*Macromolecules* **1995**, *28*, 1586−1591

# 2D-INADEQUATE NMR Evidence for the Termination Mechanism of Styrene Free-Radical Polymerization

**Darlene R. Hensley,[†] Stephen D. Goodrich,[‡] April Y. Huckstep,[‡] H. James Harwood,[‡] and Peter L. Rinaldi*,[†]**

*Department of Chemistry, Knight Chemical Laboratory, and The Maurice Morton Institute of Polymer Science, Department of Polymer Science, The University of Akron, Akron, Ohio 44325-3601*

*Received September 30, 1994; Revised Manuscript Received December 9, 1994*[⊗]

ABSTRACT: 1D- and 2D-INADEQUATE NMR data for two poly(styrene-α-$^{13}C$) samples are presented. They represent the first recorded detection of the head-to-head enchainments in polystyrene that result when polystyrene radicals terminate by combination. Resonances that are attributable to structures resulting from head-to-head propagation reactions and to a terminal methylene carbon, which may have been produced either by a chain transfer reaction or by a disproportionation termination reaction, have also been detected. The $^{13}$C NMR spectra of several polymers and copolymers that serve as models for head-to-head enchainments in polystyrene are also discussed.

## Introduction

High-field NMR spectroscopic studies on polymers prepared in the presence of $^{13}$C-enriched initiators and chain transfer agents have provided a wealth of information about the chemistry of initiation and transfer reactions.[1−3] Such information, coupled with NMR information about the mode and stereochemistry of monomer enchainment in homopolymerization reactions and about monomer unit sequence distributions in copolymers, provides a quite detailed picture of free-radical-induced polymerization reactions. The picture could be even more complete if structures that result from termination reactions could also be characterized spectroscopically. Unfortunately, NMR has not been used for this purpose hitherto.

Since information about the mode of termination in free-radical-initiated polymerizations is important for considerations of telechelic polymer synthesis[4] and the thermal stability of polymers as well as for the development of a fundamental understanding of termination processes, we have embarked on a series of investigations on the use of NMR spectroscopy to characterize the structures that result from termination reactions. In this paper we report 1D- and 2D-INADEQUATE studies on poly(styrene-α-$^{13}C$) that enable detection of head-to-head enchainments which result from termination-by-coupling reactions.

A large body of indirect evidence indicates that polystyrene radicals terminate predominantly by combination rather than by disproportionation.[5,6] This evidence is based on determinations of the number of initiator fragments present per molecule by radiotracer,[7,8] spectroscopic,[9−11] and elemental analysis methods,[12−15] on comparisons of kinetic chain lengths[16−19] with experimentally measured degrees of polymerization,[4,20] on molecular weight distribution data,[4,20] on gelation studies[21] involving polymerizations utilizing polyfunctional macroinitiators or studies on polymerizations utilizing bifunctional initiators,[21] on polycondensation studies involving polystyrene prepared using initiating radicals that bear alcohol or acid groups,[16,20,22−30,17,31] on the results of fractionation studies, and on the behavior of model radicals.[32−35] There is at present no direct evidence for the head-to-head enchainments which must be present in polystyrene that has terminated by combination. Our approach to obtain direct evidence was to prepare two samples of poly(styrene-α-$^{13}C$) having different molecular weights and to investigate the $^{13}$C NMR spectra of the polymers using 1D- and 2D-INADEQUATE[36,37] experiments.

## Experimental Section

**Materials.** The 99%-enriched styrene-α-$^{13}C$ was obtained from MSD Isotopes and rinsed twice with a 10% (wt/vol) NaOH solution prior to being polymerized. Cupric octanoate ($Cu^{II}[OOC(CH_2)_6CH_3]_2$) was synthesized by a reported method.[38] The styrene and stilbene were washed three times with a 10% (wt/vol) NaOH solution and then twice with distilled water, dried with $MgSO_4$, filtered, and then fractionally distilled from $CaH_2$ under vacuum; the monomers were tested for peroxides with KI/starch indicator prior to being polymerized. Dibenzyl ketone and acetylacetone were tested for peroxides using the KI/starch detection method; peroxides were removed by shaking with 0.4 M ferrous sulfate in 0.2 M $H_2SO_4$. After removal of peroxides, the liquids were fractionally distilled under vacuum. Pyridine was fractionally distilled from $CaH_2$. Triethylamine was refluxed with phthalic anhydride for 6 h and then refluxed with $CaH_2$ for 1 h prior to being fractionally distilled. Methanol used as a polymerization solvent was fractionally distilled prior to use. Benzene, tetrahydrofuran, benzoyl peroxide, azobis(isobutyronitrile) (AIBN), and methanol used for polymer isolation were used as received.

