagation may also be initiated on other active bonds such as M–CH_3, M–H (arising from β-hydrogen abstraction), or even M–$CH_2C_6H_5$. The end groups resulting from these possible initiation steps are less easily observed due to the low natural abundance of ^{13}C. However, weak resonances attributable to unenriched end groups can be observed in the spectra of low molecular weight samples. Figure 1 shows the ^{1}H-decoupled ^{13}C NMR spectrum of a sample of highly syndiotactic polystyrene prepared in the presence of TBT/MAO (without any addition of ^{13}C enriched $Al(C_2H_5)_3$), according to ref 2, and soluble in boiling butanone (sample 1). The main resonances are due to the carbons of the inner monomer units: quaternary aromatic carbons at 143.5 ppm, ortho and meta aromatic carbons at 125.9 ppm, para aromatic carbon at 123.6 ppm, aliphatic methylene carbon at 42.4 ppm, and methine carbon at 39.2 ppm. In the vertical expansion (Figure 1B) one can also observe additional weak resonances both in the region of the saturated carbons at 20.9, 35.7, and 43.8 ppm and in that of the unsaturated carbons at 127.4 and 132.8 ppm. The off-resonance spectrum shows that the unsaturated carbons are methines and that the saturated carbons are CH_3's (20.9 ppm), CH_2's (43.8 ppm), and CH's (35.7 ppm). It is also worthwhile to point out that these resonances have approximately the same intensity and that no resonance, diagnostic of irregular arrangements of the styrene monomer units, is observed either in the range 26–30 ppm [–($CH_2CH(C_6H_5)CH(C_6H_5)CH_2$]–] or at 47–51 ppm [–($CH(C_6H_5)CH_2CH_2CH(C_6H_5)$–] as anticipated by Weill and Vogl.[4] The resonances of two unsaturated methine carbons can be accounted for by the presence of 2,4-diphenylbuten-3-yl end groups (PB): $CH(C_6H_5){=}CHCH(C_6H_5)\text{-}CH_2$–. The resonances of the saturated carbons can be attributed to C(1) (43.8 ppm), C(2) (35.7 ppm), and C(3) (20.9 ppm) of 2-phenylpropyl end groups (PP): –C(1)H_2C(2)H(C_6H_5)C(3)H_3. In fact the chemical shifts become very close to those of the C(3), C(4), and C(5) of 4,6,8-triphenylundecane (TPU) reported in the literature,[5] C(1)H_3C(2)H_2C(3)H_2C(4)H(C_6H_5)C(5)$H_2CH(C_6H_5)CH_2CH(C_6H_5)CH_2CH_2CH_3$, after addition of the contribution of C(2) and C(1) according to the rules of Grant and Paul, i.e.:

$$\delta_{\text{C}(1)}(\text{PP}) + \delta_\gamma = 41.3 \approx \delta_{\text{C}(5)}(\text{TPU}) = 42.5$$

$$\delta_{\text{C}(2)}(\text{PP}) + \delta_\beta + \delta_\gamma = 42.6 \approx \delta_{\text{C}(4)}(\text{TPU}) = 41$$

$$\delta_{\text{C}(3)}(\text{PP}) + \delta_\alpha + \delta_\beta = 39.4 \approx \delta_{\text{C}(3)}(\text{TPU}) = 38$$

By considering that polymerization is a polyinsertion on metal–carbon bonds, the PB end groups can only arise from β-hydrogen abstraction involving growing polymer chains bonded to the metal through monomer units inserted in secondary fashion, according to the scheme

$$\text{M}-\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2- \rightarrow \text{M}-\text{H} + \text{C}_6\text{H}_5\text{CH}{=}\text{CHCH}(\text{C}_6\text{H}_5)\text{CH}_2-$$

The presence of trans-substituted unsaturations has been also confirmed by infrared analysis (absorption at 965 cm^{-1}). Reinitiation on the M–H bond via secondary insertion of the monomer accounts for the observed PP end groups:

$$\text{M}-\text{H} + \text{C}_8\text{H}_8 \rightarrow \text{M}-\text{CH}(\text{C}_6\text{H}_5)\text{CH}_3$$

