Supplementary Material Available: Details of the preparation and characterization of the isobutylene copolymers (Table I), carboxylation of the isobutylene/methylstyrene copolymers (Table II), and grafting of pivalolactone to the carboxylated isobutylene/methylstyrene copolymers (Table III) (13 pages). Ordering information is given on any current masthead page.

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Model Copolymerization Reactions. Determination of the Relative Rates of Addition of Styrene and Acrylonitrile to the 1-Phenylethyl Radical

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ABSTRACT: 1,1′-Azobis(1-phenyl[1-^{13}C]ethane) (1) was prepared in 15% overall yield, starting from [1-^{13}C]acetic acid (99 atom %). Analysis of end-group concentrations in styrene–acrylonitrile copolymers prepared with 1 as initiator allows accurate determination of the relative rates of addition of these monomers to the 1-phenylethyl radical. We obtain $k_S/k_A = 0.20 \pm 0.02$, a result consistent with the penultimate model treatment of the styrene–acrylonitrile copolymerization by Hill, O'Donnell, and O'Sullivan.

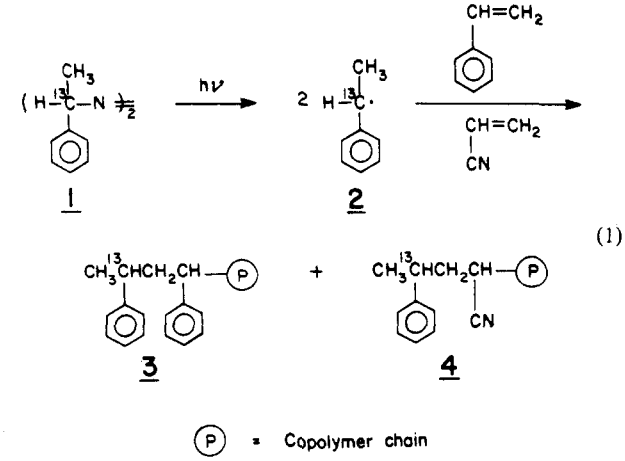
Introduction

Much of what is known about the addition of alkyl radicals to olefins has been learned from studies of radical copolymerization. In 1944 Mayo and Lewis outlined a kinetic framework for the prediction of copolymer composition, in which two kinetically distinct macroradicals compete for two olefinic comonomers.[1,2] Their "terminal" kinetic model quickly became the standard treatment of radical copolymerization, and the reactivity ratios derived from it now number in the thousands.[3] The success of the terminal model in predicting copolymer compositions has led to its widespread acceptance and to a belief that macroradical reactivity is governed in most systems only by the identity of the terminal comonomer unit.

There are good reasons to question this view. First of all, it was pointed out as early as 1946 that deviations from the predictions of the terminal model should be detected most readily in measurements of *sequence*, rather than *composition*.[4] Because sequence measurements even now are not routinely accessible, stringent tests of the terminal model have been applied only in a relatively small number of copolymerization systems. Second, the terminal model does not provide a satisfactory description of the *overall rate* of radical copolymerization. Until recently it was thought that the problem lay in inadequate treatment of the termination step, but rate measurements by Fukuda and co-workers have shown that, in the copolymerization of styrene and methyl methacrylate, it is the propagation rate constant that does not conform to the predictions of the terminal model.[5]

Problems of this kind have prompted us to renew investigation of the factors that control reactivity in radical addition to olefins. We have shown recently that the addition of primary alkyl radicals to styrene and acrylonitrile is sensitive to the nature of substituents placed γ to the radical center and that the magnitude of the effect is remarkably similar to that inferred from an application of the penultimate kinetic model to the copolymerization of these monomers.[6,7] But primary radicals are hardly realistic models of the macroradicals responsible for the growth of copolymer chains. We report in this paper a method by which one can assess the reactivity of the 1-phenylethyl radical, a plausible model of styryl-terminated macroradicals.