**Procedures.** NMR spectra were obtained on a Varian UNITYplus 600 MHz spectrometer, with temperature regulation at $30.0 \pm 0.1$ °C, using 33% wt/vol solutions of polymer in $CDCl_3$ contained in 5 mm tubes. The 2D-INADEQUATE spectrum was obtained from the low molecular weight poly(styrene-α-$^{13}C$) sample utilizing the following parameter set: a 90° $^{13}$C pulse width of 10.9 μs, a 25 000 Hz spectral window in $f_2$, a 50 000 Hz spectral window in $f_1$, 0.164 s acquisition time, and a 1.000 s relaxation delay; 448 transients were averaged for each of 125 $t_1$ increments. The data were processed with shifted sine bell weighting and zero filling to form an 8192 × 1024 matrix prior to Fourier transformation.

Molecular weights were determined via GPC analysis, using samples dissolved in tetrahydrofuran at a concentration of 5 mg/mL. Retention times were compared with a calibration curve constructed from the analyses of standard polystyrene

---

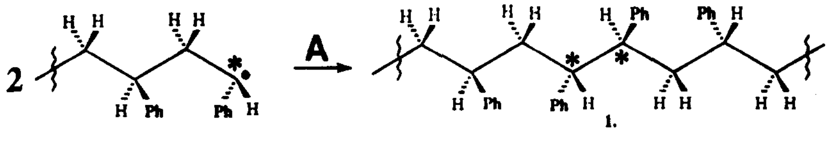
[†] Department of Chemistry, Knight Chemical Laboratory.

[‡] The Maurice Morton Institute of Polymer Science, Department of Polymer Science.

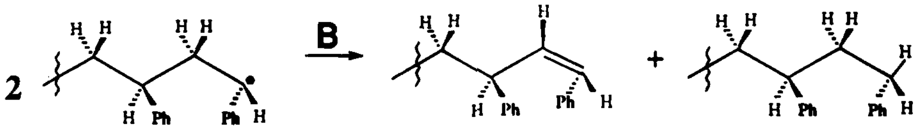
[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1995.

0024-9297/95/2228-1586$09.00/0

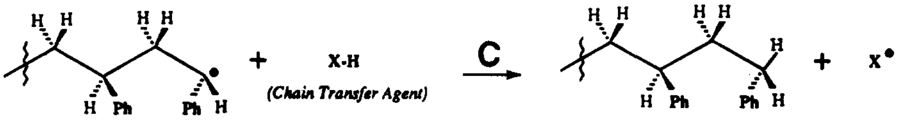
Scheme 1



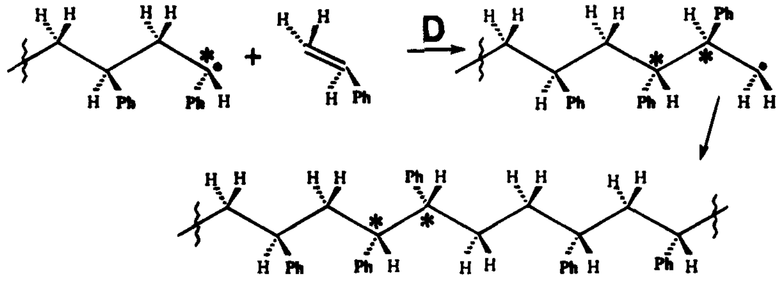
**Termination via Combination (Head-to-Head Termination Reaction)**



**Termination via Disproportionation (Note: Terminal Methylene and Olefinic Carbons)**



**Termination via Chain Transfer Reaction (Note: Terminal Methylene Carbon)**



**Head-to-Head Propagation Reaction**

samples having molecular weights of 4000, 25 000, 200 000, 400 000, and 900 000.

**Low Molecular Weight Poly(styrene-α-$^{13}C$) (1).** Styrene-α-$^{13}C$ (0.75 g, 7.2 mmol), cupric octanoate (0.05 g, 0.15 mmol), dibenzyl ketone (0.20 g, 1.1 mmol), pyridine (0.20 g, 2.5 mmol), triethylamine (0.05 g, 0.49 mmol), and benzene (1.5 g, 19.2 mmol) were placed in a glass bottle (1 oz) that was sealed with a rubber septum. The reaction vessel was purged for 5 min with $N_2$ and then suspended in a mineral oil bath at 70 °C for 24 h. Several drops of tetrahydrofuran and acetylacetone were then added to the reaction mixture which was then added dropwise to 200 mL of methanol. The poly(styrene-α-$^{13}C$) that precipitated was collected by filtration and dried at 60 °C under vacuum. The yield was 0.57 g (76%). GPC measurement indicated the polymer to have a number-average molecular weight of $7.6 \times 10^3$ and a weight-average molecular weight of $1.8 \times 10^4$.

**High Molecular Weight Poly(styrene-α-$^{13}C$) (1).** Styrene-α-$^{13}C$ (0.75 g, 7.2 mmol), AIBN (0.16 g, 1.0 mmol), and benzene (1.5 g, 19.2 mmol) were placed in a glass bottle (1 oz) that was sealed with a rubber septum. The reaction vessel was purged for 5 min with $N_2$ and then suspended in a mineral oil bath at 70 °C for 24 h. The reaction mixture was added dropwise with stirring to 200 mL of methanol. The poly(styrene-α-$^{13}C$) that precipitated was collected by filtration. The yield was 0.11 g (14%). GPC measurement indicated the polymer to have a number-average molecular weight of $2.08 \times 10^4$ and a weight-average molecular weight of $4.3 \times 10^4$.

