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

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A large body of indirect evidence indicates that polystyrene radicals terminate predominantly by combination rather than by disproportionation (Scheme 1).[1,2] Since the mode of termination is important for considerations of telechelic polymer synthesis[3] and the thermal stability of polymers, it is desirable that direct methods be developed for determining the structures that are incorporated in polymers by termination processes. In this paper NMR experimental data are presented which offer the first detection of the head-to-head enchainments in polystyrene (**1**) that result when polystyrene radicals terminate by combination. Resonances due to the presence of 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 approach taken in this study was to prepare two samples of poly(α-^{13}C-styrene) having different molecular weights and to analyze them using 1D- and 2D-NMR experiments. It was hoped that 99% ^{13}C enrichment would enable α-^{13}C present in structures that result from termination to be observed directly in 1D ^{13}C NMR spectra. Due to the high dynamic range of NMR, it is possible to detect resonances of components present in amounts as low as 0.05 mol %. This means that it should be possible to detect structures that result by termination or transfer reactions if the polymers have molecular weights less than 10^6.

In applying 2D techniques, the INADEQUATE[4] experiment was selected as it would favor the detection of head-to-head structures that would form. This is possible because the INADEQUATE technique uses multiple quantum coherence to selectively detect signals from homonuclear-coupled spins such as ^{13}C–^{13}C while suppressing signals from isolated ^{13}C's.[5] Since the ^{13}C-isotope comprises only 1.1% of the naturally occurring carbon atoms, ^{13}C–^{13}C fragments account for only $1/10^4$ of the C–C bonds in polymers containing ^{13}C in natural abundance. Due to the infrequent occurrence of the ^{13}C–^{13}C linkages under normal conditions, the INADEQUATE experiment is very insensitive and requires relatively long signal averaging times. Incorporation of 99% ^{13}C label at the α-position of styrene units uniformly enhances all of the α-^{13}C resonances in a normal 1D ^{13}C NMR spectrum. However, the signals from isolated ^{13}C nuclei are filtered from INADEQUATE spectra. Since every coupling of two polystyrene chains produces a ^{13}C–^{13}C spin pair, these resonances are enhanced 10 000-fold and are enhanced 100-fold relative to resonances of α-^{13}C signals of styrene units incorporated in the polymer chain via head-to-tail propagation. The INADEQUATE spectrum of poly(α-^{13}C-styrene) should contain signals representing junctions of α-carbons (ca. 100% enriched) with methylene and quaternary aromatic carbons that contain the ^{13}C-isotope in natural abundance as well as signals representing junctions that involve pairs of α-carbons. The latter signals

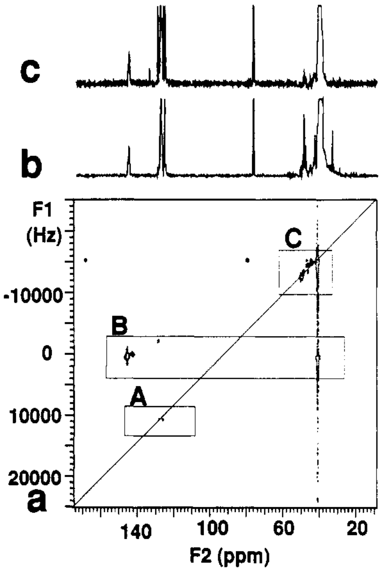

Figure 1. (a) 2D-INADEQUATE spectrum of poly(α-^{13}C-styrene) full sweep width in each dimension with 1D ^{13}C spectra across the top; (b) spectrum of a low molecular sample used to obtain the 2D-INADEQUATE spectrum; (c) spectrum of a high molecular weight sample of the polymer. The spectra were recorded on a Varian UNITYplus 600-MHz spectrometer using a 33% w/v solution in CDCl$_3$ contained in a 5-mm NMR tube. The 2D-INADEQUATE spectrum was obtained from the low molecular weight sample utilizing the following parameters: a ^{13}C 90° pulse of 10.9 μs, 25 000-Hz spectra window, 0.164-s acquisition time, and a 1.0-s relaxation delay; 448 transients were averaged for each of the 125 t_1 increments. The data were processed with shifted sine bell weighting and zero filling to a 8192 × 1024 matrix before being Fourier transformed. Cross-peaks in area A are due to C$_2$–C$_3$ and C$_3$–C$_4$ bonds, those in area B correspond to C$_1$–C$_\alpha$ h–t bonds, and those in area C corresopnd to C$_\alpha$–C$_\alpha$ bonds, C$_\beta$–C$_\alpha$ h–h bonds and C$_\alpha$–C$_\beta$ h–t bonds.