The method uses 1,1′-azobis(1-phenyl[1-^{13}C]ethane) (1) as a source of the 1-phenylethyl radical (2). Photolysis of 1 in a mixture of styrene and acrylonitrile leads to free radical copolymerization and to the formation of the two chemically distinct ^{13}C-enriched end-group diads 3 and 4 (eq 1). Four distinct diads are expected if end-group



stereochemistry is taken into account. Careful integration of the corresponding ^{13}C NMR signals allows determination of the relative end-group concentrations and thereby a calculation of the monomer reactivity ratios for 2. We describe these experiments in the present paper. Bevington and co-workers have reported the use of ^{13}C-en-

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Table I
Polymerization Data for ^{13}C-Enriched SAN Copolymers[a]

copolymer	styrene, mmol	acrylonitrile, mmol	styrene/acrylonitrile ([S]/[A])	polymer, mg	convn, %	[3]/[4]
1	7.827	2.554	3.06	101	10.6	0.568
2	7.884	2.350	3.35	97	10.3	0.736
3	8.048	2.177	3.70	95	10.1	0.971
4	8.230	1.692	4.86	90	9.5	0.971
5	8.381	1.513	5.54	87	9.1	0.991
6	8.428	1.314	6.41	87	9.2	1.29
7	8.580	1.187	7.23	83	8.7	1.46
8	8.594	0.9404	9.14	82	8.7	1.90

[a] Conditions: 14.5 mg of 1; 2.62 g of benzene; 33 °C; 3 h.

riched azobis(isobutyronitrile) in a series of investigations of the reactivity of the 2-cyano-2-propyl radical.[8]

Experimental Section

Preparations. [1-^{13}C]Acetyl Chloride. To a 10-mL round-bottom flask was added 1.0 g (16.4 mmol) of 99 atom % [1-^{13}C]acetic acid. A stream of dry N_2 was directed into the open flask. The flask was cooled to 0 °C, and 2.2 g (18.8 mmol) of freshly distilled thionyl chloride was added dropwise, with stirring, over a period of 15 min. After the addition, the reaction was stirred at 25 °C for 30 min, the flask was fitted with a condenser, and the reaction mixture was refluxed under N_2 for 1 h. After the mixture cooled to room temperature, the reflux condenser was replaced with a still head. Distillation (50–52 °C) under N_2 yielded 1.0 g (12.7 mmol, 77%) of [1-^{13}C]acetyl chloride.

[1-^{13}C]Acetophenone. To a 25-mL round-bottom flask was added 1.0 g (12.7 mmol) of [1-^{13}C]acetyl chloride and 7 mL of dry benzene. After the flask was cooled to −5 °C, 1.98 g (14.8 mmol) of anhydrous $AlCl_3$ was added in small portions over 40 min with stirring. After the addition, the reaction was stirred at 25 °C for 4 h. Throughout the addition and subsequent reaction, dry N_2 was bubbled through the mixture, which was contained in an open flask. Benzene was added periodically to make up for losses due to evaporation. The reaction mixture was then poured into 30 mL of 1 N HCl and extracted with three 30-mL portions of ether. The combined ether extracts were washed with 20 mL of 10% NaOH and then with 20 mL of water. After drying over $MgSO_4$ and removal of the ether, 1.35 g of crude yellow acetophenone (77% pure, 67% yield) was obtained.

[1-^{13}C]Acetophenone Azine. The crude acetophenone from above (1.35 g, 8.66 mmol, 77% pure) was dissolved in 2.5 mL of absolute ethanol to which 10 mg of acetic acid had been added. Hydrazine hydrate (0.208 g, 4.16 mmol of hydrazine) was then added dropwise, with stirring, to the solution contained in an open 10-mL round-bottom flask. The reaction was stirred at 60 °C for 2 h, by which time copious amounts of crystals had separated. The precipitated yellow crystals were collected by filtration, washed with 10 mL of cold methanol, and dried in vacuo to give 0.95 g (93%) [1-^{13}C]acetophenone azine: mp 122–123 °C.

1,2-Bis(1-phenyl[1-^{13}C]ethyl)hydrazine. [1-^{13}C]Acetophenone azine (0.95 g, 3.99 mmol) was suspended in 30 mL of acetic acid in a 250-mL bottle, and 110 mg of $PtO_2 \cdot H_2O$ was added. Hydrogenation was then accomplished by using a Paar hydrogenator, the theoretical amount of hydrogen being absorbed in about 10 min at 25 °C and an initial pressure of 34 psi. After filtration of the catalyst and removal of the acetic acid under vacuum, the oily residue was dissolved in 30 mL of ether and stirred for 2 h with 20 mL of 10% NaOH to remove any remaining acid. After separation of the organic layer and removal of the ether, 0.93 g (98%) of crude 1,2-bis(1-phenyl[1-^{13}C]ethyl)hydrazine was obtained.

