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# Selectivity of the Reaction of Free Radicals with Styrene

**Graeme Moad,* Ezio Rizzardo, and David H. Solomon**

*Division of Applied Organic Chemistry, CSIRO, Melbourne, Australia 3001.*

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ABSTRACT: The reactions of *tert*-butoxy, benzoyloxy, and phenyl radicals with styrene have been determined by examining the products formed when di-*tert*-butyl peroxalate, benzoyl peroxide, or triphenylmethylazobenzene is decomposed in styrene at 60 °C in the presence of an efficient alkyl radical trapping agent (1,1,3,3-tetramethylisoindolinyl-2-oxy). *tert*-Butoxy and benzoyloxy radicals either add to styrene or undergo $\beta$ scission. The latter process gives methyl and phenyl radicals, respectively, which, in turn, may also react with styrene. While *tert*-butoxy radicals give exclusive addition to the less substituted end of the double bond (tail addition), the reaction of benzoyloxy is nonselective, affording products from tail addition, head addition, and aromatic substitution in the ratio of 79:6:14. Phenyl radicals give tail addition and aromatic substitution (99:1). The types of functionality that may be introduced into polystyrene through lack of selectivity in the reactions of initiator-derived radicals with styrene are discussed.

## Introduction

An understanding of the interaction of free radicals with olefins is of importance in polymer chemistry, in organic synthesis, and in other fields. However, only recently have methods become available for studying the selectivity of these reactions. The literature in this area is summarized in reviews by Bevington,[1] Minisci,[2] Rüchardt,[3] and Tedder.[4]

In recent communications[5–7] we have reported nitroxide trapping experiments which show the pathways for the reaction of benzoyloxy radicals with styrene and of *tert*-butoxy radicals with acrylates. Our method owes its success to the extremely fast rate at which nitroxides combine with alkyl radicals ($k = 10^7$–$10^9$ M$^{-1}$ s$^{-1}$).[8,9] This enables, with a suitable choice of nitroxide concentration, the complete inhibition of the propagation step of vinyl polymerization ($k = 10^2$–$10^4$ M$^{-1}$ s$^{-1}$). On the other hand, because of the relatively rapid rate at which most initiator-derived radicals add to monomers ($k = 10^4$–$10^8$ M$^{-1}$ s$^{-1}$), only a fraction of (for example) methyl and phenyl radicals are trapped directly, and oxygen-centered radicals (*tert*-butoxy, benzoyloxy) appear to undergo no irreversible reactions with nitroxides. Thus a near-quantitative yield of low molecular weight products which stem from the reactions of the initiator-derived radicals and single monomer units can be obtained. In the present paper we use this method to detail the reactions of phenyl and *tert*-butoxy radicals with styrene and expand on our previous study of benzoyloxy radicals with styrene.[5]

## Experimental Section

**General Data.** NMR spectra were recorded with a Bruker WM250, a Varian CFT100, or a Varian HA100 spectrometer and, unless stated otherwise, deuteriochloroform was used as solvent. Chemical shifts are reported in ppm from internal tetramethylsilane. High-performance liquid chromatography (HPLC) was performed with a DuPont model 850 liquid chromatograph equipped with a variable-wavelength UV detector which was coupled to an LDC 308 computing integrator or a Vista 401 data system. Altex Ultrasphere ODS or Zorbax (DuPont) ODS columns were employed. Gas chromatography (GC) was carried out with a Vista 4600 instrument using a 2 m × 2 mm 0.1% SP1000 on Carbopack C column and nitrogen (20 mL min$^{-1}$) as carrier gas. Chemical ionization mass spectra (CI/MS) were obtained with a Finnigan 3300 spectrometer using methane as reagent gas. Microanalyses were performed by AMDEL, Melbourne.