**Poly(styrene-*co*-stilbene) (3).** Styrene (7.5 g, 72.0 mmol), stilbene (12.5 g, 69.3 mmol), benzoyl peroxide (4.79 g, 19.7 mmol), and toluene were placed in a glass bottle (4 oz) that was sealed with a butyl rubber-lined cap. The reaction vessel was purged for 5 min with $N_2$. The bottle was then rotated in a water bath at 60 °C for 8 h. The reaction mixture was poured into methanol to precipitate the polymer. This was then reprecipitated three times from toluene solution into methanol and collected by filtration. The yield of poly(styrene-*co*-stilbene) was 0.83 g (10.9%) based on the amount of styrene in the polymerization mixture.

## Results and Discussion

**Basic Considerations.** During the free-radical-initiated polymerization of styrene, propagating polystyrene radicals may terminate by combination (Scheme 1, path A) or by disproportionation (Scheme 1, path B) or they may abstract a hydrogen or halogen atom from another molecule in a chain transfer step (Scheme 1, path C). Structures resulting from such processes can be measured in principle, but they are likely to be present in low concentration and difficult to detect. An additional difficulty is the fact that the head-to-head structures that result from path A must be distinguished from those structures that result from head-to-head propagation reactions (Scheme 1, path D). By studying polymers derived from styrene-α-$^{13}C$, the detection of structures that result from the reactions depicted in Scheme 1 can be facilitated because the sensitivity of 1D measurements of the α-carbon resonances is enhanced approximately 100-fold compared to measurements made on conventional polystyrene in which only 1.1% of the carbon atoms are the $^{13}C$ isotope. Additionally, as the following discussion will reveal, the sensitivity of 2D-INADEQUATE experiments that would detect head-to-head linkages is enhanced $10^4$-fold by studying polymers derived from styrene-α-$^{13}C$.

The INADEQUATE experiment selectively detects signals from homonuclear-coupled spins, such as $^{13}C-^{13}C$ which appear as satellites in a normal $^{13}C$ spectrum, by exploiting multiple-quantum coherence.[36,37] Since the $^{13}C$ isotope comprises only 1.1% of the naturally

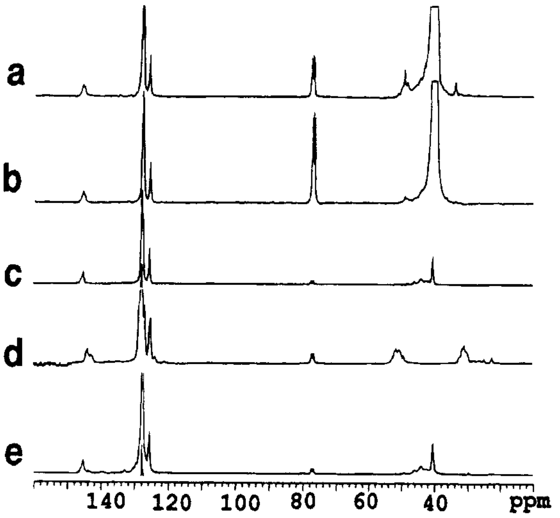


**Figure 1.** 1D $^{13}$C NMR spectra of polystyrene and model polymers: (a) low molecular weight poly(styrene-α-$^{13}$*C*), (b) high molecular weight poly(styrene-α-$^{13}$*C*), (c) unlabeled polystyrene, (d) poly(2,3-diphenyl-1,4-butylene) (**2**), and (e) poly(styrene-*co*-stilbene) (**3**).

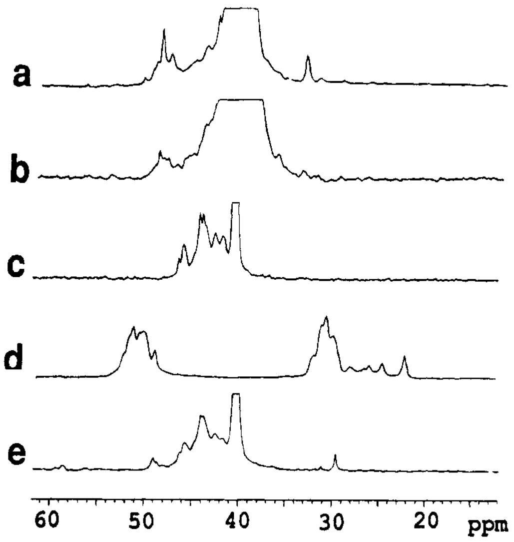


**Figure 2.** Expansions from the aliphatic regions of the $^{13}$C NMR spectra shown in Figure 1: (a) low molecular weight poly(styrene-α-$^{13}$*C*) (b) high molecular weight poly(styrene-α-$^{13}$*C*), (c) unlabeled polystyrene, (d) poly(2,3-diphenyl-1,4-butylene) (**2**), and (e) poly(styrene-*co*-stilbene) (**3**).

occurring carbon atoms, only 10$^{-4}$ of the C−C bonds in substances without $^{13}$C enrichment are $^{13}$C−$^{13}$C bonds. Due to the infrequent occurrence of $^{13}$C−$^{13}$C linkages under normal conditions, the INADEQUATE experiment is very insensitive and requires long signal averaging times. Since every coupling of two poly(styrene-α-$^{13}$*C*) chains produces a coupled $^{13}$C−$^{13}$C spin pair, the sensitivity of the INADEQUATE experiment toward such pairs is enhanced 100-fold relative to head-to-tail enchainments in an experiment that would involve unenriched polystyrene.