1,1′-Azobis(1-phenyl[1-^{13}C]ethane). The crude 1,2-bis(1-phenyl[1-^{13}C]ethyl)hydrazine (0.93 g, 3.88 mmol) was added to 15 mL of H_2O in a 50-mL round-bottom flask, and 0.90 g (4.2 mmol) of yellow HgO was then added in portions over 10 min. After stoppering the flask and shaking for 20 min, 0.22 g (1.0 mmol) of additional HgO was added and shaking was continued for 90 min. A 20-mL portion of ether was then added to the mixture, and the HgO was removed by filtration. The filtrate was extracted with ether and the extract dried over $MgSO_4$. After removal of the ether in vacuo a yellow solid residue of crude azo compound was obtained. Recrystallization twice from methanol (45 to −28 °C) gave 0.287 g (31%) of 1-phenyl[1-^{13}C]ethane in the form of white crystals. The azo compound containing ^{13}C in naturally abundant amounts was synthesized in the same way from acetophenone [the data that follow are for the ^{13}C-enriched compound; data for the compound containing naturally abundant ^{13}C may be found in ref 9 (mp) and 10 (^1H NMR)]: mp 71–72 °C; ^1H NMR (300 MHz, acetone-d_6) δ 1.46 (doublet, 3 H), 1.49 (doublet, 3 H), 4.40 (quartet, 1 H), 4.86 (quartet, 1 H), 7.3–7.4 (multiplet, 10 H). Anal. Calcd for $^{13}C_2{}^{12}C_{14}H_{18}N_2$: C, 80.79; H, 7.55; N, 11.66. Found: C, 80.32; H, 7.53; N, 11.82.

Polymerizations. Copolymers. To 14.5 mg of 1 dissolved in 2.6 g of benzene in a septum-capped, N_2 flushed glass tube was added by syringe a total of 0.945 g (10–16 mmol) of N_2-sparged monomer (styrene and acrylonitrile). The tube was placed in a Rayonet Model RMR 400 photochemical reactor (350-nm lamps) for 3 h at 33 °C. The solution was then added dropwise to 150 mL of methanol to precipitate about 95 mg (10%) of polymer, which was filtered, redissolved in $CHCl_3$, reprecipitated into methanol, and filtered before drying to constant weight under vacuum. The polymerization data for the eight enriched copolymers used in our analysis are listed in Table I. Eight copolymers containing naturally abundant ^{13}C were also prepared exactly as above, except for the use of unenriched 1. The monomer feed ratios for these copolymers differ from the ratios given in Table I by no more than 2%.

Polystyrene. The same general procedure as that given above for the copolymers was used, except the polymerization was performed in bulk for 90 min with 26 mg of 1 added as initiator.

Poly(acrylonitrile). The same general procedure as that given above for the copolymers was used, except that the amounts of solvent and reagents were as follows: 1.8 g of benzene, 9.7 mg of 1, and 0.25 g of monomer. The polymerization time was 90 min. Because poly(acrylonitrile) precipitated from benzene, it was necessary to dissolve the polymer in dimethyl sulfoxide (Me_2SO) before precipitation into methanol. The polymer was reprecipitated twice from *N,N*-dimethylformamide (DMF) into methanol before drying to constant weight under vacuum.

Measurements. Homopolymer spectra were obtained on a Varian XL-200 NMR spectrometer using a single pulse sequence (1.5-s acquisition time) and broad-band ^1H decoupling.

The spin–lattice relaxation time (T_1) of end group **3** in $CDCl_3$ was determined on a Varian XL-300 NMR spectrometer by using the enriched homopolymer of styrene (Figure 1). From inversion–recovery experiments a T_1 value of 0.23 ± 0.04 s was obtained. Owing to its insolubility in $CDCl_3$, the enriched homopolymer of acrylonitrile could not be used similarly for end group **4**. Copolymer 1 in Table I, which has the largest signal from end group **4**, was used instead to obtain a value of 0.24 ± 0.08 s for the T_1 of end group **4**.

