Determination of the Relative Rates of Addition of Styrene and Acrylonitrile to the 1-(1,3-Diphenylpropyl) and 1-(3-Cyano-1-phenylpropyl) Radicals. Evidence for a Penultimate Effect in Radical Copolymerization

Douglas A. Cywar† and David A. Tirrell*

Contribution from the Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003. *Received March 14, 1989*

Abstract: 1,1′-Azobis(1,3-[1-^{13}C]diphenylpropane) (**1b**) and 4,4′-azobis(4-phenyl[4-^{13}C]butyronitrile) (**1c**) were prepared in overall yields of 10% and 1.2%, respectively, both starting from $Ba^{13}CO_3$ (99 atom %). Analysis of end-group concentrations in styrene–acrylonitrile (SAN) copolymers prepared with **1b** as initiator allows accurate determination of the relative rates of addition of these monomers (k_S/k_A) to the 1-(1,3-diphenylpropyl) radical (**2b**); similarly, analysis of SAN copolymers prepared with **1c** allows determination of k_S/k_A for the 1-(3-cyano-1-phenylpropyl) radical (**2c**). Significantly different preferences of the radicals for addition of styrene and acrylonitrile were observed; we obtain $k_S/k_A = 0.21 \pm 0.01$ for **2b** and $k_S/k_A = 0.52 \pm 0.03$ for **2c**. These results show that k_S/k_A for 1-(1-phenylalkyl) radicals is sensitive to substitution γ to the radical center and provide strong support for the existence of a penultimate unit effect in SAN copolymerization. The results are consistent with the penultimate model analysis of SAN copolymerization by Hill, O'Donnell, and O'Sullivan.

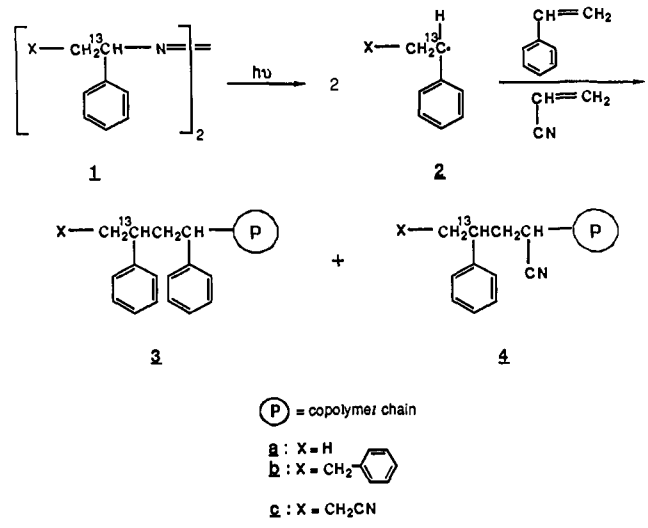
Introduction

Although the radical copolymerization of alkenes forms the basis of a large segment of the chemical industry, important problems remain in the description of copolymerization processes at the fundamental level.[1] The standard terminal model of copolymerization[2-4] has proven successful in the prediction of copolymer composition for the great majority of radical copolymerizations investigated to date. However, this does not mean that the primary assumption of this model (i.e., that the terminal monomeric unit is the sole determinant of macroradical reactivity) is generally true; measurements of composition do not in general provide a sensitive test of copolymerization mechanism.

It has long been recognized that measurements of comonomer *sequence* provide a more sensitive method than composition measurements for distinguishing among alternative kinetic models of copolymerization processes. For example, Farmer, Hill, and O'Donnell have shown that measurements of sequence can be used to distinguish among the terminal, penultimate, and complex-participation models for the styrene–maleic anhydride and styrene–acrylonitrile (SAN) systems.[4] Hill and co-workers have reported sequence measurements for SAN copolymerization and conclude on that basis that the penultimate model provides the best description of this system.[5] They find that all three kinetic models provide adequate descriptions of the composition data but that the predicted sequences vary significantly. For example, a copolymer prepared from an equimolar mixture of monomers is predicted in all three cases to contain a mole fraction of styrene units of 0.57. On the other hand, the number fraction of styrene sequences that consist of an isolated styrene residue is predicted to be 0.74 for the terminal model, 0.61 for the penultimate model, and 0.18 for the complex-participation model. Clearly these are quite different chemical substances, and the synthesis of well-defined copolymer structures requires a precise understanding of copolymerization mechanism. Relatively few systems have been investigated in this manner.

Additional concern about the assumptions of the terminal model is raised by the recent work of Fukuda, Ma, and Inagaki.[7] These workers have shown that the terminal model fails to predict the composition dependence of the overall propagation rate constant (k_p) for the copolymerization of styrene and methyl methacrylate, despite the fact that the terminal model correlates satisfactorily the composition data for this system. A penultimate model treatment, on the other hand, fits both composition and k_p.

Scheme I



The distinction between the terminal and penultimate models lies in consideration of the effect of remote substituents on radical reactivity. In view of (i) the controversy surrounding copolymerization mechanism and (ii) the critical dependence of copolymer structure on the mechanism of the chain growth process, we have sought to measure directly remote substituent effects for simple radicals of structures analogous to the propagating ends of some common macroradicals. In 1985,[8] we reported the results of trapping experiments on a set of γ-substituted primary alkyl radicals, in which we used the competitive "mercury method" developed largely by Giese.[9] These experiments revealed a γ-substituent effect in these simple radicals that is in remarkable accord with the penultimate effect proposed by Hill.[5] Nevertheless,

* To whom correspondence should be addressed.
† Present address: IBM Corp., 1701 North Street, Endicott, NY 13760.

(1) For a recent review: Tirrell, D. A. In *Comprehensive Polymer Science*; Pergamon Press: Oxford, 1989; Vol. 3, p 195.
(2) Mayo, F. R.; Lewis, F. M. *J. Am. Chem. Soc.* **1944**, *66*, 1594.
(3) Alfrey, T.; Goldfinger, G. *J. Chem. Phys.* **1944**, *12*, 205.
(4) Wall, F. T. *J. Am. Chem. Soc.* **1944**, *66*, 2050.
(5) Farmer, R. G.; Hill, D. J. T.; O'Donnell, J. H. *Macromol. Sci. Chem.* **1980**, *14*, 51.
(6) Hill, D. J. T.; O'Donnell, J. H.; O'Sullivan, P. w. *Macromolecules* **1982**, *15*, 960.
(7) Fukuda, T.; Ma, Y. D.; Inagaki, H. *Macromolecules* **1985**, *18*, 17.
(8) Jones, S. A.; Prementine, G. S.; Tirrell, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 5275.
(9) For a review: Giese, B. *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*; Pergamon Press: Oxford, 1986.

0002-7863/89/1511-7544$01.50/0

inferences drawn from measurements on reactive primary radicals can be applied only with the greatest caution to the behavior of the resonance-stabilized macroradicals involved in the copolymerization of styrene and acrylonitrile. Unfortunately, use of the mercury method with stabilized alkyl radicals (e.g., benzyl) is complicated by rapid coupling of alkyl fragments and concomitant low yields of products derived from monomer addition.[10]

A simple alternative method by which the relative rates of addition of a comonomer pair [e.g., styrene (S) and acrylonitrile (A)] to a stabilized alkyl radical can be evaluated is illustrated in Scheme I.[11] Photolysis of a ^{13}C-enriched azoalkane **1** in a comonomer mixture of known composition produces the corresponding radical **2**, which adds either of the monomers and continues to propagate. The resultant SAN copolymer contains the two chemically distinct ^{13}C-enriched end groups **3** and **4**, distinguished by the identity of the monomer to have added to the primary radical **2**. By ^{13}C NMR analysis of the copolymer one can determine the relative concentrations of **3** and **4**, and thereby the rate constant ratio k_S/k_A for the addition of styrene and acrylonitrile to the radical **2**.

We have used this method previously to determine k_S/k_A (=0.20 ± 0.02) for the 1-phenylethyl radical **2a**.[12] The present paper describes determination of k_S/k_A for the 1-(1,3-diphenylpropyl) radical (**2b**) and the 1-(3-cyano-1-phenylpropyl) radical (**2c**), generated from the respective azoalkanes **1b** and **1c**. Through comparison of k_S/k_A for **2a–c**, we sought an understanding of the role of γ-substitution in determining the relative rates of addition of styrene and acrylonitrile to a set of simple, plausible models for the styryl-terminated macroradicals involved in the growth of SAN copolymer chains. The results provide a basis for an assessment of the penultimate model as a physically meaningful description of SAN copolymerization.

Experimental Section

Preparations. [1-^{13}C]Benzoic Acid. A modification of the procedure of Dauben, Reid, and Yankwich[13] was used. Gaseous $^{13}CO_2$ (generated from 50 g of $Ba^{13}CO_3$ by dropwise addition of H_2SO_4 and subsequently trapped in a liquid N_2 cooled glass tube) was condensed at −25 °C into 400 mL of an ethereal solution of 0.28 mol of phenylmagnesium bromide. The solution was warmed to 0 °C. After 15 min, the reaction mixture was cautiously acidified with 150 mL of 2 N HCl. The organic layer was separated, washed with 50 mL of 2 N HCl and 2 × 50 mL of H_2O, and dried over $MgSO_4$. The ether was removed and the residue recrystallized from benzene to yield 25.8 g (84%) of [1-^{13}C]benzoic acid, mp 122–123 °C. Anal. Calcd for $^{13}CC_6H_7O_2$: C, 69.10; H, 4.91. Found: C, 68.80; H, 4.93. ^1H NMR (200 MHz, $CDCl_3$): δ 7.48 (m, 2 H), 7.63 (m, 1 H), 8.14 (m, 2 H). IR (KBr pellet): 3400–2200 br, 1650, 1460, 1420, 1330, 1280, 1190, 930, 810, 700 cm^{-1}.

[1-^{13}C]Benzoyl Chloride. A 500-mL round-bottom flask was fitted with a condenser and N_2 inlet and outlet. To this flask was added 51.59 g (0.419 mol) of [1-^{13}C]benzoic acid, 39 mL (0.535 mol) of $SOCl_2$, and 97 mL of CH_2Cl_2. The mixture was refluxed with stirring under a slow N_2 flush for 4 h and then allowed to stir overnight at 35 °C, also under a slow N_2 flush. The condenser was replaced with a still head, and the CH_2Cl_2 and excess $SOCl_2$ were distilled off. The remaining liquid was vacuum distilled [bp 50 °C (2 mm Hg)] to yield 54.49 g (92%) of [1-^{13}C]benzoyl chloride. ^1H NMR (200 MHz, $CDCl_3$): δ 7.51 (m, 2 H), 7.69 (m, 1 H), 8.12 (m, 2 H). IR (neat): 3060, 1720, 1590, 1450, 1320, 1200, 1180, 850, 770, 660 cm^{-1}.