**1,1,3,3-Tetramethylisoindolinyl-2-oxy (1).** The preparation of this material is described elsewhere.[7]

**2-Oxo-1,1,3,3-tetramethylisoindolinium Chloride (13b).** The procedure of Golubev[10] was used. A solution of chlorine in carbon tetrachloride was added dropwise during 10 min to a solution of 1 (500 mg) in carbon tetrachloride (20 mL) under nitrogen at −20 °C. The resultant deep red precipitate (570 mg, 96%) was collected by filtration, washed with carbon tetrachloride, and dried under vacuum. This material was used without further purification.

The oxoammonium chloride (**13b**) is immediately decolorized on dissolution in acetone[11] and gives a near-quantitative yield (95%) of **10**.

**Trapping Experiments.** The general procedure is as follows. An appropriate amount (45% of the nitroxide concentration unless stated otherwise in the text) of the initiator was added to a solution of the nitroxide (**1** or **2**) in freshly distilled styrene or styrene/acetone (the addition of benzoyl peroxide to neat nitroxide should be avoided since a vigorous reaction ensues). The resultant solution was degassed by the freeze–thaw technique and then sealed under vacuum (0.01 mmHg) and placed in a constant-temperature bath at 60 (±0.1) °C for 2–30 h, depending on initiator, nitroxide concentration, and solvent composition. Following removal of most (90–95%) of the styrene by evaporation under reduced pressure, the mixture was analyzed by HPLC. Peak areas determined by integration of the HPLC trace were converted to product ratios using response ratios determined by analysis of standard solutions. The results of these experiments are summarized in Table I or in the text.

**Reaction of Di-*tert*-butyl Peroxalate and 1 in Styrene.** A solution of di-*tert*-butyl peroxalate[12] (120 mg) and **1** (218 mg) in styrene (50 mL) was heated at 60 °C in vacuo for 3 h. The mixture was then cooled and the styrene removed at 40 °C (0.1 mmHg). The residue was shown by HPLC to contain **3**, **4**, and **9** (relative yields: 98.7, 0.2, and 1.1%, respectively) along with residual nitroxide. The major component (**3**) (200 mg, 54%) crystallized from the mixture on addition of methanol.

**Reaction of Di-*tert*-butyl Peroxalate and 1 in 50% Styrene/Acetone.** A solution containing di-*tert*-butyl peroxalate (242 mg) and **1** (123 mg) in styrene (25 mL) and acetone (25 mL) was heated at 60 °C in vacuo for 3 h. The mixture was then cooled and the solvent evaporated (35 °C (0.1 mmHg)) to leave a residue containing **3**, **4**, **9**, **5**, and **10** (relative yields: 93.6, 0.4, 2.6, 0.5, and 3.4%, respectively). The compounds **9** and **10** are volatile and a portion of these compounds can be lost if all the styrene is removed. The compounds **3**, **4**, **9**, **5**, and **10** were isolated by preparative HPLC using acetonitrile/water as the eluant. The properties of these compounds are given below.

**2-(2-*tert*-Butoxy-1-phenylethoxy)-1,1,3,3-tetramethylisoindoline (3)**: mp 93–94 °C; CI/MS *m/e* 368 (M + 1); $^1$H NMR (100 MHz) $\delta$ 0.77 (s, 3 H), 1.22 (s, 9 H), 1.26 (s, 3 H), 1.51 (s, 3 H), 1.69 (s, 3 H), 3.40 (dd, $J$ = 4, 10 Hz, 1 H), 3.79 (dd, $J$ = 8.5, 10 Hz, 1 H), 4.86 (dd, $J$ = 4, 8.5 Hz, 1 H), 6.8–7.5 (m, 9 H). Anal. ($C_{24}H_{31}NO$): C, H, N.

**2-(1-Phenylpropoxy)-1,1,3,3-tetramethylisoindoline (4)**: mp 26–27 °C; CI/MS *m/e* 310 (M + 1); $^1$H NMR (250 MHz) $\delta$ 0.73 (s, 3 H), 0.89 (t, $J$ = 7.5 Hz, 3 H), 1.22 (s, 3 H), 1.45 (s, 3 H), 1.62 (s, 3 H), 1.80 (qdd, $J$ = 7.5, 8, 13.5 Hz, 1 H), 2.17 (qdd, $J$ = 7.5, 6, 13.5 Hz, 1 H), 4.61 (dd, $J$ = 6, 8 Hz, 1 H), 6.9–7.4 (m, 9 H). Anal. ($C_{21}H_{27}NO$): C, H, N.