Spectra of styrene–acrylonitrile (SAN) copolymers were obtained on a Varian XL-300 NMR spectrometer by using a single pulse sequence with gated decoupling to suppress the nuclear Overhauser effect (NOE). A delay of 3.75 s between pulses was used, which is more than 10 times the longest possible end-group relaxation time. End-group signals were assigned by comparison of copolymer spectra with spectra of styrene and acrylonitrile homopolymers and from the variation in signal intensity with changes in monomer feed composition. Peak areas were apportioned between end groups **3** and **4** in each spectrum by drawing vertical lines from local spectral minima to the base line of the

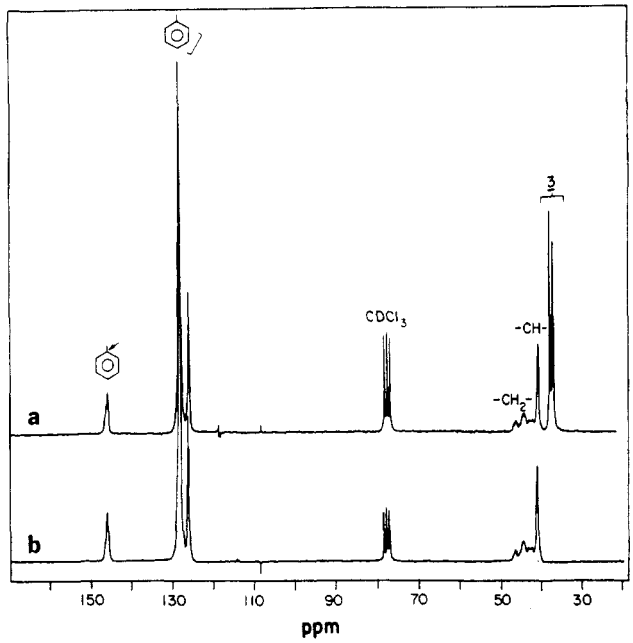

Figure 1. 50-MHz ^{13}C NMR spectra of (a) enriched and (b) natural-abundance polystyrene in $CDCl_3$ (2% w/w). The numbered labels correspond to the end groups in eq 1.

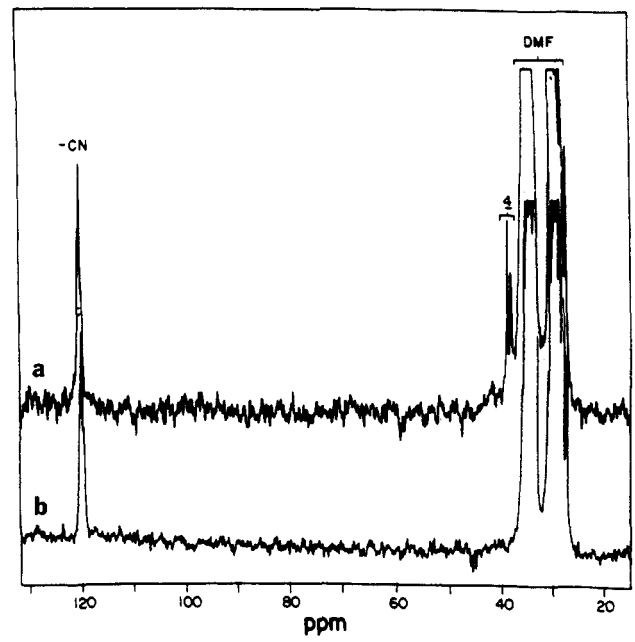

Figure 2. 50-MHz ^{13}C NMR spectra of (a) enriched and (b) natural-abundance poly(acrylonitrile) in DMF-d_7 (2% w/w). The numbered labels correspond to the end groups in eq 1.

normalized spectrum of the corresponding unenriched copolymer. An alternative procedure, in which a horizontal base line was drawn at the level of the deepest local minimum, gave identical results. Peak areas were determined by a cut-and-weigh method.

Results and Discussion

1,1′-Azobis(1-phenyl[1-^{13}C]ethane) (1) was prepared in 15% overall yield, starting from [1-^{13}C]acetic acid (99 atom %), as shown in Scheme I. The proton-decoupled ^{13}C NMR spectrum of enriched 1 showed an intense signal at 77.1 ppm—the same chemical shift as was observed for the methine carbon in the spectrum of unenriched 1 prepared from acetophenone.