1,3-Diphenyl-1-[1-^{13}C]propanone. A Grignard solution prepared from 2.50 g (103 mmol) of Mg, 19.10 g (103 mmol) of (2-bromoethyl)-benzene, and 125 mL of anhydrous ether was decanted into a 250-mL three-neck round-bottom flask fitted with an addition funnel, mechanical stirrer, reflux condenser, and N_2 inlet and outlet. After cooling to 0 °C in an ice–water bath, 9.44 g (51.5 mmol) of anhydrous $CdCl_2$ was added with stirring over 5 min. The reaction mixture was stirred for an additional 10 min at 0 °C, allowed to warm to room temperature, and then refluxed for 10 min. The condenser was then replaced with a still head and the ether distilled off until a nearly dry residue remained. (*Caution!* Evaporation to dryness of ether solutions that contain peroxides may result in an explosion.) At this time 80 mL of dry benzene was added and distilled off until a nearly dry residue remained, and a final addition of 110 mL of dry benzene was made. The reaction mixture was cooled to room temperature, and 7.10 g (50.2 mmol) of [1-^{13}C]benzoyl chloride was added dropwise over 2 min with vigorous stirring. The reaction was then refluxed for 1.5 h. After it was cooled to room temperature, the reaction mixture was opened to the air and 80 mL of ice–water was added. After enough aqueous 1 N H_2SO_4 was added to dissolve a white precipitate, the phases were separated. The aqueous phase was extracted with 30 mL of benzene and the extract added to the organic phase. The organic phase was then washed with 30 mL each of H_2O, aqueous 5% (w/w) NaOH, and H_2O twice more. After the solution was dried over $MgSO_4$, the solvent was removed in vacuo and the residue recrystallized from 95% ethanol to yield 5.23 g (49%) of 1,3-diphenyl-1-[1-^{13}C]-propanone as white plates; mp 67–68 °C. ^1H NMR (200 MHz, $CDCl_3$): δ 3.08 (m, 2 H), 3.30 (m, 2 H), 7.27 (m, 5 H), 7.49 (m, 3 H), 7.96 (m, 2 H). IR (KBr): 3030, 2930, 1640, 1450, 1370, 1290, 970, 750, 690 cm^{-1}. The natural-abundance compound 1,3-diphenyl-1-propanone was prepared from benzoyl chloride in the same manner. ^1H NMR (200 MHz, $CDCl_3$): δ 3.07 (m, 2 H), 3.30 (m, 2 H), 7.27 (m, 5 H), 7.49 (m, 3 H), 7.96 (m, 2 H). IR (KBr): 3030, 2930, 1680, 1370, 1300, 1210, 980, 740, 690 cm^{-1}.

1,3-Diphenyl-1-[1-^{13}C]propanone Azine. A solution of 4.93 g (23.4 mmol) of 1,3-diphenyl-1-[1-^{13}C]propanone, 0.374 g (11.7 mmol) of anhydrous hydrazine, and 1 drop of acetic acid in 31 mL of absolute ethanol was refluxed under N_2 for 2.5 h. The solution was then allowed to stand at room temperature for 2 days. The solid that had precipitated was then filtered, washed with 20 mL of ice-cold anhydrous ethanol, and dried under vacuum to give 3.22 g (66%) of 1,3-diphenyl-1-[1-^{13}C]propanone azine as yellow prisms; mp 114–115 °C. Anal. Calcd for $^{13}C_2C_{28}H_{28}N_2$: C, 86.56; H, 6.74; N, 6.69. Found: C, 86.43; H, 6.71; N, 6.58. ^1H NMR (200 MHz, $CDCl_3$): δ 2.82 (m, 2 H), 3.18 (m, 7.20 (m, 5 H), 7.45 (m, 3 H), 7.93 (m, 2 H). IR (KBr): 3020, 2930, 1550, 1500, 1450, 1280, 1180, 1030, 750, 690 cm^{-1}. The natural-abundance compound 1,3-diphenyl-1-propanone azine was prepared from 1,3-diphenyl-1-propanone in the same manner. ^1H NMR (200 MHz, $CDCl_3$): δ 2.82 (m, 2 H), 3.18 (m, 2 H), 7.20 (m, 5 H), 7.45 (m, 3 H), 7.93 (m, 2 H). IR (KBr): 3030, 2950, 1600, 1570, 1500, 1450, 1290, 1180, 1030, 750, 690 cm^{-1}.

***N,N'*-Bis(1,3-diphenyl[1-^{13}C]propyl)hydrazine.** A 100-mL three-neck round-bottom flask fitted with a reflux condenser, addition funnel, and N_2 inlet and outlet was charged with a solution of 3.13 g (7.45 mmol) of 1,3-diphenyl-1-[1-^{13}C]propanone azine in 27 mL of dry toluene. After the system was flushed with N_2, the solution was heated to reflux and 1.65 mL of 10 M $BH_3{\cdot}Me_2S$ (16.5 mmol of BH_3) was added dropwise over 10 min. The reaction was refluxed for an additional 6 h and cooled to room temperature, and 5.0 mL of methanol was added dropwise over 30 min with stirring (vigorous foaming). After it was stirred overnight at room temperature, the solution was cooled to 0 °C in an ice–water bath and anhydrous HCl was bubbled through the solution for 5 min (vigorous foaming). After it was stirred overnight at room temperature, the solvent was removed in vacuo to leave 4.9 g of a colorless oil. This was dissolved in 30 mL of CH_2Cl_2, and the solution was transferred to a separatory funnel and washed with 30 mL of aqueous 10% (w/w) NaOH. After it was ensured that the pH of the aqueous phase was >10, the phases were separated. The aqueous phase was extracted with 30 mL of CH_2Cl_2 and the extract added to the organic phase. The organic phase was then washed with 30 mL of H_2O and 30 mL of saturated aqueous NaCl. After the organic phase was dried over $MgSO_4$, the solvent was removed in vacuo to yield 3.14 g (100%) of crude *N,N'*-bis(1,3-diphenyl[1-^{13}C]propyl)hydrazine as a colorless oil. This was used in the next step without further purification. ^1H NMR (200 MHz, $CDCl_3$): δ 1.7–2.8 (m, 10 H, 8 H after D_2O exchange), 3.45 (m, 1 H), 4.12 (m, 1 H), 7.24 (m, 20 H). IR (neat): 3100–3400 br, 3070, 3030, 2930, 2860, 1610, 1500, 1460, 750, 700 cm^{-1}. The natural-abundance compound *N,N'*-bis(1,3-diphenylpropyl)hydrazine was prepared from 1,3-diphenyl-1-propanone azine in the same manner. ^1H NMR (80 MHz, $CDCl_3$): δ 1.9 (m, 4 H), 2.3–3.2 (m, 6 H, 4 H after D_2O exchange), 3.7 (m, 2 H), 7.1 (m, 20 H). IR (neat): 3100–3400 br, 3070, 3030, 2930, 2860, 1610, 1500, 1460, 750, 700 cm^{-1}.

1,1'-Azobis(1,3-[1-^{13}C]diphenylpropane) (1b). In a 100-mL round-bottom flask was mixed 3.14 g (7.45 mmol) of *N,N'*-bis(1,3-diphenyl-[1-^{13}C]propyl)hydrazine and 20 mL of H_2O. After the addition of 2.20 g (10.2 mmol) of yellow HgO, the flask was stoppered and shaken for 1.5 h. At the end of this time 30 mL of CH_2Cl_2 was added and the mixture filtered through a Celite pad. The organic phase was separated and dried for 30 min over $MgSO_4$. The solvent was subsequently removed in vacuo and the crude residue left in an open flask in the dark for 3 days. The solid thus obtained was recrystallized twice from 25 mL

(10) Prementine, G. S.; Tirrell, D. A. *Macromolecules* **1989**, *22*, 52.
(11) This approach was introduced by Bevington and co-workers for azobis(isobutyronitrile): Bevington, J. C.; Huckerby, T. N.; Hutton, N. W. E. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*(9), 2655.
(12) Cywar, D. A.; Tirrell, D. A. *Macromolecules* **1986**, *19*, 2908.
(13) Dauben, W. G.; Reid, J. C.; Yankwich, P. E. *Anal. Chem.* **1947**, *19*, 828.
(14) Gilman, H.; Zoellner, E. A.; Dickey, J. B. *J. Am. Chem. Soc.* **1929**, *51*, 1576.

of 5:1 methanol/benzene and dried under vacuum to give 1.30 g (42%) of 1,1′-azobis(1,3-[1-^{13}C]diphenylpropane) as white needles; mp 78–100 °C. Anal. Calcd for $^{13}C_2C_{28}H_{30}N_2$: C, 86.15; H, 7.19; N, 6.66. Found: C, 86.34; H, 7.15; N, 6.48. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.43 (m, 8 H), 4.18 (m, 1 H), 4.86 (m, 1 H), 7.20 (m, 20 H). IR (KBr): 3070, 3030, 2950, 2890, 1600, 1500, 1460, 1030, 750, 700 cm^{-1}. ^{13}C NMR (75 MHz, $CDCl_3$): δ 81.66, 81.74. UV (0.033 M benzene solution): ϵ_{max} (362 nm) = 48 M^{-1} cm^{-1}. The natural-abundance compound 1,1′-azobis(1,3-diphenylpropane) was prepared from *N,N′*-bis(1,3-diphenylpropyl)hydrazine in the same manner. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.43 (m, 8 H), 4.53 (m, 2 H), 7.20 (m, 20 H). IR (KBr): 3080, 3030, 2940, 2890, 1600, 1500, 1460, 1030, 750, 700 cm^{-1}. ^{13}C NMR (75 MHz, $CDCl_3$): δ 31.97, 32.24, 36.22, 36.72, 81.66, 81.75, 125.80, 125.92, 127.48, 127.61, 127.88, 127.92, 128.26, 128.38, 128.56, 128.66, 139.76, 140.05, 141.38, 141.51. UV (0.032 M benzene solution): ϵ_{max}(362 nm) = 48 M^{-1} cm^{-1}.

Ethyl 3-Phenyl-3-keto[3-^{13}C]propionate. The procedure of Straley and Adam[15] for the preparation of the compound naturally abundant in ^{13}C was used.

Ethyl 3-Phenyl-3-(methoxylmino)[3-^{13}C]propionate. The procedure of Secor and Sanders[16] for the preparation of the compound naturally abundant in ^{13}C was used.

3-Amino-3-phenyl-1-[3-^{13}C]propanol. The procedure of Secor and Sanders[16] for the preparation of the compound naturally abundant in ^{13}C was used.

3-Phenyl-3-phthalimido-1-[3-^{13}C]propanol. A finely ground, intimate mixture of 20.23 g (0.134 mol) of 3-amino-3-phenyl-1-[3-^{13}C]propanol and 19.84 g (0.134 mol) of phthalic anhydride was heated at 170 °C under N_2 with magnetic stirring in a 500-mL round-bottom flask for 1.5 h. After cooling, the solid was dissolved in 250 mL of CH_2Cl_2 and the solution dried over $MgSO_4$. The CH_2Cl_2 was subsequently removed and the residue crystallized upon standing overnight; no further purification was necessary. The yield of 3-phenyl-3-phthalimido-1-[3-^{13}C]propanol was 35.90 g (95%); mp 95–100 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.64 (br s, 1 H, exchanged with D_2O), 2.54 (m, 1 H), 2.82 (m, 1 H), 3.71 (m, 2 H), 5.27 (m, 0.5 H), 5.96 (m, 0.5 H), 7.30 (m, 3 H), 7.54 (m, 2 H), 7.68 (m, 2 H), 7.79 (m, 2 H). IR (KBr): 3420, 2930, 2870, 1770, 1700, 1390, 1350, 1080, 1040, 710 cm^{-1}. The natural-abundance compound 3-phenyl-3-phthalimido-1-propanol was prepared from 3-amino-3-phenyl-1-propanol in the same manner. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.99 (br s, 1 H, exchanged with D_2O), 2.52 (m, 1 H), 2.81 (m, 1 H), 3.68 (m, 2 H), 5.59 (m, 1 H), 7.30 (m, 3 H), 7.54 (m, 2 H), 7.67 (m, 2 H), 7.79 (m, 2 H). IR (KBr): 3530, 3450 s, 2940, 1770, 1700, 1390, 1360, 1090, 1060, 710 cm^{-1}.