This compound (**4**) was also available from the reaction of methyl radicals with styrene in dimethyl sulfoxide. A solution of 35% (w/v) aqueous hydrogen peroxide (0.15 mL) in dimethyl

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Table I
Products from the Interaction of Benzoyloxy Radicals with Styrene (%)

| | [nitroxide], M | | | | | |
|---|---|---|---|---|---|---|
| | $0.05^{a-d}$ | $0.01^{a-d}$ | $0.005^{a-d}$ | $0.237^{e}$ | $0.043^{e}$ | $0.005^{e}$ |
| **6** | 79.6 | 83.0 | 84.8 | 79 | 80 | 95 |
| **21** | 6.0 | 4.3 | 2.6 | 5 | 5 | 3 |
| **22** | trace | 1.0 | 2.0 | — | — | — |
| **23** | trace | trace | trace | — | — | — |
| **15** | 2.8 | 1.0 | 0.8 | 6 | 5 | 1 |
| **16** | 0.9 | 0.3 | 0.2 | 2 | 2 | 0.2 |
| **17** | 3.8 | 3.5 | 2.4 | 7 | 7 | 1 |
| **7** | 6.8 | 6.8 | 6.9 | — | — | — |
| **18, 19, 20** | 0.07 | 0.07 | 0.07 | — | — | — |

[a] The initial benzoyl peroxide concentration was half the nitroxide concentration. The experiments using 0.05, 0.01, and 0.005 M nitroxide were carried with reaction times of 20, 28, and 27 h to give 100, 90, and 85% conversion of peroxide, respectively. [b] Other products, not mentioned in the table, include benzoic acid (from induced decomposition), **10**, and products from thermal initiation (see text); benzene is not formed. [c] The total yield of products is >95% based on benzoyl peroxide. [d] The phenoxyamine **11** was not determined by should be ca. 0.3% of the product at 0.05 M nitroxide and less at lower nitroxide concentrations based on our observation of the fraction of phenyl radicals trapped directly by nitroxide in the experiments using triphenylmethylazobenzene (see text). [e] Data taken from ref 5. These reactions were carried out with nitroxide **2**. Product amounts indicated by a dash were not evaluated.

sulfoxide (10 mL) was added over 20 min to a solution containing **1** (100 mg), titanium trichloride (160 mg), dimethyl sulfoxide (10 mL), and styrene (50 mL) at room temperature. After 5 min the mixture was diluted with water and extracted with petroleum ether. The organic phase was washed with water and saturated sodium chloride, dried ($MgSO_4$), and evaporated to leave an orange oil (180 mg) from which the required compound (25 mg, 15%) was isolated by preparative HPLC.

A further sample of **4** was obtained as follows. A solution of di-*tert*-butyl peroxalate (138 mg) and **1** (217 mg) in propylbenzene (25 mL) was heated at 60 °C for 2 h. The solvent was then evaporated and the required compound (100 mg, 55%) was isolated by preparative HPLC, using acetonitrile/water as the eluant.

**2-Methoxy-1,1,3,3-tetramethylisoindoline (9)**: mp 39–40 °C; CI/MS *m/e* 206 (M + 1); $^1$H NMR (250 MHz) $\delta$ 1.44 (br s, 12 H), 3.80 (s, 3 H), 7.0–7.3 (m, 4 H). Anal. ($C_{13}H_{19}NO$): C, H, N.

**2-(1-Phenyl-4-oxopentoxy)-1,1,3,3-tetramethylisoindoline (5).** This compound was isolated in insufficient quantity for a complete characterization. It has been assigned the structure **5** on the basis of its CI/MS, which shows *m/e* 392 (M + 41), 370 (M + 29), 352 (M + 1), 161 (M − 190 = loss of nitroxide) as well as the typical fragmentation pattern for the tetramethylisoindolinyloxy group: *m/e* 190, 174, 160, 147, 119.