The 2D-INADEQUATE NMR experiment is capable of detecting three types of $^{13}$C−$^{13}$C linkages in poly(styrene-α-$^{13}$*C*). First there are the structures that result from termination-by-combination reactions (Scheme 1, path A) and those that result from head-to-head propagation reactions (Scheme 1, path D). In addition, this experiment will detect $^{13}$C−$^{13}$C pairs that connect α-$^{13}$C carbons (enriched) with methylene carbons (natural abundance) that are the $^{13}$C isotope. To distinguish the resonance of $^{13}$C−$^{13}$C pairs that result from termination-by-combination reactions from those of other $^{13}$C−$^{13}$C pairs, the spectra of poly(styrene-α-$^{13}$*C*) samples having considerably different molecular weights were compared. It was expected that the concentrations of $^{13}$C−$^{13}$C pairs that are associated with α-carbon−methylene carbon junctions or that are the result of head-to-head propagation reactions would be the same for high and low molecular weight polymers but that the concentrations of $^{13}$C−$^{13}$C pairs that result from termination-by-combination reactions would be larger in the low molecular weight polymer than in the high molecular weight polymer sample.

**1D-NMR Measurements.** Spectra a−c of Figure 1 show the 1D $^{13}$C NMR spectra of poly(styrene-α-$^{13}$*C*) having a molecular weight of 7.6 × 10$^3$, of poly(styrene-α-$^{13}$*C*) having a molecular weight of 2.1 × 10$^4$, and of polystyrene. The spectra were measured under identical conditions as is indicated by the similarity of the quaternary aromatic carbon resonance areas at 143 ppm. The resonances of α-carbons dominate the aliphatic carbon resonance areas of spectra shown in Figure 2a,b. Noteworthy are resonances in the 33.6−33.8 and 47−52 ppm regions that are very strong in the spectrum of the lower molecular weight poly(styrene-α-$^{13}$*C*) (Figure 2a), are weaker in the spectrum of the higher molecular weight poly(styrene-α-$^{13}$*C*) (Figure 2b), and are not evident in the spectrum of polystyrene (Figure 2c). The fact that the relative intensities of these resonances vary considerably with molecular weight indicates that they represent structures associated with termination or transfer reactions.

Based on the results of empirical chemical shift calculations and other evidence that will be discussed below, the signals at 47−52 ppm are attributed to methine carbons present in −CH(Ph)CHPh− linkages resulting from termination-by-combination reactions and the resonances at 33.6−33.8 ppm may be attributed to terminal methylene carbons. The latter could be produced via either termination-by-disproportionation or chain transfer reactions. If a termination-by-disproportionation reaction had taken place to a significant degree, an olefinic resonance of intensity comparable to that of the terminal methylene would occur in the $^{13}$C NMR spectrum of the polymer at ca. 137 ppm. As such a resonance was not detected, it was concluded that in this case the terminal methylene carbon is due primarily to a chain transfer reaction.

It is not surprising that resonances due to termination and transfer reactions were evident in the spectra of the poly(styrene-α-$^{13}$*C*) samples. Due to the high dynamic range of NMR, it is possible to detect resonances at levels as low as 0.001 mol %. This means that it should be possible to detect structures that result by terminations or transfer reactions if the polymers have molecular weights less than one million. Since the α-carbon resonances constitute almost 99% of the aliphatic carbon resonances observed in the spectra of the poly(styrene-α-$^{13}$*C*) samples, it proved possible to calculate the number-average molecular weights ($M_n$) of these samples from the relative intensities of the resonances observed at 47−52 and 32−35 ppm compared to all the aliphatic carbon resonances observed. The following formula was used, where $A$ represents the resonance area of the regions indicated in the subscript.

$$M_n = (104.14\ \text{g/mol}) \times A_{32-52}/[0.5A_{47-52} + A_{32-35}] \quad (1)$$

Although quantitative methods were not used to collect these spectra (i.e., gated decoupling to suppress

**Table 1. Molecular Weights of Poly(styrene-α-$^{13}$*C*) Samples As Determined by NMR and GPC**

| sample | $M_n$ from GPC | $M_n$ from NMR | fraction of termination from path A |
|---|---|---|---|
| high MW | $2.08 \times 10^4$ | $5.1 \times 10^4$ | 0.87 |
| low MW | $7.6 \times 10^3$ | $8.2 \times 10^3$ | 0.82 |