3-Phenyl-3-phthalimido-1-[3-^{13}C]propyl 4-Methylphenylsulfonate. In a 2-L round-bottom flask was placed 35.50 g (0.126 mol) of 3-phenyl-3-phthalimido-1-[3-^{13}C]propanol and 1 L of anhydrous pyridine. After the solid had dissolved, the solution was cooled to 0 °C and 28.10 g (0.147 mol) of *p*-toluenesulfonyl chloride was added in several portions over 2 min. The flask was then capped with a rubber septum, flushed with N_2, and left at 0 °C for 48 h. The solution was then poured into 1.5 L of ice–water and extracted with 3 × 200 mL of $CHCl_3$. The combined $CHCl_3$ extracts were then washed with ice-cold 200-mL portions of aqueous 3 N HCl until a wash remained acidic. It was necessary to cool the $CHCl_3$ solution several times to keep it below 35 °C. The $CHCl_3$ solution was then washed with 2 × 100 mL of saturated aqueous $NaHCO_3$ and 100 mL of saturated aqueous NaCl. After the mixture was dried over $MgSO_4$, the $CHCl_3$ was removed in vacuo to leave 51.44 g (90%) of 3-phenyl-3-phthalimido-1-[3-^{13}C]propyl (4-methylphenyl)-sulfonate as a light green oil. This crude product was used directly in the next step. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.36 (s, 3 H), 2.68 (m, 1 H), 2.98 (m, 1 H), 4.07 (m, 2 H), 5.08 (m, 0.5 H), 5.78 (m, 0.5 H), 7.48 (m, 13 H). IR (neat): 3050, 2980, 1770, 1700, 1600, 1460, 1360, 1180, 1100, 920, 730 cm^{-1}. The natural-abundance compound 3-phenyl-3-phthalimido-1-propyl (4-methylphenyl)sulfonate was prepared from 3-phenyl-3-phthalimido-1-propanol in the same manner. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.37 (s, 3 H), 2.69 (m, 1 H), 2.97 (m, 1 H), 4.06 (m, 2 H), 5.44 (m, 1 H), 7.51 (m, 13 H). IR (neat): 3040, 2940, 1770, 1700, 1590, 1350, 1180, 1090, 990, 920, 750 cm^{-1}.

4-Phenyl-4-phthalimido[4-^{13}C]butyronitrile. In a 250-mL round-bottom flask was placed 51.04 g (0.113 mol) of 3-phenyl-3-phthalimido-1-[3-^{13}C]propyl (4-methylphenyl)sulfonate and 45 mL of DMSO. After the oil had dissolved, the solution was heated to 40 °C and a suspension of 6.52 g (0.133 mol) of NaCN in 30 mL of DMSO was added all at once. The mixture was maintained at 40 °C with stirring for 1 h, then heated to 60 °C for 0.5 h, and finally allowed to cool to room temperature. The mixture was then poured into 700 mL of H_2O and extracted with 6 × 100 mL of $CHCl_3$. The combined $CHCl_3$ extracts were washed with 100 mL of aqueous 1 N HCl, 3 × 100 mL of H_2O, and 100 mL of saturated aqueous NaCl. After the mixture was dried over $MgSO_4$, the $CHCl_3$ was subsequently removed to leave 21.64 g (65%) of 4-phenyl-4-phthalimido[4-^{13}C]butyronitrile as a white solid; mp 125–127 °C. (Occasionally when performing this reaction with natural-abundance starting material, a thick brown liquid rather than solid material was obtained at this point. In this case trituration with ether was found to be effective. It is noted that this difficulty is least likely to occur when the starting material is free of pyridine and the DMSO and NaCN are dry.) ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.41 (m, 2 H), 2.75 (m, 1 H), 2.97 (m, 1 H), 5.07 (m, 0.5 H), 5.76 (m, 0.5 H), 7.34 (m, 3 H), 7.55 (m, 2 H), 7.71 (m, 2 H), 7.82 (m, 2 H). IR (KBr): 3060, 2940, 2250, 1770, 1700, 1390, 1350, 1110, 1090, 710 cm^{-1}. The natural-abundance compound 4-phenyl-4-phthalimidobutyronitrile was prepared from 3-penyl-3-phthalimido-1-propyl (4-methylphenyl)sulfonate in the same manner. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.40 (m, 2 H), 2.74 (m, 1 H), 2.96 (m, 1 H), 5.42 (m, 1 H), 7.34 (m, 3 H), 7.54 (m, 2 H), 7.70 (m, 2 H), 7.82 (m, 2 H). IR (KBr): 3070, 2940, 2250, 1770, 1700, 1390, 1360, 1110, 1090, 710 cm^{-1}.

4-Amino-4-phenyl[4-^{13}C]butyronitrile. In a 1-L Erlenmeyer flask were placed 21.44 g (73.9 mmol) of 4-phenyl-4-phthalimido[4-^{13}C]butyronitrile, 625 mL of 95% ethanol, and 7.98 g of hydrazine hydrate (160 mmol of hydrazine). The mixture was heated at 60 °C for 2 h with stirring, and then 350 mL of aqueous 1 N HCl was added. Heating at 60 °C with stirring was continued for an additional 2 h. The mixture was then cooled to 0 °C and filtered. The filtrate was transferred to a 2-L round-bottom flask and placed on a rotary evaporator to remove the ethanol. Solid NaOH was then added to the aqueous mixture, which remained until the pH was greater than 10. The temperature of the mixture was kept below 40 °C during this addition by means of an ice bath. The mixture was then extracted with 4 × 125 mL of $CHCl_3$, and the combined extracts were dried over $MgSO_4$. The $CHCl_3$ was subsequently removed, and the liquid that remained was dissolved in 1.0 L of anhydrous ether. Dry HCl was bubbled through this solution until no further solid was observed to precipitate. The mixture was then filtered and the solid thus obtained dried in vacuo to yield 13.61 g (94%) of 4-amino-phenyl[4-^{13}C]butyronitrile hydrochloride; mp 178–184 °C. The hydrochloride salt was then converted to the base by placing 13.46 g (68.5 mmol) of the HCl salt in a 125-mL separatory funnel and adding 50 mL of aqueous 15% (w/w) of NaOH. The free amine separated as the top layer and was extracted into 7 × 15 mL of $CHCl_3$. To the combined $CHCl_3$ extracts was added 100 mL of benzene. This solution was dried over $MgSO_4$, the solvent was subsequently removed, and the liquid product that remained was left on a vacuum line (0.5 mmHg) overnight before use in the next step. The final yield of 4-amino-4-phenyl[4-^{13}C]butyronitrile as a clear yellow liquid was 10.93 g (94% based on 4-phenyl-4-phthalimido[4-^{13}C]butyronitrile). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.49 (br s, 2 H, exchanged with D_2O), 1.98 (m, 2 H), 2.34 (m, 2 H), 3.68 (t, 0.5 H), 4.36 (t, 0.5 H), 7.31 (m, 5 H). IR (neat): 3380, 3310, 3030, 2930, 2250, 1600, 1460, 890, 770, 710 cm^{-1}. The natural-abundance compound 4-amino-4-phenylbutyronitrile was prepared from 4-phenyl-4-phthalimidobutyronitrile in the same manner. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.50 (br s, 2 H, exchanged with D_2O), 1.98 (m, 2 H), 2.34 (m, 2 H), 4.03 (t, 1 H), 7.32 (m, 5 H). IR (neat): 3380, 3320, 3030, 2930, 2250, 1600, 1460, 890, 770, 710 cm^{-1}.

***N,N′*-Bis(1-phenyl[1-^{13}C]-3-cyanopropyl)sulfonamide.** A 250-mL three-neck round-bottom flask was fitted with a 25-mL addition funnel, a N_2 inlet, and a N_2 outlet. A solution of 10.79 g (67.4 mmol) of 4-amino-4-phenyl[4-^{13}C]butyronitrile and 6.82 g (67.4 mmol) of dry triethylamine in 38 mL of dry, ethanol-free $CHCl_3$ was placed in the flask. The solution was cooled to −30 °C by means of a dry ice–isopropyl alcohol bath, and a solution of 4.55 g (33.7 mmol) of freshly distilled sulfuryl chloride in 14 mL of dry, ethanol-free $CHCl_3$ was added dropwise over 45 min. During this addition a fast N_2 flush was maintained and the solution magnetically stirred as vigorously as possible using an egg-shaped stir bar. After the addition was complete, the reaction mixture was stirred for an additional 1 h at −30 °C and then stirred at room temperature overnight. At this point the reaction mixture was transferred to a separatory funnel with the aid of 30 mL of additional $CHCl_3$, and washed with 2 × 20 mL of H_2O. After the mixture was dried over $MgSO_4$, the $CHCl_3$ solution was concentrated to a volume of 20 mL and the sulfonamide was isolated by column chromatography on a 5 × 18 cm column of Kieselgel 60 (230–400 mesh) silica gel with elution by 9:1 ether/hexane. Thus obtained was 7.28 g (56%) of *N,N′*-bis(1-phenyl[1-^{13}C]-3-cyanopropyl)sulfonamide as a white solid; mp 130–132 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.05 (m, 8 H), 3.92 (m, 1 H), 4.61 (m, 1 H), 4.94 (m, 2 H, exchanged with D_2O), 7.19 (m, 10 H). IR (KBr): 3250, 2250, 1450, 1330, 1160, 1070, 1010, 950, 770, 710

(15) Straley, J. M.; Adams, A. C. In *Organic Syntheses*; Rabjohn, N., Ed.; Wiley: New York, 1963; Collect. Vol. IV, p 415.
(16) Secor, H. V.; Sanders, E. B. *J. Org. Chem.* **1978**, *43*, 2539.

Table I. Polymerization Data for ^{13}C-Enriched SAN Copolymers Derived from **1b**[a]

copolymer	styrene, mmol	acrylonitrile, mmol	styrene–acrylonitrile ([S]/[A])	polymer, mg	conversn, %	time,[b] min	$M_p \times 10^{-3}$ [c]	[**3b**]/[**4b**]
1	15.84	7.821	2.02	152	7.4	148	29	0.391
2	17.30	5.090	3.40	236	11.4	215	26	0.763
3	17.55	4.387	4.00	137	6.6	186	29	0.855
4	17.95	3.707	4.84	162	7.8	186	24	1.04
5	18.24	3.215	5.67	167	8.1	203	22	1.20
6	18.40	2.863	6.43	165	8.0	203	19	1.34
7	18.55	2.557	7.26	164	7.9	216	19	1.45
8	18.69	2.341	7.98	151	7.3	216	19	1.69
9[d]	6.37	7.71	0.83	111	10.3	146		

[a] Conditions: 80 mg of **1b**; 5.0 g of benzene; 33 °C. [b] Time of irradiation with 350-nm light. [c] Molecular weights are reported as polystyrene molecular weights of elution volume equal to that of the peak in the observed GPC elution profile. [d] Copolymer 9 was prepared with 40 mg of **1b**; 2.6 g of benzene.