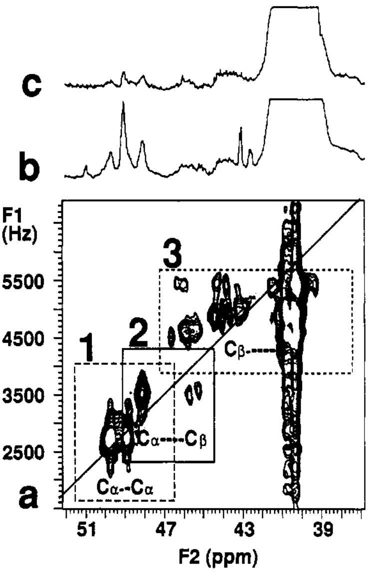

Figure 2. (a) Expansion of region C from the 2D-INADEQUATE spectrum depicted in Figure 1 with corresponding regions of the 1D ^{13}C NMR spectra of the low (b) and high (c) molecular weight polymers. Cross-peaks in region 1 arise from C$_\alpha$–C$_\alpha$ bonds, those in region 2 correspond to C$_\beta$–C$_\alpha$ bonds (C$_\alpha$ from a h–h segment), and those in region 3 correspond to C$_\beta$–C$_\alpha$ bonds (C$_\alpha$ from a h–t segment).

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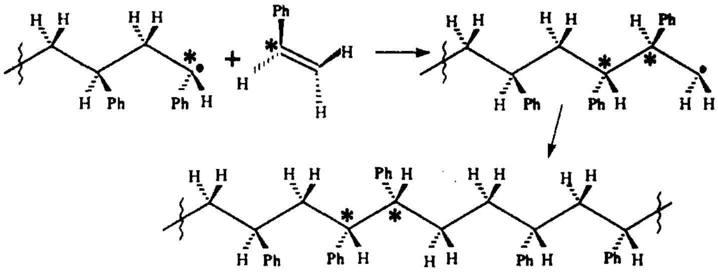
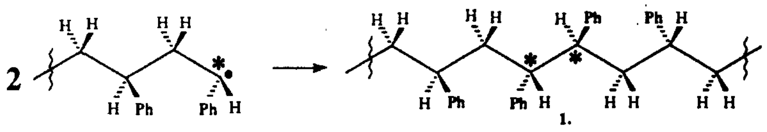
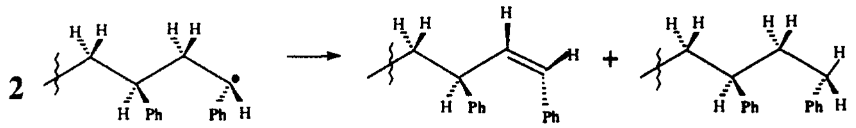
Scheme 1



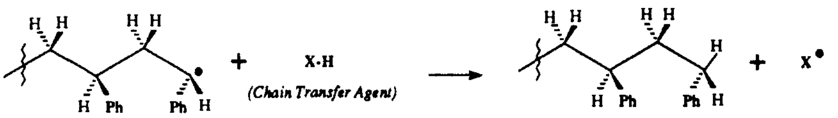
Head-to-Head Propagation Reaction



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)

can result from head-to-head propagation reactions or from termination by coupling of propagating radicals (Scheme 1). Although these signals should have different chemical shifts, they are more easily distinguished by comparing their relative intensities in the 1D ^{13}C NMR spectra of polymers having different molecular weights. Signals due to structures from random head-to-head propagation should be of the same relative intensity in spectra of all the polymers, regardless of molecular weight, whereas signals due to head-to-head structures that are the result of termination reactions will be of greater relative intensity in the spectra of low molecular weight polymers than in those of high molecular weight polymers. It should be noted that, for a poly(α-^{13}C-styrene) with a molecular weight of 20 800 (DP = 200) that has terminated predominately by combination, signals due to α-^{13}C–β-^{13}C junctions should be nearly the same intensity as those due to α-^{13}C–α-^{13}C junctions. Because almost 100% of the α-carbons are labeled with ^{13}C, every termination by combination will produce a $-CH_2(Ph)^{13}CH^{13}CH(Ph)CH_2-$ fragment; however, ^{13}C is present in the β-positions in only 1.1% natural abundance so that only $^1/_{50}$ main-chain repeat units will contain an α-^{13}C–β-^{13}C fragment. For higher molecular weight polymers, the α-^{13}C–β-^{13}C signals will be stronger than the α-^{13}C–α-^{13}C signals.