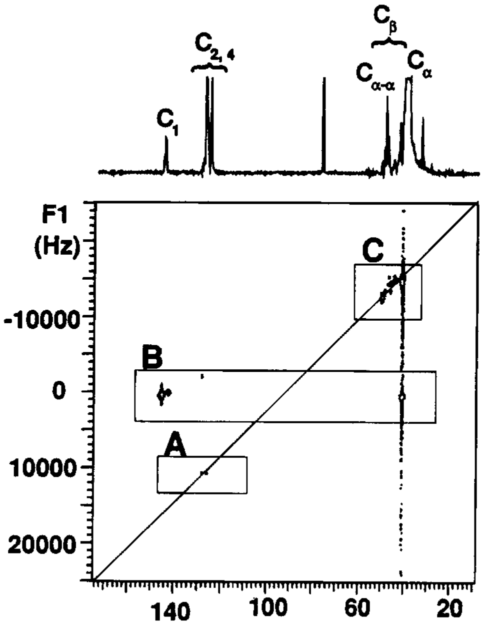


**Figure 3.** 2D-INADEQUATE spectrum of poly(styrene-α-$^{13}$*C*) with the full spectral window in each dimension and the 1D $^{13}$C NMR spectrum plotted across the top.

the nuclear Overhauser effect (NOE) and a very long relaxation delay to permit complete recovery of the nuclear magnetization were not used), the NOE and relaxation properties of the α-$^{13}$C nuclei are likely to be similar. The results from NMR and GPC molecular weight determination are summarized in Table 1 and are in reasonably good agreement. Based on the relative intensities of the resonances at 32–35 and 47–52 ppm, it was estimated that 13–18% of the chains had terminated by chain transfer.

**2D-INADEQUATE NMR Measurements.** The 2D-INADEQUATE spectrum (full spectral width) of the low molecular weight poly(styrene-α-$^{13}$*C*) is shown in Figure 3 with the corresponding region from the 1D $^{13}$C NMR spectrum plotted across the top. Correlations which indicate direct attachment of two $^{13}$C atoms are identified by the presence of two sets of resonances along a horizontal line, equally spaced from the diagonal. The chemical shifts of the attached $^{13}$C atoms can be identified by extending a vertical line to the 1D spectrum along the top. Correlations of the main chain resonances are seen between $C_2$ and $C_3$, and $C_3$ and $C_4$ (region A); between $C_1$ and $C_α$ (region B); and between $C_α$ and $C_β$ (region C).

An expansion of region C is shown in Figure 4. The appearance of some sets of cross-peaks is different from the usual pair of doublets spaced equidistant from the diagonal; this is caused by the similarity of the $^{13}$C shifts. The two doublets appear as an AB pattern with weak outer peaks in the doublets rather than as an AX pattern. Consequently, in 2D-INADEQUATE spectra, the weak outer signals are very often not detected and the inner lines of the doublets are shifted toward the shifts of the $^{13}$C signal as they are in an AB pattern of a 1D spectrum. As a consequence of stereochemistry in both the head–head styrene units and adjacent repeat units, separate $^{13}$C resonances are observed for the α-$^{13}$C atoms in $-CH_2{}^{13}CH(Ph){-}^{13}CH(Ph)CH_2-$; *they are not equivalent*.

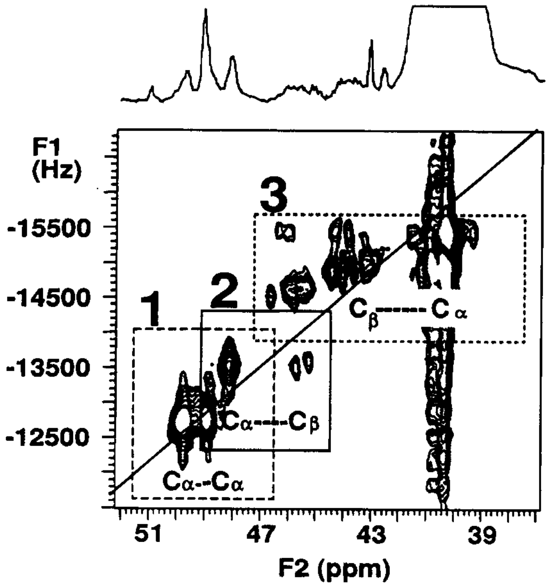


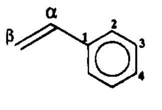
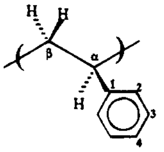
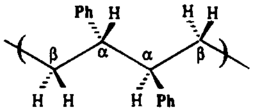
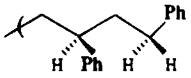
**Figure 4.** Expansion of region C from the 2D-INADEQUATE spectrum depicted in Figure 3 with corresponding region of the 1D $^{13}$C NMR spectrum of the low molecular weight polymer plotted across the top. Cross-peaks in region 1 arise from $C_α$–$C_α$ bonds, those in region 2 correspond to $C_β$–$C_α$ bonds ($C_α$ from a h–h segment), and those in region 3 correspond to $C_β$–$C_α$ bonds ($C_α$ from a h–t segment).