Table II. Polymerization Data for ^{13}C-Enriched SAN Copolymers Derived from **1c**[a]

copolymer	styrene, mmol	acrylonitrile, mmol	styrene–acrylonitrile ([S]/[A])	polymer, mg	conversn, %	time,[b] min	$M_p \times 10^{-3}$ [c]	[**3c**]/[**4c**]
10	7.805	2.835	2.75	72	7.5	190	29	1.40
11	7.561	3.141	2.41	79	8.3	190	26	1.32
12	7.464	3.492	2.14	7.8	8.1	180	29	1.08
13	7.391	3.952	1.87	86	8.8	180	36	0.870
14	6.954	4.269	1.63	89	9.4	180	29	0.813
15	6.646	4.800	1.38	82	8.7	162	32	0.661
16	6.610	5.818	1.14	90	9.0	144	44	0.576
17	5.836	6.694	0.872	91	9.4	137	44	0.444
18[d]	6.431	5.735	1.12	98	10.1	165		

[a] Conditions: 25 mg of **1c**; 2.62 g of benzene; 33 °C. [b] Time of irradiation with 350-nm light. [c] Molecular weights are reported as polystyrene molecular weights of elution volume equal to that of the peak in the observed GPC elution profile. [d] Copolymer 18 was used only for NOE measurements.

cm^{-1}. The natural-abundance compound *N,N'*-bis(1-phenyl-3-cyanopropyl)sulfonamide was prepared from 4-amino-4-phenylbutyronitrile in the same manner. ^1H NMR (200 MHz, $CDCl_3$): δ 1.82 (m, 4 H), 2.13 (m, 4 H), 4.24 (m, 2 H), 5.20 (br, 2 H, exchanged with D_2O), 7.19 (m, 10 H). IR (KBr): 3250, 2260, 1450, 1340, 1160, 1100, 1080, 950, 770, 710 cm^{-1}.

4,4'-Azobis(4-phenyl[4-^{13}C]butyronitrile) (1c). A mixture of 0.88 g (2.30 mmol) of finely ground *N,N'*-bis(1-phenyl[1-^{13}C]-3-cyanopropyl)sulfonamide, 0.18 g (4.50 mmol) of NaOH, 7.0 mL of Clorox (4.94 mmol of NaOCl), and 7.0 mL of H_2O was stirred for 72 h in an open 30-mL beaker. At the end of this time, the precipitated crude azo compound was filtered from the mixture and recrystallized twice from methanol (55–20 °C). The yield of 4,4'-azobis(4-phenyl[4-^{13}C]butyronitrile) as white needles was 0.110 g (15%); mp 124–125 °C. Anal. Calcd for $^{13}C_2C_{18}H_{20}N_4$: C, 76.07; H, 6.33; N, 17.60. Found: C, 75.81; H, 6.32; N, 17.57. ^1H NMR (200 MHz, $CDCl_3$): δ 2.08 (m, 4 H), 2.34 (m, 4 H), 4.26 (t, 1 H), 4.95 (t, 1 H), 7.40 (m, 10 H). IR (KBr): 3030, 2940, 2900, 2260, 1500, 1450, 1430, 1310, 1040, 770, 710 cm^{-1}. ^{13}C NMR (75 MHz, acetone-d_6): δ 81.14. UV (0.027 M benzene solution): ϵ_{max}(363 nm) = 43 M^{-1} cm^{-1}. The natural-abundance compound 4,4'-azobis(4-phenylbutyronitrile) was prepared from *N,N'*-bis(1-phenyl-3-cyanopropyl)sulfonamide in the same manner. ^1H NMR (200 MHz, $CDCl_3$): δ 2.08 (m, 4 H), 2.35 (m, 4 H), 4.61 (t, 2 H), 7.39 (m, 10 H). IR (KBr): 3040, 2950, 2910, 2260, 1500, 1450, 1430, 1310, 1050, 770, 710 cm^{-1}. ^{13}C NMR (75 MHz, acetone-d_6): δ 14.19, 31.13, 81.13, 119.74, 128.61, 128.88, 129.68, 139.73. UV (0.026 M benzene solution): ϵ_{max}(363 nm) = 43 M^{-1} cm^{-1}.

Polymerizations. Polystyrene (PS). Polystyrene samples derived from 1,1'-azobis(1,3-[1-^{13}C]diphenylpropane) (**1b**) and natural abundance **1b** were prepared using the following procedure: To 0.9 g of styrene in a glass tube were added 3.2 g of benzene and 40 mg of the azo compound. The tube was capped with a septum and the solution deoxygenated with N_2. The tube was then placed in a Rayonet Model RMR 400 photochemical reactor (350-nm lamps) for 6 h at 33 °C. After irradiation the solution was added dropwise to 150 mL of rapidly stirred methanol to precipitate about 70 mg (8%) of polymer, which was filtered, redissolved in $CHCl_3$, reprecipitated into methanol, and filtered before drying to constant weight under vacuum.

PS samples derived from 4,4'-azobis(4-phenyl[4-^{13}C]butyronitrile) (**1c**) and natural abundance **1c** were similarly prepared except for the use of 2.6 g of benzene, 25 mg of the azo compound, and an irradiation time of 12 h.

Poly(acrylonitrile) (PAN). Poly(acrylonitrile) samples derived from 1,1'-azobis(1,3-[1-^{13}C]diphenylpropane) (**1b**) and natural abundance **1b** were prepared using the following procedure: To 1.0 g of acrylonitrile in a glass tube were added 2.6 g of benzene and 14.5 mg of the azo compound. The tube was capped with a septum and the solution deoxygenated with N_2. The tube was then placed in a Rayonet Model RMR 400 photochemical reactor (350-nm lamps) for 3 h at 33 °C. Because PAN precipitated from benzene, it was necessary to dissolve the polymer in about 25 mL of dimethyl sulfoxide before precipitation into 500 mL of rapidly stirred methanol. After the solution was filtered and the polymer was allowed to dry in the air for 2 h, the polymer was redissolved in about 10 mL of *N,N*-dimethylformamide and reprecipitated into 500 mL of methanol before drying to constant weight under vacuum. Approximately 300 mg (30%) of PAN was thus obtained.

PAN samples derived from 4,4'-azobis(4-phenyl[4-^{13}C]butyronitrile) (**1c**) and natural abundance **1c** were similarly prepared except for the use of 0.7 g of acrylonitrile, 15 mg of **1c**, and an irradiation time of 4 h.

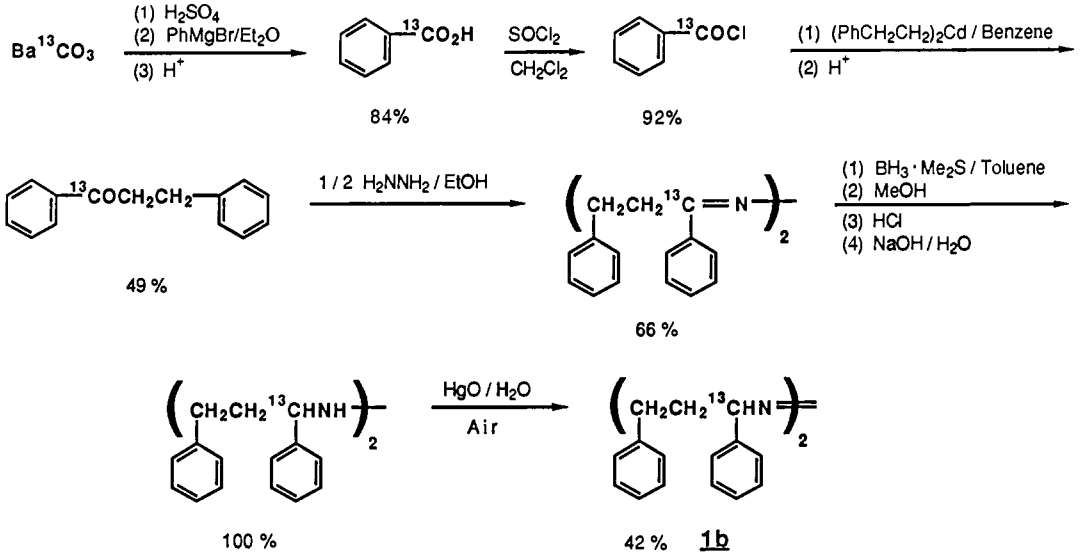
Copolymers. Styrene–acrylonitrile (SAN) copolymers derived from 1,1'-azobis(1,3-[1-^{13}C]diphenylpropane) (**1b**) and natural abundance **1b** were prepared as follows: To 80 mg of **1b** dissolved in 5.0 g of benzene in a septum-capped, N_2-flushed glass tube was added by syringe a total of 2.1 g (21–24 mmol) of N_2-sparged monomer (styrene and acrylonitrile). The tube was then placed in a Rayonet Model RMR 400 photochemical reactor (350-nm lamps) for 140–220 min at 33 °C.

After irradiation the solution was added dropwise to 350 mL of rapidly stirred methanol to precipitate about 170 mg (8%) of polymer, which was filtered, redissolved in $CHCl_3$, reprecipitated into methanol, and filtered before drying to constant weight under vacuum. Polymerization data for nine enriched copolymers derived from **1b** are listed in Table I; eight of these, numbered 1–8 in Table I, were used in the **3b**/**4b** end-group analysis. For each of these eight copolymers, there was prepared an unenriched copolymer at the same monomer feed ratio. The copolymers containing ^{13}C in naturally abundant amounts were prepared exactly as above, except for the use of unenriched **1b**.

SAN copolymers derived from 4,4'-azobis[4-^{13}C]butyronitrile (**1c**) and natural abundance **1c** were similarly prepared except for the use of 25 mg of **1c**, 2.6 g of benzene, 0.96 g of total monomer, and 200 mL of methanol as precipitant. Polymerization data for nine enriched copolymers derived from **1c** are listed in Table II; eight of these, numbered 10–17 in Table II, were used in the **3c**/**4c** end-group analysis. Again, a natural-abundance copolymer was prepared for every enriched polymer at identical monomer feed compositions.

Measurements. All ^{13}C NMR spectra were obtained on a Varian XL-300 NMR spectrometer using 2% (w/w) solutions of the polymers. For homopolymer spectra a standard single-pulse sequence, broad-band ^1H decoupling, an 80° pulse width, a 1.9-s delay between pulses, and an acquisition time of 0.90 s were used. For copolymer spectra a standard single-pulse sequence, broad-band ^1H decoupling, a 90° pulse width, an

Scheme II



acquisition time of 0.90 s, and a pulse delay equal to 5 times the longest possible end-group spin–lattice relaxation time (T_1) were used.

Inversion–recovery experiments were performed on ^{13}C-enriched copolymers to determine T_1 values of the end groups. For end groups **3b** and **4b**, measurements using copolymer 2 (see Table I) in deuterated diglyme at 140 °C gave T_1 values ranging from 1.23 to 1.76 s. A pulse delay of 8.80 s (=5 × longest T_1) was thus used for spectra of copolymers derived from **1b** to ensure complete relaxation of the nuclei. For end groups **3c** and **4c**, measurements using copolymer 14 (see Table II) in deuterated bromobenzene at 136 °C gave T_1 values ranging from 0.87 to 1.63 s. A pulse delay of 8.16 s (=5 × longest T_1) was thus used for spectra of copolymers derived from **1c**.