PP end groups could in principle arise also from primary insertion on M–CH_3 bonds according to the hypothetical initiation

$$\text{M}-\text{CH}_3 + \text{C}_8\text{H}_8 \rightarrow \text{M}-\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)\text{CH}_3$$

This possibility, however, can be disregarded not only in view of the fact that secondary insertion has been observed in the initiation on M–$^{13}CH_2CH_3$ bonds[3] but also because no irregularly arranged monomer units are observed in the spectrum of the sample. In fact head-to-head arranged units –($CH(C_6H_5)CH_2CH_2CH(C_6H_5)$)– should necessarily be observed in the case of macromolecules started with primary insertion and bonded to the metal of the catalytic complexes by secondary inserted units at the moment of the β-hydrogen abstraction:

$$\text{M}-\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2-\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)\text{CH}_3 \rightarrow \text{M}-\text{H} + \text{CH}(\text{C}_6\text{H}_5){=}\text{CHCH}(\text{C}_6\text{H}_5)\text{CH}_2-\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)\text{CH}_3$$

The amount of regioirregular arrangements should be at least equal to that of the end groups. Regioirregular units are undetectable not only in the spectrum of sample 1 but even in the spectrum of sample 2 (number-average degree of polymerization 15) prepared at 90 °C with the catalytic system tetrabenzylzirconium (TBZ)–MAO and soluble in acetone at room temperature. In fact the ^{13}C NMR spectrum of this sample, reported in Figure 2, shows, with fair intensity, the resonances expected for PB and PP end groups in equal amount but no resonances at all diagnostic of irregularly arranged monomer units. Moreover, it is worth noting that one cannot observe any resonance attributable to end groups resulting from secondary insertion either on M–CH_3 or M–$CH_2C_6H_5$ bonds. This fact gives the additional information that most of the polymer chains, at least in the absence of trialkylaluminum and at relatively high polymerization temperature, are initiated on M–H bonds and terminate via β-hydrogen abstraction. In addition, it is observed that the number-average polymerization degree of sample 2 determined by GPC almost coincides with the ratio between the area of the resonance, e.g., of the chain methine carbons at 39.2 ppm and that of the resonance of the methine carbon of the PP end groups at 35.2 and 35.7 ppm. This sample is less stere-

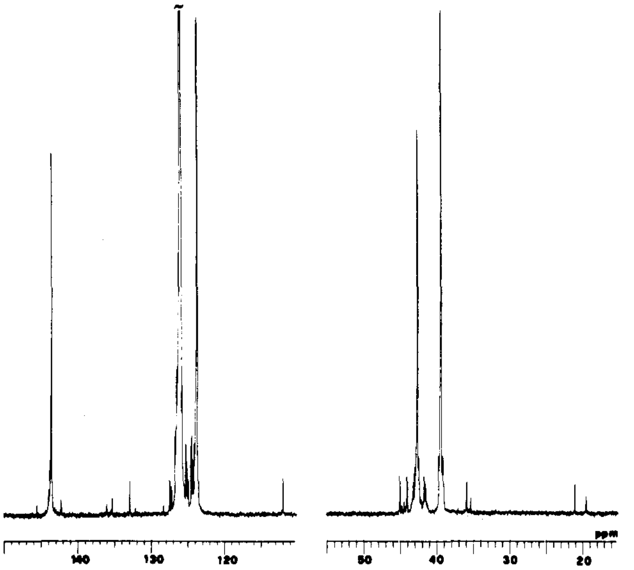
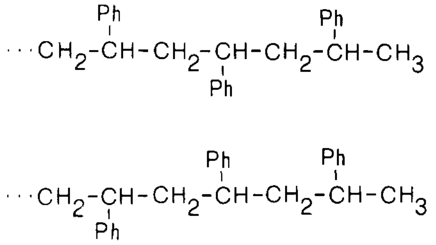