Correlations are observed which are attributed to resonances of $C_α$–$C_α$ fragments (region 1). One of these $C_α$ resonances exhibits a correlation to a $C_β$ resonance (region 2) which in turn exhibits a correlation to a $C_α$ resonance of a repeat unit that has added in the normal head–to-tail fashion. Correlations are also observed which are attributed to $C_β$ and $C_α$ that reside in the head-to-tail enchainments (region 3).

Correlations are also observed that indicate bonding between α and β carbons. These are comparable in intensity to the $C_α$–$C_α$ correlations because 1.1% of the β carbons contain the $^{13}$C isotope and all α-carbons are labeled. It should be noted that for a poly(styrene-α-$^{13}$*C*) with a molecular weight of 20 800 (DP ≤ 200) that has terminated predominantly by combination, signals due to β-$^{13}$C's of (α-$^{13}$C)–(β-$^{13}$C) junctions (43.5–47 ppm) should be no greater in intensity than those due to α-$^{13}$C's of (α-$^{13}$C)–(α-$^{13}$C) junctions (47–51 ppm). For higher molecular weight (DP > 200) polymers, the signals due to the β-$^{13}$C's of (α-$^{13}$C)–(β-$^{13}$C) junctions will be stronger than those signals due the α-$^{13}$C's of (α-$^{13}$C)–(α-$^{13}$C) fragments. Such is the case if the resonances from the aliphatic region of the low and high molecular weight poly(styrene-α-$^{13}$*C*) are compared (spectra a and b of Figure 2, respectively).

The 2D-INADEQUATE spectra definitively establish the presence of (α-$^{13}$C)–(α-$^{13}$C) fragments expected from termination-by-combination, confirm that these fragments are attached to repeat units which have added to polystyrene in a normal head-to-tail fashion, and exhibit relative resonance intensities which are consistent with the fraction of repeat units which should exist in this environment. Resonance assignments which are obtained from this spectrum are summarized in Table 2.

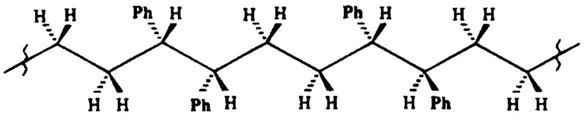
**Table 2. $^{13}$C Resonance Assignments**

| | | chemical shift (δ) | | | | |
|---|---|---|---|---|---|---|
| structure | carbon | lit. (exptl) | lit. (calcd) | calcd | exptl | DEPT assignments[f] |
| <br>*Styrene* | $C_1$ | 137.3[a] | | | | |
| | $C_2$ | 127.9[a] | | | | |
| | $C_3$ | 127.9[a] | | | | |
| | $C_4$ | 126.2[a] | | | | |
| | α-CH | 136.7[a] | | | | |
| | β-$CH_2$ | 113.2[a] | | | | |
| <br>*Polystyrene* | $C_1$ | 147−145[b] | | | 145.6−145.0 | s |
| | $C_2$ | 128.4, 127.9[b] | | | 128.9−126.8 | d |
| | $C_3$ | 128.4[b] | | | 128.9−126.8 | d |
| | $C_4$ | 126[b] | | | 126.7−125.5 | d |
| | α-CH | 41.5, 41.3[b] | | 39.9 | 40.40 | d |
| | β-$CH_2$ | 46−43[b] | | | 47.4−42.5 | t |
| <br>*Head-to-Head Polystyrene* | α-CH | 51[c] | 49.2[c] | 48.9 | 48.5, 49.5[d] | d |
| | | | | | 51.1−48.1[e] | d |
| | β-$CH_2$ | 31[c] | 33.2[c] | | | t |
| <br>*Terminal Methylene* | $CH_2$ | | | 33.9 | 33.8, 33.6 | t |

[a] Reference 21. [b] Reference 22. [c] Reference 20. [d] Poly(stilbene-*co*-styrene) $^{13}$C NMR spectrum; α-CH of the stilbene units. [e] Poly(styrene-α-$^{13}$C) $^{13}$C NMR spectra. [f] s = C, d = CH, t = $CH_2$, q = $CH_3$.

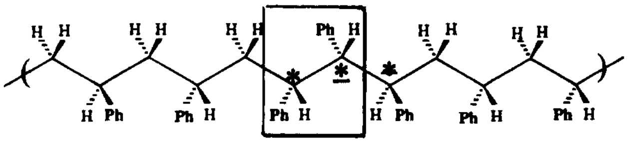
**$^{13}$C NMR Spectra of Related Polymers.** Additional supporting evidence for the resonance assignments rendered above for carbons in head-to-head enchainments that result from either propagation or combination reactions is provided by comparisons with $^{13}$C NMR spectra of 1,4-poly(2,3-diphenylbutane) (**2**) and poly(styrene-*co*-stilbene) (**3**), polymers which have structures very similar to head-to-head enchainments in polystyrene.