The end-group peak area ratios (**3b**/**4b** and **3c**/**4c**) of the copolymers were found to be negligibly different whether the spectra were recorded with the nuclear Overhauser effect (using broad-band decoupling) or with suppression of the NOE (using a gated decoupling sequence). Measurements using copolymer 2 in deuterated diglyme at 140 °C showed only a 1.2% difference in **3b**/**4b** for spectra recorded with and without the NOE. Similarly, measurements using copolymer 18 in deuterated bromobenzene at 136 °C showed only a 0.2% difference in **3c**/**4c** for spectra recorded with and without the NOE. Spectra shown were recorded without NOE suppression.

The end-group signals of enriched SAN copolymers were assigned by comparison of copolymer spectra with homopolymer spectra and from variations in signal intensity with changes in monomer feed composition. Peak areas were apportioned between end groups in each spectrum by drawing vertical lines from the local spectral minima occurring between signals of differing assignment to the base line of the normalized spectrum of the corresponding natural-abundance copolymer. Peak areas were determined by a cut-and-weight method.

Chemical shifts recorded for $CDCl_3$ solutions were measured with reference to the center peak of the $CDCl_3$ triplet that occurs at 77.00 ppm. [All solvent shifts quoted here are relative to tetramethylsilane (TMS)]. Spectra obtained for dimethyl-d_6 sulfoxide (DMSO-d_6) solutions were referenced using the center line of the DMSO-d_6 multiplet at 39.50 ppm; those obtained from *N*,*N*-dimethylformamide-d_7 (DMF-d_7) solutions were referenced using the center line of the DMF-d_7 multiplet at 35.20 ppm. For polymer solutions prepared with "deuterated diglyme", a 3:2 mixture of diglyme and diglyme-d_{14} was used. Spectra recorded at 140 °C for these solutions were referenced using a natural-abundance diglyme signal that occurs at 70.88 ppm relative to TMS at room temperature. Solutions of polymer in "deuterated bromobenzene" were prepared with a 3:2 mixture of bromobenzene and bromobenzene-d_5. Spectra recorded at 136 °C for these solutions were referenced using a bromobenzene-d_5 signal that occurs at 130.89 ppm relative to TMS at room temperature.

Results and Discussion

Preparation of Azoalkanes. 1,1′-Azobis(1,3-[1-^{13}C]diphenylpropane) (**1b**) was prepared in 10% overall yield starting from $Ba^{13}CO_3$ (99 atom %), as outlined in Scheme II. Natural abundance **1b** was prepared by the same route starting from benzoyl chloride. This is believed to be the first report of this azo compound. The synthesis of **1b** as described in the Experimental Section calls for two recrystallizations of the crude product from methanol–benzene and gives a purified product that is a mixture of the *dl* and meso forms.[17] The proton-decoupled 75-MHz ^{13}C NMR spectrum of enriched **1b** consists of two nearly equally intense signals at 81.66 and 81.74 ppm—the same chemical shifts as are observed for the methine carbons of natural abundance **1b**.

4,4′-Azobis(4-phenyl[4-^{13}C]butyronitrile) (**1c**) was prepared in 1.2% overall yield starting from $Ba^{13}CO_3$ (99 atom %) as outlined in Scheme III. Natural abundance **1c** was prepared in the same manner starting from ethyl 3-phenyl-3-ketopropionate (ethyl benzoylacetate). This is believed to be the first report of this azo compound. The synthesis of **1c** as described in the Experimental Section calls for two recrystallizations of the crude product from methanol and gives a purified product that is either the pure meso or pure *dl* form.[18] The proton-decoupled 75-MHz ^{13}C NMR spectrum of ^{13}C-enriched **1c** consists of an intense signal at 81.13 ppm—the same chemical shift as is observed for the methine carbon of natural abundance **1c**.

Rate Constant Ratio Determinations. The relative rates of addition of styrene and acrylonitrile (k_S/k_A) to the 1-(1,3-diphenyl[1-^{13}C]propyl) (**2b**) and 1-(3-cyano-1-phenyl[1-^{13}C]propyl) (**2c**) radicals were determined by the method shown in Scheme

(17) This conclusion is based on the following observations made for samples of natural abundance **1b**: First, a sample purified by two recrystallizations melted over a broad temperature range (78–100 °C), while a sample recrystallized six times melted sharply at 109 °C. Identical elemental analyses, IR spectra, and UV spectra were obtained for these two samples, and all are consistent with the expected structure. Second, a proton-decoupled 75-MHz ^{13}C NMR spectrum of the lower melting sample consists of twice as many signals as that of the higher melting compound; within 0.5 ppm of every signal that appears in the spectrum of the higher melting sample there occurs an additional signal in the spectrum of the lower melting sample. Finally, samples of crude azo compound recrystallized between two and six times have melting and spectral characteristics intermediate between those described above. Thus, both samples are chemically pure, but the lower melting compound is a *dl*/meso mixture and the higher melting is either pure meso or pure *dl*. The sample of ^{13}C-enriched **1b** used to prepare SAN copolymers was purified by just two recrystallizations and was thus a *dl*/meso mixture.

(18) This conclusion is based on the following observations made for samples of ^{13}C-enriched **1c**: First, a sample that was purified by only one recrystallization melted over a broad temperature range (68–80 °C) compared to a sample purified by two recrystallizations (mp 124–125 °C). Although the lower melting material contains an impurity of unknown composition, identical IR and UV spectra are obtained for the two samples, and the elemental analysis of the higher melting material is consistent with the formula of **1c**. Second, a proton-decoupled 75-MHz ^{13}C NMR spectrum of the higher melting sample has a single intense signal in the region expected for the methine carbon, while in this region the spectrum of the lower melting sample has two intense signals separated by 0.40 ppm. Finally, two overlapping triplets are observed for each signal from the methine protons in a 200-MHz ^1H NMR spectrum of the lower melting sample, while a single triplet appears for each in the spectrum of the higher melting compound. The higher melting sample of ^{13}C-enriched **1c** was used to prepare SAN copolymers.

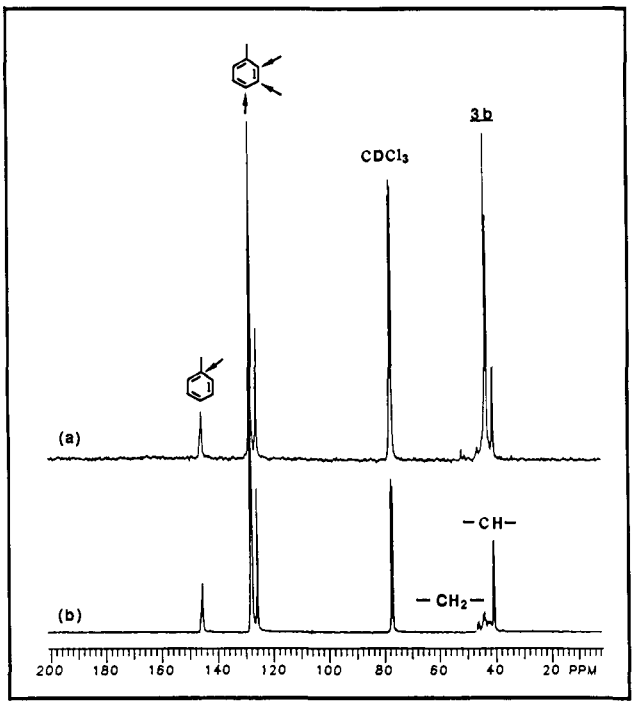


Figure 1. 75-MHz ^{13}C NMR spectra of (a) enriched and (b) natural-abundance polystyrene derived from **1b** in $CDCl_3$ at 20 °C.

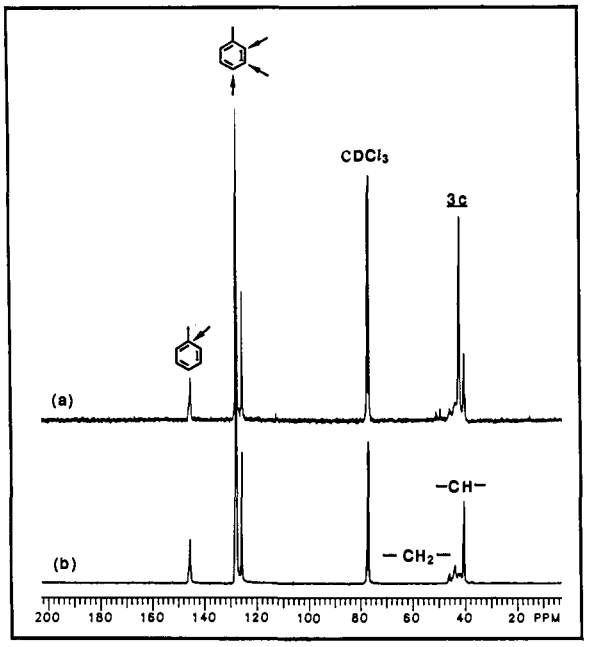


Figure 2. 75-MHz ^{13}C NMR spectra of (a) enriched and (b) natural-abundance polystyrene derived from **1c** in $CDCl_3$ at 20 °C.

I. (The results and abbreviations for the ^{13}C-enriched radicals will be generalized to include the natural-abundance radicals, although k_S/k_A determinations were made only for the enriched radicals.) The radicals were generated by photolysis of 1,1′-azobis(1,3-diphenyl[1-^{13}C]propane) (**1b**) and 4,4′-azobis(4-phenyl[4-^{13}C]butyronitrile) (**1c**) in the presence of known amounts of styrene and acrylonitrile, and styrene–acrylonitrile (SAN) copolymers containing ^{13}C-enriched end groups **3** and **4** were produced. These experiments were performed at 33 °C in benzene solution under steady-state irradiation, and all copolymers remained soluble throughout the reaction. To minimize drift in monomer feed composition, monomer conversions were limited to 7–11% (Tables I and II). The molecular weights of the enriched copolymers were estimated by comparison of their gel permeation chromatograms with those of polystyrene samples of known molecular weights and narrow molecular weight distributions

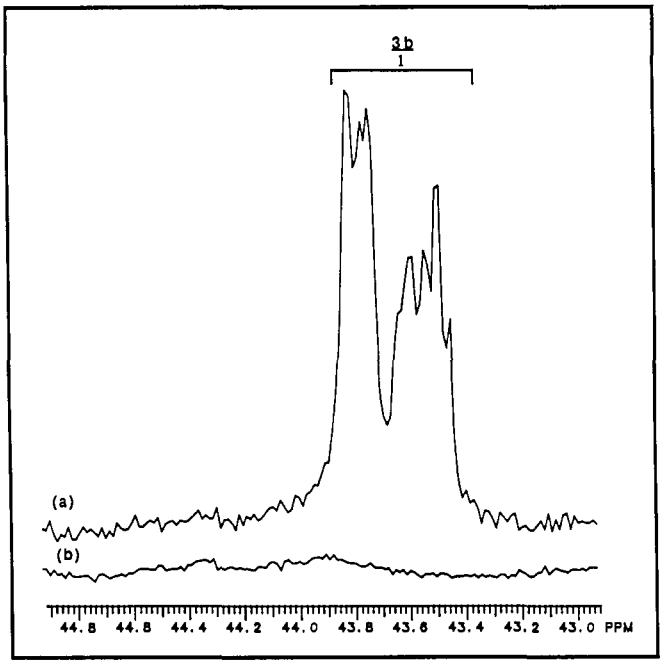


Figure 3. 75-MHz ^{13}C NMR spectra (expanded plots) of (a) enriched and (b) natural-abundance polystyrene derived from **1b** in deuterated diglyme at 140 °C.