Figure 2. ^1H-decoupled ^{13}C NMR spectrum of sample 2 (HMDS scale). The resonances at 111.9, 127.1, 135.2, and 136.0 ppm are due to the presence of traces of styrene monomer in the sample.



$$\cdots CH_2-\overset{Ph}{CH}-CH_2-\underset{Ph}{CH}-CH_2-\overset{Ph}{CH}-CH_3$$

$$\cdots CH_2-\underset{Ph}{CH}-CH_2-\overset{Ph}{CH}-CH_2-\overset{Ph}{CH}-CH_3$$

Figure 3. Fischer projection of the 2,4,6-triphenylheptyl end groups resulting after the insertion of three monomer units on M–H bonds. The two reported configurations are the only ones detected in the end groups of sample 2; Ph = C_6H_5.

oregular than sample 1. In fact, in the spectrum one can observe the resonances of some irregular stereosequences.[2] The amount of rrr stereochemical tetrads, evaluated according to the literature,[5] from the relative intensity of the resonances of the backbone methylene carbons is 80% in comparison with 99% for sample 1. Correspondingly the resonances of the PP end group also appear split due to different stereochemical environments (see Figures 2 and 3).

From the data reported in this paper it is therefore concluded that in the presence of the homogeneous syndiotactic catalysts TBT–MAO and TBZ–MAO the insertion of styrene is 100% secondary both in the propagation and in the initiation steps, even where it occurs on M–H bonds. The most important chain-transfer process involves β-hydrogen abstraction. Under our conditions most of the polymer chains are initiated on M–H bonds. The stereoregularity of the arrangement of the phenyl substituents of the end groups, with respect with those of the first neighboring monomer units, parallels that of the polymer chain.

Experimental Section. TBT, TBZ, and MAO were prepared according to the literature.[7,8] Sample 1 was prepared at 60 °C with TBT/MAO catalytic system as previously described,[2] collecting the boiling butanone-soluble fraction. Sample 2 was prepared by polymerizing at 90 °C for 4 h 0.17 mol of styrene dissolved in 40 mL of toluene, using 1.0×10^{-4} mol of TBZ and 0.45 g of MAO as catalyst. After the polymerization was stopped with 5 mL of methanol, the reaction mixture was poured into 200 mL of acetone. The precipitated solid was filtered, and the solution was cooled at −18 °C overnight. The solid crystallized at −18 °C was collected and dried, giving 0.5 g of oligomeric polystyrene ($M_n = 1635$; $M_w = 2421$). The ^{13}C NMR spectra were performed on an AM 250 Bruker Spectrometer, either at 120 °C (sample 1) or at 25 °C (sample 2), in solution of tetrachlorodideuterioethane containing hexamethyldisiloxane (HMDS) as internal chemical shift reference. Molecular weight of sample 2 was measured by GPC in o-dichlorobenzene.

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Registry No. TBT, 17520-19-3; TBZ, 24356-01-2; PhCH=CH_2, 100-42-5.

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Electronic Spectra of Hindered Silyl- and Organo-Substituted Polysilylenes†

High molecular weight polysilylenes are receiving considerable attention as photoresists[1] and photoconductors.[2] We have examined the absorption and emission spectra of a large number of linear polysilylenes[3] in order to provide photophysical evidence for the underlying causes for the photosensitivity of these unusual σ-backbone polymers and to gain insight into the mechanisms of charge and energy transport. These studies indicated that increasing the size of the substituent moieties bonded to the silicon main chain both reduced the transition energy for the first UV absorption[3] and increased the photosensitivity[1a,b] for alkyl-substituted polymers.

Although increasing the size of the substituent moiety has a pronounced effect on photosensitivity, this was not strongly reflected in the fluorescence quantum yields for these polymers. The small observed effect on the fluorescence quantum yields with substituent size increase (0.42 in poly(cyclohexylmethylsilylene) vs. 0.76 in poly(n-propylmethylsilylene)) may result from either an increased intersystem crossing rate or from more efficient internal conversion as the transition energy decreases. The phosphorescence behavior suggested that the immediate

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