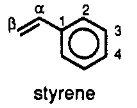
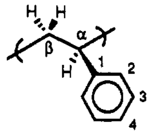
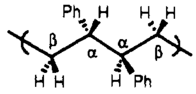
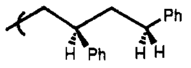
The 2D-INADEQUATE spectrum of the poly(α-^{13}C-styrene) is shonw in Figure 1a. The corresponding 1D ^{13}C NMR spectrum of the sample used to obtain the spectrum in Figure 1a is plotted in Figure 1b, and the ^{13}C NMR spectrum of a poly(α-^{13}C-styrene) sample with approximately 4 times higher molecular weight is shown in Figure 1c. Correlations between C_2 and C_3, between C_3 and C_4 (region A), between C_1 and C_α (region B), and between C_α and C_β (region C) are evident. An expansion of region C is shown in Figure 2. Correlations are observed which are attributed to C_α–C_α resonances (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 was added in the normal head-to-tail fashion.

Evidence that the C_α–C_α linkages responsible for the resonances in region 1 are formed by coupling of two chains rather than by chance head-to-head polymerization is obtained by comparing ^{13}C NMR spectra (Figure 2b,c) of two poly(α-^{13}C-styrene) samples with greatly different molecular weights. The 1D ^{13}C NMR spectrum of the polymer with ca. 4-fold higher molecular weight (Figures 1c and 2c) has greatly reduced signals which are attributed to C_α–C_α resonances (δ_C = 48–51 ppm) when compared with the spectrum of lower molecular weight polymer (Figures 1b and 2b). If these fragments arose from random head-to-head polymerization, their intensities, relative to other peaks in the spectrum, would not change with molecular weight.

The ^{13}C resonance assignments for styrene, polystyrene, and model structures for head-to-head polystyrene fragments are summarized in Table 1. Experimental ^{13}C chemical shifts were obtained from a one-pulse experiment, and the ^{13}C multiplicities were verified by DEPT[6] NMR experiments; 1D- and 2D-INADEQUATE experiments were used to verify the identity of sites containing adjacent ^{13}C labels. The presence of resonances at 33.8–33.6 ppm, indicating the presence of terminal CH_2 segments, suggested some termination via disproportionation. But this possibility was discounted since ^{13}C resonances from vinyl methine carbons, which must also be a result of disproportionation, are not detected. Thus, the methylene resonance at 33.8–33.6 ppm is probably the result of a single propagating polystyrene radical abstracting a hydrogen atom in a chain-transfer reaction rather than from disproportionation with a second propagating radical.

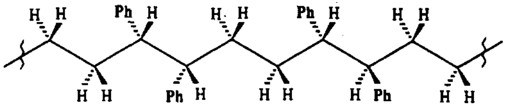
The C_α–C_α resonance assignments described above are consistent with the shifts reported by Vogl[9,10] for hydrogenated poly[1,4-poly-(2,3-diphenylbutadiene)] (**2**) which

Table 1. ^{13}C Resonance Assignments for Polystyrene Fragments

carbon		chemical shift (δ)				DEPT assignment[f]
		literature (ppm)				
		exptl	calcd	calcd (ppm)	exptl (ppm)	
 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]				
 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
 head–head	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]			
 terminal methylene	CH_2			33.9	33.8, 33.6	t

[a] Reference 7. [b] Reference 8. [c] Reference 10. [d] Poly(stilbene-*co*-styrene) ^{13}C NMR spectrum; α-CH of the stilbene units. [e] Poly(α-^{13}C-styrene) ^{13}C NMR spectra. [f] s = C, d = CH, t = CH_2, q = CH_3.

contains a reasonable model structure for head-to-head enchainments in polystyrene. Furthermore, some C_α resonances of poly(stilbene-*co*-styrene)[11] (**3**) that fall between 48 and 51 ppm correspond to the minor resonances observed in the spectrum of conventionally prepared polystyrene. These resonances also arise from structures which are a good model for head-to-head polystyrene enchainments.



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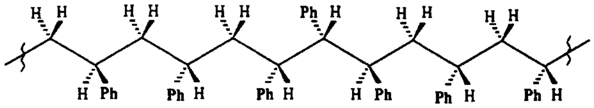

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In summary, the presence of methine carbon resonances in 48–51 ppm region coupled with the results of chemical shift calculations and 2D INADEQUATE data show the presence of two styrene repeat units bonded together by a head-to-head enchainment, offering the first direct evidence which supports the belief that the principal mode of termination of polystyrene radicals is combination.

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References and Notes

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