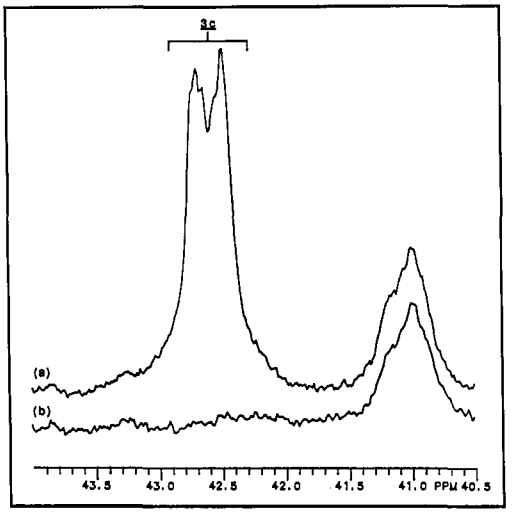


Figure 4. 75-MHz ^{13}C NMR spectra (expanded plots) of (a) enriched and (b) natural-abundance polystyrene derived from **1c** in deuterated bromobenzene at 136 °C.

($M_w/M_n < 1.1$); the results are listed in Tables I and II.

Presented in Figure 1 are ^{13}C NMR spectra of polystyrenes prepared by using enriched and natural abundance **1b**. Two new signals appear at 36.78 and 37.39 ppm in the spectrum of the enriched polymer and are assigned to the two alternative stereochemical configurations of end group **3b**. Similarly, Figure 2 shows polystyrenes derived from **1c**. Two new, partially resolved signals appear at 42.17 and 42.48 ppm and are assigned to **3c**. In each case, the chemical shifts of the signals assigned to end groups **3** are within 2 ppm of those calculated using additive shift parameters.[19,20] The integrated areas of the two signals observed

(19) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; Wiley: New York, 1981; p 258.

(20) The spectra of ^{13}C-enriched copolymers shown in Figures 1 and 2 also contain new signals in the region of 48–50 ppm. In each case the total integrated area of these signals is less than 7% of that of the corresponding end-group signals assigned above. The origin of these signals is unknown, but they almost certainly arise from ^{13}C-enriched initiator fragments incorporated into the polymer. Spectra taken after several reprecipitations of the polystyrenes showed that the relative intensities of the signals did not change, so it is unlikely that these signals arise from occluded low molecular weight impurities.

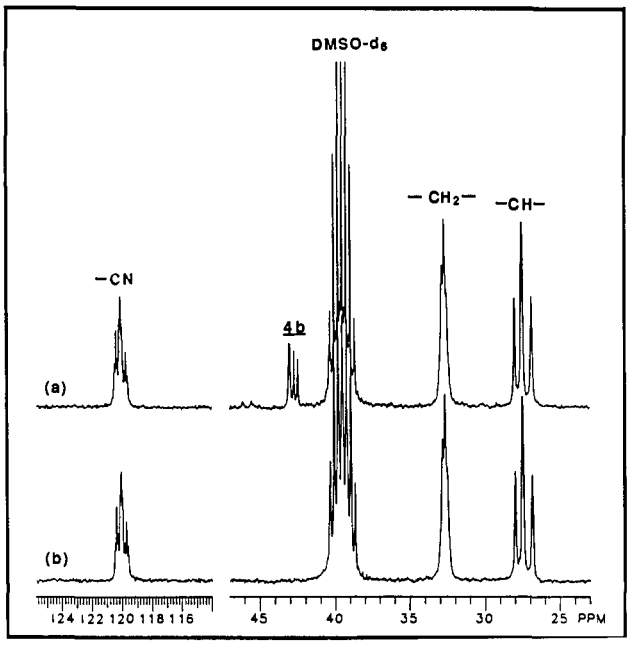


Figure 5. 75-MHz ^{13}C NMR spectra of (a) enriched and (b) natural-abundance poly(acrylonitrile) derived from **1b** in DMSO-d_6 at 20 °C. Spectral regions not shown contain no sample signals.

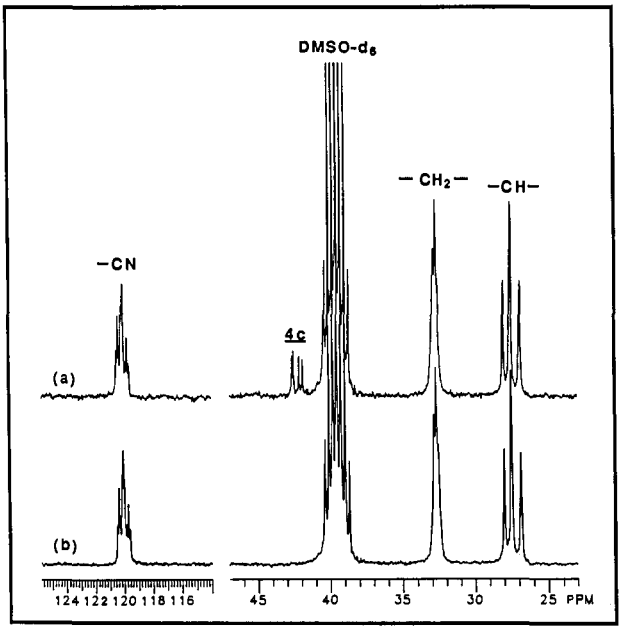


Figure 6. 75-MHz ^{13}C NMR spectra of (a) enriched and (b) natural-abundance poly(acrylonitrile) derived from **1c** in DMSO-d_6 at 20 °C. Spectral regions not shown contain no sample signals.

for each of the end groups **3** are equal, indicating that the stereochemistry in each case is the result of random placement of styrene monomer.

Expanded plots of polystyrene (PS) spectra in the regions of the end-group signals are presented in Figures 3 and 4. Note that these spectra are not expansions of the spectra in Figures 1 and 2, which were recorded at 20 °C using $CDCl_3$ solutions. The spectra in Figures 3 and 4 were recorded using different solvents and temperatures to facilitate comparison to SAN copolymer spectra (vide infra). Spectra of polystyrenes derived from **1b** (Figure 3) were obtained at 140 °C using deuterated diglyme solutions, and the signals assigned to **3b** occur under these conditions at 43.54 and 43.77 ppm. Considerable fine structure is evident. For polystyrenes derived from **1c** (Figure 4), spectra were obtained using deuterated bromobenzene solutions at 136 °C. Under these conditions the two signals assigned to **3c**, which were partially resolved in $CDCl_3$ solution, overlap to such an extent

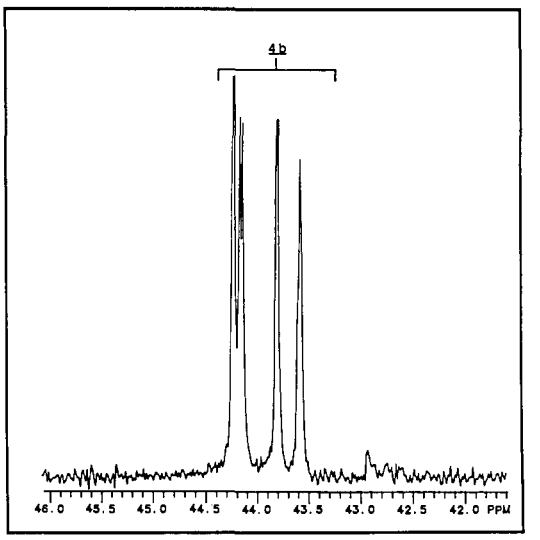


Figure 7. 75-MHz ^{13}C NMR spectrum (expanded plot) of enriched poly(acrylonitrile) derived from **1b** in DMF-d_7 at 20 °C.

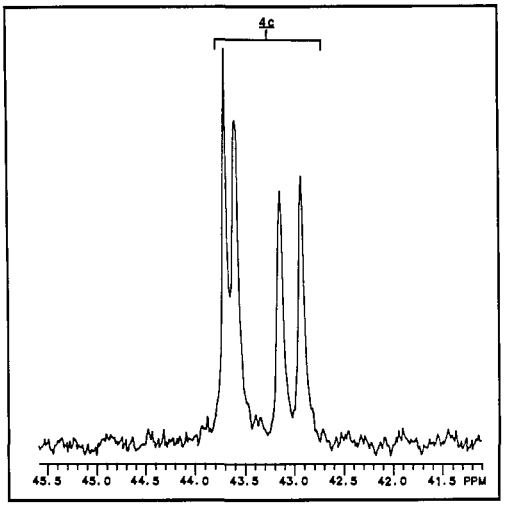


Figure 8. 75-MHz ^{13}C NMR spectrum (expanded plot) of enriched poly(acrylonitrile) derived from **1c** in DMF-d_7 at 20 °C.

that essentially one signal centered at 42.58 ppm is observed.

^{13}C NMR spectra of poly(acrylonitrile) (PAN) samples prepared by using enriched and natural abundance **1b** and **1c** are shown in Figures 5 and 6. In each case new signals arise in the spectrum of the enriched polymer and are assigned to **4b** (Figure 5) or **4e** (Figure 6). The natural-abundance signals were assigned according to Pichot and Pham.[21] The spectral region obscured by dimethyl-d_6 sulfoxide was observed for each PAN sample in *N,N*-dimethylformamide-d_7 and shown to be free of signals. Expanded plots of spectra obtained using DMF-d_7 solutions are presented in Figures 7 and 8. Four distinct signals appear in each spectrum: at 43.56, 43.78, 44.13, and 44.21 ppm for **4b** and at 42.94, 43.16, 43.60, and 43.72 ppm for **4c**. The chemical shifts of the end-group signals all occur within 2 ppm of their calculated positions.[19] The integrated intensities of the lines are again consistent with random stereochemical placement of monomer near the chain end.

Spectra of SAN copolymers recorded under conditions necessary to resolve the end-group signals, and expanded in the regions of interest, are presented in Figures 9 and 10. Each figure includes spectra of copolymers prepared with ^{13}C-enriched initiator **1b** or **1c** at two different monomer feed compositions. Natural-abundance copolymers were prepared to ensure correct base-line assignment in the spectral regions corresponding to end groups **3** and **4**. In each case, the natural-abundance copolymer spectrum

(21) Pichot, C.; Pham, Q. T. *Makromol. Chem.* **1979**, *180*, 2539.