Scheme I

$$CH_3{}^{13}CO_2H \xrightarrow{SOCl_2} CH_3{}^{13}COCl \xrightarrow[AlCl_3]{C_6H_6}$$

$$CH_3{}^{13}COPh \xrightarrow[EtOH]{H_2NNH_2\cdot H_2O} (CH_3(C_6H_5)^{13}C{=}N)_2 \xrightarrow[PtO_2\cdot H_2O]{H_2}$$

$$(CH_3(C_6H_5)^{13}CNH)_2 \xrightarrow{HgO} (CH_3(C_6H_5)^{13}CH{-}N)_2$$

1,1′-Azobis(1-phenylethane) is known to be an effective initiator of free radical polymerization[11,12] and was used here in both ^{13}C-enriched and natural-abundance forms to prepare homopolymers and copolymers of styrene and acrylonitrile. Copolymerizations were run in benzene solution at 33 °C under steady-state irradiation (Rayonet minireactor, 350-nm lamps). All of the copolymers remained soluble throughout the reaction. Conversions were limited to 8–11% (cf. Table I), and molecular weights varied within the range 20 000–40 000 as determined by gel permeation chromatography.

Figure 1 shows ^{13}C NMR spectra of polystyrenes prepared by using enriched and unenriched 1. Two new signals appear at 36.75 and 37.42 ppm in the spectrum of the enriched polymer and are assigned to the two alternative stereochemical configurations of end group 3.[13] Similarly, the resonances of end group 4 appear at 36.42 and 38.44 ppm in the spectrum of enriched poly(acrylonitrile) (PAN) in DMF-d_7 (Figure 2). The spectral regions obscured by DMF-d_7 in Figure 2 were observed for enriched and unenriched poly(acrylonitrile) in Me_2SO-d_6 (which obscures the signal from 4) and were found to be identical with each other and to a published spectrum of PAN.[14]

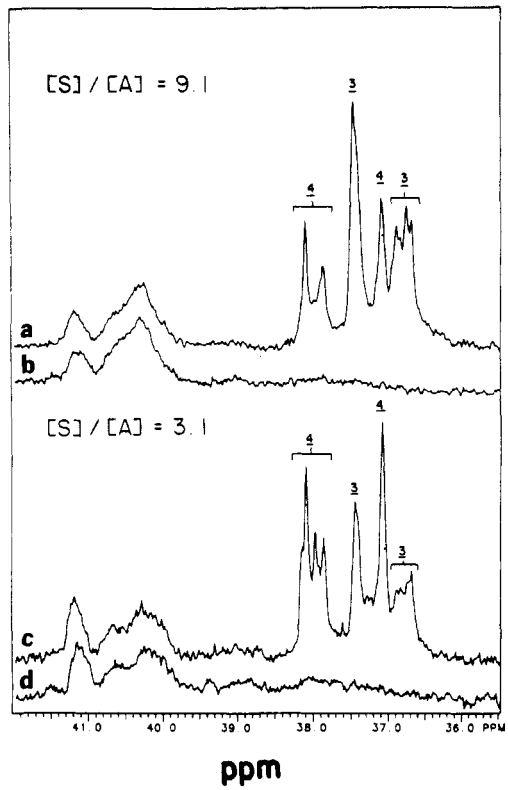

Figure 3. 75-MHz ^{13}C NMR spectra (expanded plots) of natural-abundance (b and d) and enriched (a and c) SAN copolymers in $CDCl_3$ (2% w/w) prepared with monomer feed ratios ([S]/[A]) of 9.1 (top) and 3.1 (bottom). The numbered labels correspond to the end groups in eq 1.

Figure 3 shows ^{13}C NMR spectra of styrene–acrylonitrile copolymers prepared by using two different monomer feed compositions. In each case, copolymers were prepared both with natural-abundance 1 and with enriched 1 to ensure correct base-line assignment in the spectral regions

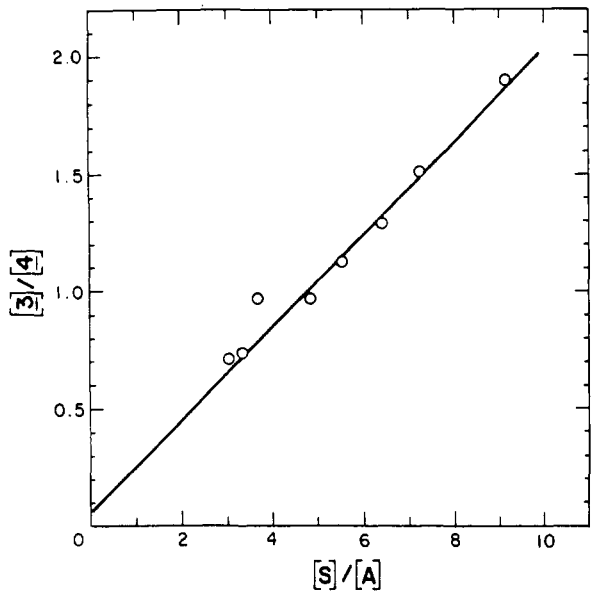

Figure 4. Plot of relative end-group concentration ([3]/[4]) vs. monomer feed ratio ([S]/[A]) for enriched SAN copolymers 1–8 listed in Table I.