Vogl and co-workers[39−44] synthesized head-to-head/tail-to-tail polystyrene, poly(2,3-diphenyl-1,4-butylene), by hydrogenating 1,4-poly(2,3-diphenylbutadiene). Although this material's structure is slightly different from the structures that result from head-to-head propagation or from termination-by-combination reactions (Scheme 1), it was of interest to compare the chemical shifts of the α-carbons in this polymer with the chemical shifts assigned to head-to-head structures in the previous discussion. Figure 1d shows the 150 MHz $^{13}$C NMR spectrum of a sample of poly(2,3-diphenyl-1,4-butylene) that was kindly provided by Professor Otto Vogl with an expansion of the aliphatic region shown in Figure 2d. The α-carbon resonances are observed at 48−53 ppm, which is slightly downfield from the resonances of head-to-head junctions in polystyrene. Since Vogl's polymer lacks phenyl substitution on β- and γ-carbons that neighbor the methine carbons, an exact correspondence of the chemical shifts of the carbons present in −CH(Ph)−CH(Ph)− structures in the polymers is not expected.



**2**

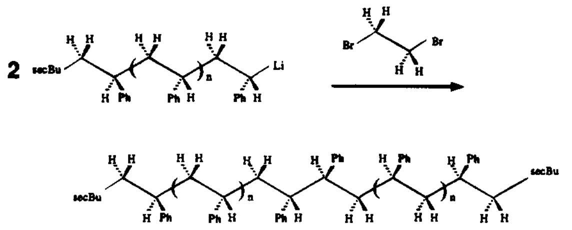
Copolymers of stilbene with styrene also contain −CH(Ph)−CHPh− linkages in environments similar to those of −CH(Ph)−CHPh− linkages in polystyrene that has terminated by combination. This is shown by structure **3**, where the stilbene unit is enclosed in a box. Since the reactivity ratio of stilbene is zero, stilbene units are present as isolated units in the copolymers and polymers with high concentrations. A comparison of the aliphatic regions from the $^{13}$C NMR spectra of poly(styrene-α-$^{13}$*C*) (Figure 2a,b) and poly(styrene-*co*-stilbene) (**3**) (Figure 2e) provides further evidence that signals observed slightly downfield of those due to the methylene carbon of the polystyrene, in the 47−51 ppm region, are due to the carbons of α-$^{13}$C−α-$^{13}$C junctions. Confirmation that these resonances are due to methine carbons is shown via DEPT[45] NMR spectra.



**Poly(stilbene-co-styrene): [ * h-h fragments; $\underline{*}$ stilbene units]**

**3**

Additionally, Quirk and Hasegawa[46] have recently found that polystyryllithium is converted to a coupled polystyrene dimer on treatment with either ethylene oxide or 1,2-dibromoethane (eq 2). The dimer, which is apparently formed by an electron transfer reaction that yields free radicals which subsequently couple, can be expected to have a structure identical to that obtained when polystyrene radicals terminate by combination. Indeed, the $^{13}$C NMR spectrum of the dimer contains a signal at 49.5 ppm that they attribute to a head-to-head enchainment.



(2)

## Conclusion

This work illustrates the value of combined use of isotopic labeling and modern NMR methods for the study of polymer structure and reactivity. In particular, 2D-INADEQUATE NMR experiments provided the first direct evidence that head-to-head enchainments (i.e., $-CH_2CH(Ph)-CH(Ph)CH_2-$ segments) are present in the backbone of polystyrene. Additional data obtained via this study provided the necessary evidence that these head-to-head enchainments were formed primarily at the sites where the two chains couple, thus supporting the belief that polystyrene terminates primarily via combination. The assignments of resonances from these structures is further substantiated by chemical shift calculations and the spectral analysis of model compounds.

**Acknowledgment.** We gratefully acknowledge the Kresge Foundation and the donors to the Kresge Foundation Challenge Program for supporting the purchase of the 600 MHz NMR spectrometer used in this work, the National Science Foundation (Grant DMR-9310642), the State of Ohio Board of Reagents Academic Challenge and Research Challenge Grant Programs, and the Lord Corporation for financial support of this research. We are also grateful to Professor O. Vogl for providing a sample of **2**, to Professor R. Quirk for providing NMR spectra of the polystyrene dimers that were derived from poly(styryllithium), and to Dr. S. Jolly for performing GPC measurements.