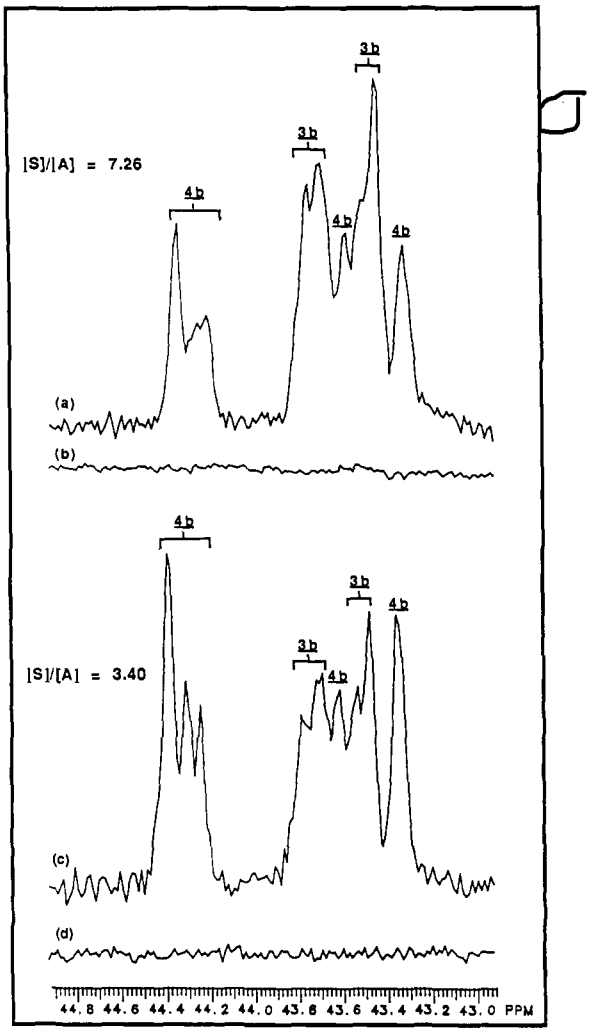


Figure 9. 75-MHz ^{13}C NMR spectra (expanded plots) of enriched (a and c) and natural-abundance (b and d) SAN copolymers derived from **1b** in deuterated diglyme at 140 °C. The copolymers were prepared with monomer feed ratios ([S]/[A]) of 7.26 (top) and 3.40 (bottom).

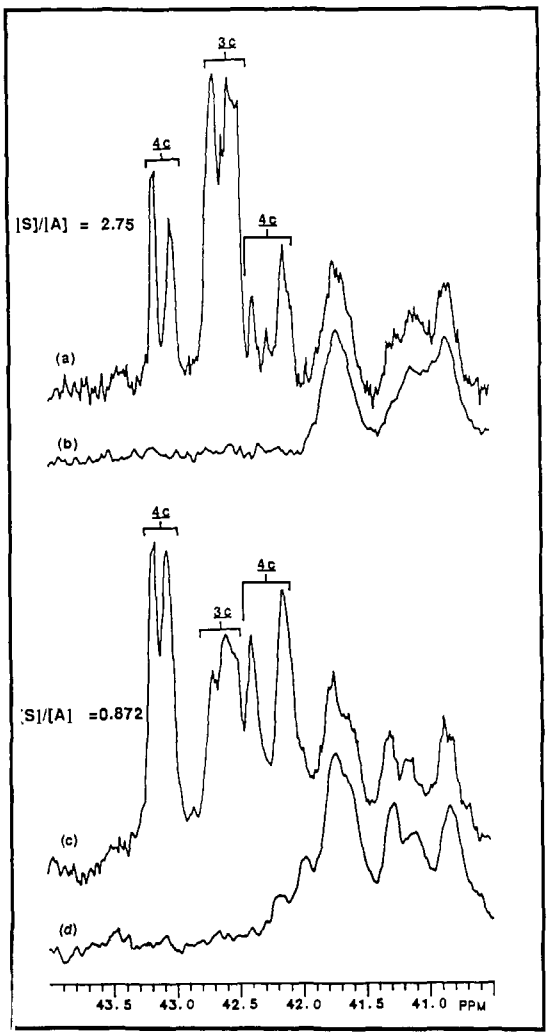


Figure 10. 75-MHz ^{13}C NMR spectra (expanded plots) of enriched (a and c) and natural-abundance (b and d) SAN copolymers derived from **1c** in deuterated bromobenzene at 136 °C. The copolymers were prepared with monomer feed ratios ([S]/[A]) of 2.75 (top) and 0.872 (bottom).

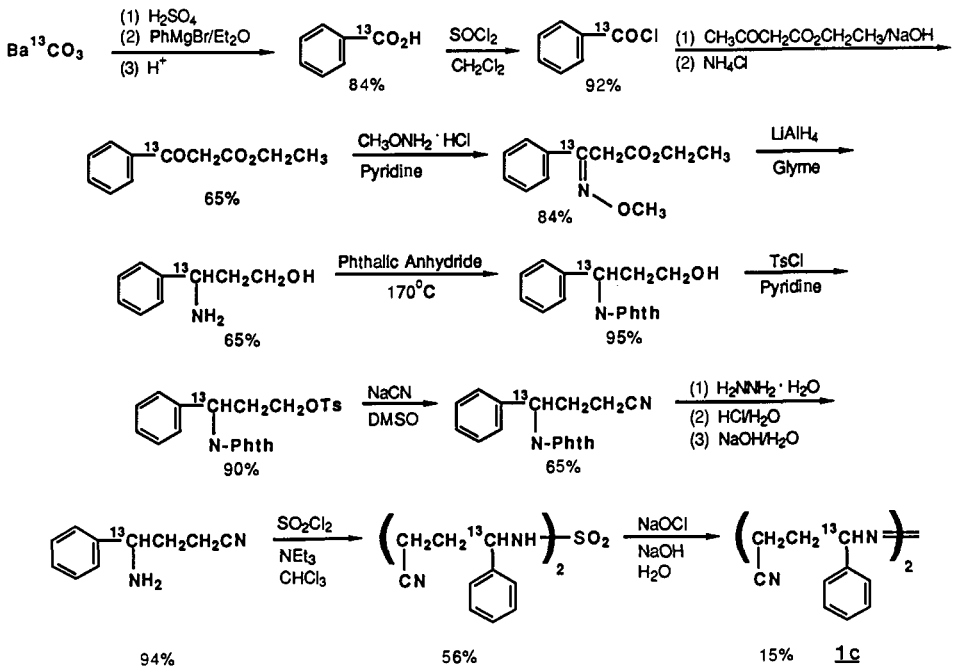
is normalized with respect to that of the enriched sample on the basis of neighboring (natural-abundance) signal intensities. These spectra were recorded under conditions suitable for quantitative signal integration, using pulse delays of at least 5 times the longest end group T_1. The spectra were recorded without NOE suppression after it was determined that the **3**/**4** peak area ratios were unaffected by the NOE.

The end-group signals were assigned by comparison of copolymer spectra with spectra of PS and PAN samples, and from variations in signal intensity with changes in monomer feed composition. The signals assigned to end group **3b** appear at 43.54 and 43.77 ppm (Figure 9) and that from **3c** appears at 42.58 ppm (Figure 10). These chemical shifts are identical with those from PS spectra recorded under the same conditions (cf. Figures 3 and 4), although the fine structures of the signals differ. Signals assigned to end group **4b** appear at 43.34, 43.60, and 44.30 ppm in Figure 9, and those from **4c** appear at 42.13, 42.38, and 43.10 ppm (Figure 10). The position and fine structure of the end-group signals are different from (although similar to) those observed for PAN samples in DMF-d_7 (cf. Figures 7 and 8) as a result of the use of different solvents and temperatures to obtain PAN and copolymer spectra. Confirmation of these assignments was facilitated by preparation of a copolymer rich enough in acrylonitrile that signals from **3b** are negligible compared to those of **4b**. This copolymer is soluble in diglyme at 140 °C (unlike PAN), and the fine structure of the end-group spectrum (Figure 11) is consistent with the assignments shown in Figure 9.

Eight enriched copolymers were prepared from each of the initiators **1b** and **1c**. The results of these experiments are summarized in Tables I and II. Figure 12 presents plots of relative end-group concentrations (i.e., **3**/**4** peak area ratios) as a function of monomer feed composition ([S]/[A]). Each plot is linear, as expected, and the linear least-squares fit line for each passes very near the origin. The slope of the line obtained in each case is the ratio of the rates of addition of styrene and acrylonitrile (k_S/k_A) to the radical **2b** or **2c**. From Figure 12, $k_S/k_A = 0.21 \pm 0.01$ for the 1-(1,3-diphenylpropyl) radical (**2b**), and $k_S/k_A = 0.52 \pm 0.03$ for the 1-(3-cyano-1-phenylpropyl) radical (**2c**). The quoted error in each case is the standard deviation of the origin-to-point slopes. The relative standard deviation of a **3**/**4** determination was about 3%, as estimated by repeated analyses undertaken for several samples.

The errors given above for k_S/k_A do not take into account drifts in monomer feed composition that may have occurred during the polymerizations. Although the conversions were low (<11%), an attempt was made to estimate errors that may have resulted from compositional drift. For any of the copolymerizations, the final feed composition can be calculated with knowledge of the conversion and the final overall copolymer composition, and an average feed composition can then be obtained. Such average values were calculated for three of the eight copolymerizations performed for each k_S/k_A determination. The initial feed compositions of these copolymerizations were representative of the entire range investigated in each case, and conversions were typical. Copolymer compositions were determined by nitrogen analysis. New three-point plots were drawn using the averaged feed compositions, and the slopes of the best fit lines gave the following: $k_S/k_A =$

Scheme III



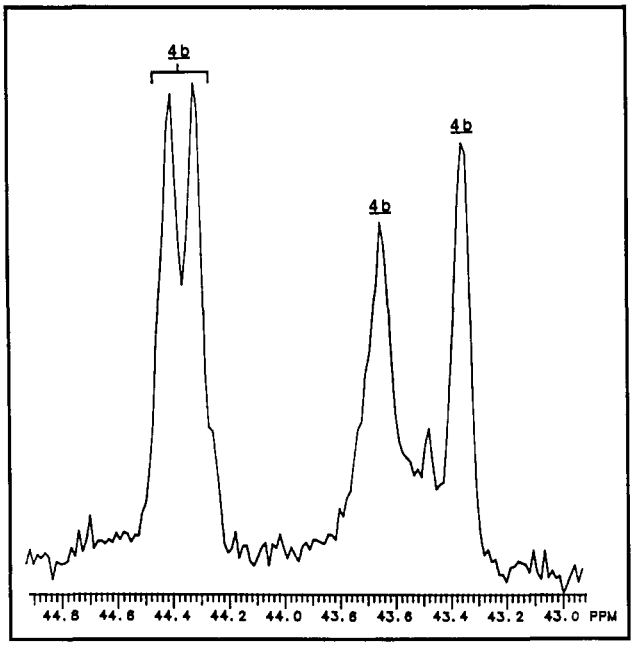


Figure 11. 75-MHz ^{13}C NMR spectrum (expanded plot) of an enriched SAN copolymer derived from **1b** in deuterated diglyme at 140 °C. The copolymer was prepared at a monomer feed ratio ([S]/[A]) of 0.83 (copolymer 9 in Table I).

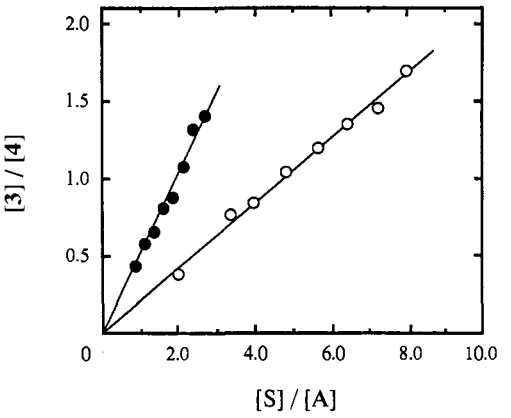


Figure 12. Plots of relative end-group concentration ([3]/[4]) vs monomer feed composition ([S]/[A]): (●) enriched SAN copolymers derived from **1c** (copolymers 10–17 in Table II); (○) enriched SAN copolymers derived from **1b** (copolymers 1–8 in Table I).