corresponding to end groups **3** and **4**. The signals due to end group **3** again appear at 36.75 and 37.42 ppm; those of end group **4** are shifted somewhat from their positions in DMF-d_7 and appear at 37.12 and 38.00 ppm. As expected, the intensities of the signals assigned to **3** decrease with decreasing [S]/[A]. The spectra in Figure 3 were recorded under conditions appropriate for quantitative signal integration, i.e., with a pulse delay of at least 10 times the longest end group T_1 and with gated decoupling to suppress the nuclear Overhauser effect.

Table I summarizes the results of eight such experiments, and Figure 4 presents a plot of the relative end-group concentrations ([**3**]/[**4**]) as a function of monomer feed composition. The plot is linear, as expected, and the best-fit line passes very near the origin. The slope of the line is k_S/k_A, the ratio of the rates of addition of styrene and acrylonitrile to the 1-phenylethyl radical. From Figure 3, $k_S/k_A = 0.20 \pm 0.02$.

The parameter k_S/k_A should be directly analogous to the terminal model reactivity ratio (r_S) for styrene in its radical copolymerization with acrylonitrile. Greenley's critical summary of copolymerization reactivity ratios[15] lists values of r_S ranging from 0.27 to 0.54 for this copolymerization, but it is perhaps most useful to compare our results with the recent careful analysis of Hill, O'Donnell, and O'Sullivan.[7] They report $r_S = 0.33$ and $r_A = 0.05$ for the best-fit terminal model and $r_{SS} = 0.23$, $r_{AS} = 0.63$, $r_{AA} = 0.04$, and $r_{SA} = 0.09$ from application of the penultimate kinetic scheme. On the basis of sequence analyses, Hill et al. propose that the penultimate model provides the best description of the radical copolymerization of styrene and acrylonitrile.

The similarity of our measured k_S/k_A and the best-fit r_{SS} of Hill and co-workers is intriguing. In earlier work on the addition of primary radicals to styrene and acrylonitrile,[6] we found virtually identical reactivity ratios for the 1-butyl and 3-phenyl-1-propyl radicals, a result that suggests k_S/k_A is insensitive to the introduction of a phenyl group γ to the radical center. Should this be so for 1-phenyl-1-alkyl radicals as well, 1-phenylethyl would be expected to serve as an excellent model of the ~~SS• chain end. We intend to test this hypothesis through examination of the reactivity of the 1,3-diphenyl-1-propyl and 3-cyano-1-phenyl-1-propyl radicals.

Conclusions

1,1′-Azobis(1-phenyl[1-^{13}C]ethane) (**1**) serves as a convenient source of the 1-phenylethyl radical. Analysis of end-group concentrations in styrene–acrylonitrile copolymers prepared with **1** as initiator allows accurate determination of the relative rates of addition of these monomers to 1-phenylethyl. We obtain $k_S/k_A = 0.20 \pm 0.02$, a result consistent with the penultimate model treatment of the styrene–acrylonitrile copolymerization by Hill, O'Donnell, and O'Sullivan.

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Registry No. $H_3C^{13}COCl$, 1520-57-6; $H_3C^{13}CO_2H$, 1563-79-7; $H_3C^{13}COPh$, 10383-88-7; C_6H_6, 71-43-2; $H_3C^{13}C(Ph)=NN=^{13}C(Ph)CH_3$, 105091-09-6; H_2NNH_2, 302-01-2; $H_3C^{13}C(Ph)NHNH^{13}C(Ph)CH_3$, 102925-68-8; $H_3C^{13}C(Ph)N=N^{13}C(Ph)CH_3$, 102925-67-7; PS, 9003-53-6; PAN, 25014-41-9; (S)(AN) (copolymer), 9003-54-7; S, 100-42-5; AN, 107-13-1.

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