## References and Notes

(1) Bevington, J. C. *Makromol. Chem. Macromol. Symp.* **1987**, *10/11*, 89.
(2) Solomon, D. H.; Moad, G. *Makromol. Chem., Macromol. Symp.* **1987**, *10/11*, 109.
(3) Bevington, J. C.; Ebdon, J. R.; Huckerby, T. N. *NMR Spectroscopy of Polymers*; Ibbett, R. N., Ed.; Blackie Academic and Professional: London 1993; Chapter 3.
(4) Dawkins, J. V.; Yeadon, G. *Polymer* **1979**, *20*, 981.
(5) Bamford, C. H. In *Encyclopedia of Polymer Science and Engineering*; John Wiley and Sons Inc: New York, 1988; Vol. 13.
(6) Moad, G.; Solomon, D. H. In *Comprehensive Polymer Science*; Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon Press: New York, 1989; Vol. 3, Chapter 8.
(7) Bevington, J. C. *Radical Polymerization*; Academic Press: New York, 1961.
(8) Avery, G. *Chem. Rev.* **1960**, *63*, 645.
(9) Bevington, J. C.; Ebdon, J. R.; Huckerby, T. N. *Eur. Polym. J.* **1985**, *21*, 685.
(10) Anisimov, Y. N.; Ivanchev, S. S.; Yurzhenko, A. I. *Polym. Sci. USSR (Engl. Transl.)* **1967**, *9*, 773.
(11) Rubio, L. H. G.; Ro, N.; Patel, R. D. *Macromolecules* **1984**, *17*, 1998.
(12) Palit, S. R.; Mandal, B. M. *J. Macromol. Sci., Rev. Macromol. Chem.* **1968**, *2*, 225.
(13) Ghosh, N. N.; Mandal, B. M. *Macromolecules* **1986**, *19*, 19.
(14) Rizzardo, E.; Solomon, D. H. *J. Macromol. Sci., Chem.* **1979**, *13*, 997.
(15) Rizzardo, E.; Solomon, D. H. *J. Macromol. Sci., Chem.* **1979**, *13*, 1005.
(16) Mayo, F. R.; Gregg, R. A.; Matheson, M. S. *J. Am. Chem. Soc.* **1951**, *73*, 1691.
(17) Johnson, D. H.; Tobolsky, A. V. *J. Am. Chem. Soc.* **1952**, *74*, 938.
(18) Olaj, O. F.; Breitenbach, J. W.; Wolf, B. *Monatsh. Chem.* **1964**, *95*, 1646.
(19) Stickler, M. *Makromol. Chem.* **1979**, *180*, 2615.
(20) Braks, J. G.; Huang, R. Y. M. *J. Appl. Polym. Sci.* **1978**, *22*, 3111.
(21) Bamford, C. H.; Dyson, R. W.; Eastmond, G. C. *Polymer* **1969**, *10*, 885.
(22) O'Driscoll, K. F.; Bevington, J. C. *Eur. Polym. J.* **1985**, *21*, 1039.
(23) Bamford, C. H.; Jenkins, A. D. J. *Nature (London)* **1955**, *176*, 78.
(24) Burnett, G. M.; North, A. M. *Makromol. Chem.* **1964**, *73*, 77.
(25) Ayrey, G.; Levitt, F. G.; Mazza, R. J. *Polymer* **1965**, *6*, 157.
(26) Dawkins, J. V.; Yeadon, G. *Polymer* **1979**, *20*, 981.
(27) Bevington, J. C.; Melville, H. W.; Taylor, R. P. *J. Polym. Sci.* **1954**, *12*, 449.
(28) Bevington, J. C.; Melville, H. W.; Taylor, R. P. *J. Polym. Sci.* **1954**, *14*, 463.
(29) Hakozaki, J.; Yamada, N. *J. Chem. Sci. Jpn.* **1967**, *70*, 1560.
(30) Hakozaki, J.; Yamada, N. *Chem. Abstr.* **1968**, *68*, 96263r.
(31) Henrici-Olivé, G.; Olivé, S. *J. Polym. Sci.* **1960**, *48*, 329.
(32) Gibian, M. J.; Corley, R. C. *J. Am. Chem. Soc.* **1972**, *94*, 4178.
(33) Gleixner, G.; Olaj, O. F.; Breitenbach, J. W. *Makromol. Chem.* **1979**, *180*, 2581.
(34) Shelton, J. R.; Liang, C. K. *J. Org. Chem.* **1973**, *38*, 2301.
(35) Overberger, C. G.; Finestone, A. B. *J. Am. Chem. Soc.* **1956**, *78*, 1638.
(36) Bax, A.; Freeman, R.; Frenkiel, T. A. *J. Am. Chem. Soc.* **1981**, *103*, 2102.
(37) Bax, A.; Freeman, R.; Frenkiel, T. A.; Levitt, M. H. *J. Magn. Reson.* **1981**, *43*, 478.
(38) Gushchin, A. V.; Rabinovich, A. M.; Sazonova, E. V.; Shnol', T. R.; Koreneva, L. N. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1990**, *35*, 1579.
(39) Inoue, H.; Helbig, M.; Vogl, O. *Macromolecules* **1977**, *10*, 1331.
(40) Weill, G.; Vogl, O. *Polym. Bull.* **1978**, *1*, 181.
(41) Bangerter, F.; Serafini, S.; Pino, P.; Vogl, O. *Makromol. Chem., Rapid Commun.* **1981**, *2*, 109.
(42) Marchal, E.; Benoit, H.; Vogl, O. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 949.
(43) Jacovic, M.; Vogl, O. *Polym. Eng. Sci.* **1978**, *18*, 875.
(44) Foldes, E.; Deak, G.; Tudos, F.; Vogl, O. *Eur. Polym. J.* **1993**, *29*, 221.
(45) Doddrell, D. M.; Pegg, D. T.; Bendall, M. R. *J. Mag. Reson.* **1982**, *48*, 323.
(46) Hasegawa, H. Master's Thesis, The University of Akron, Akron, OH, 1994.

MA941292P