0.20 for **2b** and $k_S/k_A = 0.49$ for **2c**. Each value is slightly lower than that cited above but still within the quoted error range. It is evident that conversion effects are insignificant. It is of interest to note here that the copolymer compositions determined for this analysis are quite close to those of Hill and co-workers[5] for bulk SAN copolymerization; for example, Hill obtained a styrene mole fraction of 0.77 for a copolymer prepared with a feed composition [S]/[A] = 7.98, while a value of 0.78 was obtained in this work for a copolymer prepared at this same feed composition.

The relative end-group concentrations plotted in Figure 12 were measured for each enriched copolymer by integration of the end-group signals after a base line had been assigned using the normalized spectrum of the natural-abundance copolymer prepared at the same feed ratio. This procedure was undertaken to minimize the effects of coincidence of natural-abundance and enriched signals. However, for the copolymers prepared from **1b**, the natural-abundance signals in the region of the end groups are small and quite broad compared to those of the end groups. Accordingly, it was expected for these copolymers that the base-line assignment procedure just mentioned might have been unnecessary. Indeed, identical results were obtained when an alternate method of analysis was employed in which the base lines were assigned in each spectrum by simply drawing a horizontal line at the level of the deepest local minimum that occurred between the end-group signals. On the other hand, for copolymers derived from **1c** at low [S]/[A] ratios (less than about 1.9; see c and d in Figure 10), there is significant overlap of natural-abundance and enriched signals in the region of 42.0–42.5 ppm. This affects the intensities of signals assigned to **4c** in this region (i.e., the **4c** signals upfield of the **3c** multiplet), although the **4c** multiplet that occurs further downfield at 43.10 ppm is relatively unaffected. This multiplet corresponds to the two partially resolved **4c** signals at 43.60 and 43.72 ppm in the spectrum of PAN prepared from **1c** (Figure 8), and in this spectrum the sum of the integrated areas of these signals is equal to the sum of the areas of the other **4c** signals further upfield at 42.94 and 43.16 ppm. Should this relationship hold for the corresponding signals in the copolymers, an alternate method of analysis would be to take the total integrated area for **4c** in the copolymer spectra as twice the area of the downfield

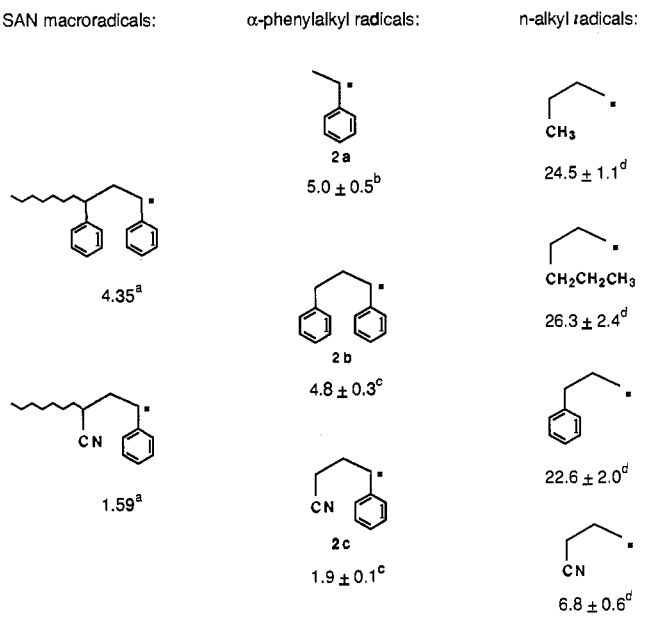


Figure 13. Comparison of k_A/k_S for addition of acrylonitrile and styrene to SAN macroradicals, α-phenylalkyl radicals, and *n*-alkyl radicals. Key: a, from ref 5; b, from ref 8; c, this work; d, from ref 7.

4c multiplet at 43.10 ppm and to disregard the **4c** signals appearing further upfield that are overlapped by natural-abundance signals. This alternate method gave a linear plot of [**3c**]/[**4c**] vs [S]/[A] that passed near to the origin; $k_S/k_A = 0.58 \pm 0.06$ was obtained from the slope. This value for **2c** agrees within experimental error with that obtained by the preceding analysis ($k_S/k_A = 0.52 \pm 0.03$), a result that serves to increase confidence that the interference of natural-abundance signals with the **4c** signals occurring upfield of the **3c** multiplet did not affect significantly the rate constant ratio determination for **2c**.

A final alternate method of analysis concerns the determination of k_S/k_A for **2b**. Inspection of spectra of enriched copolymers derived from **1b** reveals that in each case there is a well-resolved **4b** multiplet at 44.30 ppm, while the other signals occurring upfield and assigned to **4b** and **3b** are not well-resolved (Figure 9). The well-resolved multiplet at 44.30 ppm corresponds to the two partially resolved **4b** signals at 44.13 and 44.21 ppm in the spectrum of PAN prepared from **1b** (Figure 7), and in this spectrum the sum of the integrated areas of these signals is equal to the sum of the areas of the **4b** signals further upfield at 43.56 and 43.78 ppm. Should this relationship hold for the corresponding signals in the copolymers, it would be appropriate to take the total integrated area for **4b** in the copolymer spectra as twice the area of the downfield **4b** multiplet at 43.30 ppm, and thus the area for **3b** would be given by subtracting the area of the **4b** multiplet at 43.30 ppm from the summed integrated areas of the upfield **3b** and **4b** signals at 43.2–44.0 ppm. Application of this alternate method resulted in a plot of [**3b**]/[4b] vs [S]/[A] that was linear and passed near to the origin; $k_S/k_A = 0.21$ was obtained from the slope. This is identical with the result obtained by the analysis described in the Experimental Sections and suggests that failure to achieve base-line resolution of **3b** and **4b** signals in the range of 43.2–44.0 ppm does not preclude reliable determination of k_S/k_A for **2b**.

The results obtained for the addition of styrene and acrylonitrile to the 1-(1-phenylalkyl) radicals **2** can best be interpreted in the context of our previous investigation[8] of olefin addition to *n*-alkyl radicals and in the context of the penultimate model analysis of SAN copolymerization by Hill, O'Donnell, and O'Sullivan.[5] Figure 13 presents k_A/k_S values for comparison. A number of interesting points emerge. First, the 2.5-fold decrease in k_A/k_S for **2c** as compared to the nearly identical values for **2a** and **2b** is most striking and demonstrates clearly the role of the γ-cyano substituent in modulating radical selectivity. Second, this 2.5-fold decrease in k_A/k_S for **2c** is consistent with a similar 3.5-fold decrease observed in previous work for the 3-cyanopropyl radical as compared to 3-phenylpropyl, -hexyl, and -butyl.[8] Third, the decrease in k_A/k_S for **2c** as compared to **2b** agrees very well with the 2.7-fold decrease inferred by Hill for a macroradical with an SS end as compared to an AS end.[5] And finally, the actual magnitudes of k_A/k_S for **2b** and **2c** agree very well with those of the SS- and AS-terminated macroradicals, respectively; in each case, k_A/k_S for the model radical is higher than that for the corersponding macroradical by a factor of about 1.2.

The foregoing observations provide strong evidence for the existence of penultimate effects in SAN copolymerization. Indeed, it would be unusual if SS- and AS-terminated macroradicals did not exhibit the selectivity differences observed for model radicals **2b** and **2c**, which have structures essentially identical with the propagating ends of the macroradicals. The most likely explanation for the reduction in the relative rate of acrylonitrile addition to an alkyl radical bearing a γ-cyano group is the development in the transition state of dipolar repulsion between cyano groups on the monomer and radical. When the results of the separate investigations summarized in Figure 13 are taken together, the evidence is compelling that the penultimate model provides a physically meaningful description of SAN copolymerization.

Conclusions

1,1′-Azobis(1,3-[1-^{13}C]diphenylpropane) (**1b**) and 4,4′-azobis(4-phenyl[4-^{13}C]butyronitrile) (**1c**) serve as convenient sources of the corresponding radicals 1-(1,3-diphenylpropyl) (**2b**) and 1-(3-cyano-1-phenylpropyl) (**2c**). Analysis of end-group concentrations in styrene–acrylonitrile (SA) copolymers prepared with **1b** or **1c** as initiator allows accurate determination of the relative rates of addition of these monomers to **2b** or **2c**. We find $k_S/k_A = 0.21 \pm 0.01$ for **2b** and 0.52 ± 0.03 for **2c**. The 2.5-fold increase in k_S/k_A observed for **2c** as compared to **2b** or to the 1-phenylethyl radical (for which $k_S/k_A = 0.20 \pm 0.02$) indicates that a cyano group in a position γ to an α-phenylalkyl radical decreases the relative rate of acrylonitrile addition. This behavior is similar to that previously observed for primary alkyl radicals of analogous structure. These results are also consistent with the penultimate model treatment of the styrene–acrylonitrile copolymerization by Hill, O'Donnell, and O'Sullivan and offer clear evidence for the existence of a penultimate unit effect for that system.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. Support of our research by a Presidential Young Investigator Award of the National Science Foundation (to D.A.T.) is also gratefully acknowledged. NMR spectra were recorded in the University of Massachusetts NMR Laboratory, which is supported in part by the NSF Materials Research Laboratory at the University. The authors thank Dr. Douglas A. Wicks for advice and assistance.

Registry No. 1b, 122189-13-3; **1c**, 122189-20-2; **2b**, 122212-51-5; **2c**, 122189-21-3; PS, 9003-53-6; PAN, 25014-41-9; (S)(AN) (copolymer), 9003-54-7; $Ph^{13}CO_2H$, 3880-99-7; $Ba^{13}CO_3$, 51956-33-3; PhM_gBr, 100-58-3; $Ph^{13}COCl$, 52947-05-4; $Ph^{13}CO(CH_2)_2Ph$, 122189-10-0; $Br(CH_2)_6Ph$, 103-63-9; $[Ph(CH_2)_2{}^{13}C(Ph)=N]_2$, 122189-11-1; H_2NNH_2, 302-01-2; $[Ph(CH_2)_2{}^{13}CH(Ph)NH]_2$, 122189-12-2; $Ph^{13}CH(N\text{-Phth})(CH_2)_2OH$, 122189-14-4; $Ph^{13}CH(NH_2)(CH_2)_2OH$, 122189-15-5; $Ph^{13}CH(N\text{-Phth})(CH_2)_2OTs$, 122189-16-6; TsCl, 98-59-9; $Ph^{13}CH(N\text{-Phth})CH(CH_2)_2CN$, 122189-17-7; NaCN, 143-33-9; $Ph^{13}CH(NH_2)(CH_2)_2CN$, 122189-18-8; $[CN(CH_2)_2{}^{13}CH(Ph)NH]^2SO_2$, 122189-19-9; SO_2Cl_2, 7791-25-5; $PhCH=CH_2$, 100-42-5; $H_2C=CHCN$, 107-13-1; phthalic anhydride, 85-44-9.