**2-(2-Oxopropoxy)-1,1,3,3-tetramethylisoindoline (10)**: mp 83–85 °C; CI/MS *m/e* 248 (M + 1); $^1$H NMR (100 MHz) $\delta$ 1.47 (br s, 12 H), 2.26 (s, 3 H), 4.59 (s, 2 H), 7.0–7.3 (m, 4 H). Anal. ($C_{15}H_{21}NO_2$): C, H, N.

**Reaction of Benzoyl Peroxide and 1 in 50% Styrene/Acetone.** A solution of benzoyl peroxide (152 mg) and **1** (238 mg) in styrene (125 mL) and acetone (125 mL) was heated at 60 °C in vacuo for 87 h. The solvent was then evaporated and ethanol (4 mL) was added. After this mixture was allowed to stand at 4 °C for 16 h, **6** (130 mg, 50%) was collected by filtration. The products, **6**, **21**, a mixture of **22** and **23**, **15**, a mixture of **16** and **17**, **7**, **31**, and **32**, were isolated by preparative HPLC, with methanol/water as the eluant. The properties of these compounds are given below. The products **10** and **18–20** were identified by cochromatography with authentic samples.

**2-[2-(Benzoyloxy)-1-phenylethoxy]-1,1,3,3-tetramethylisoindoline (6)**: mp 94–95 °C; CI/MS *m/e* 416 (M + 1); $^1$H NMR (250 MHz) $\delta$ 0.82 (s, 3 H), 1.26 (s, 3 H), 1.45 (s, 3 H), 1.62 (s, 3 H), 4.52 (dd, $J$ = 4, 12 Hz, 1 H), 4.78 (dd, $J$ = 8, 12 Hz, 1 H), 5.16 (dd, $J$ = 4, 8 Hz, 1 H), 6.9–7.6 (m, 12 H), 8.0–8.2 (m, 2 H). Anal. ($C_{27}H_{29}NO_3$): C, H, N.

**2-(Benzoyloxy)-1-phenylethanol.** To prove its identity, a sample of the piperidine analogue of **6**[5] was reduced to the known half-ester.[13] A mixture of 1-[2-(benzoyloxy)-1-phenylethoxy]-2,2,6,6-tetramethylpiperidine (100 mg), zinc dust (100 mg), and acetic acid (1 mL) were stirred at room temperature for 80 h. The reaction mixture was then filtered, poured into the water (10 mL), and extracted with ether (3 × 10 mL). The extracts were washed with saturated sodium bicarbonate solution (4 × 10 mL) and water (10 mL) and then dried ($MgSO_4$). The product, a white waxy solid (60 mg, 87%), was identical (IR, NMR, HPLC) with material isolated from the reaction of benzoic acid with styrene oxide.[13] 2-(Benzoyloxy)-1-phenylethanol and 2-(benzoyloxy)-2-phenylethanol (see below) were observed to equilibrate on standing in chloroform solution.

**2-[2-(Benzoyloxy)-2-phenylethoxy]-1,1,3,3-tetramethylisoindoline (21).** The compound was a low-melting solid: CI/MS *m/e* 416 (M + 1); high-resolution mass spectrum, *m/e* 225.091 (M − 190 = loss of nitroxide), $C_{15}H_{13}O_2$ requires 225.092; $^1$H NMR (250 MHz) $\delta$ 1.36 (br s, 12 H), 4.24 (dd, $J$ = 6, 15 Hz, 1 H), 4.42 (dd, $J$ = 10, 15 Hz, 1 H), 6.28 (dd, $J$ = 6, 10 Hz, 1 H), 6.9–7.7 (m, 12 H), 8.1–8.2 (m, 2 H).

**2-(Benzoyloxy)-2-phenylethanol.** A mixture of 1-[2-(benzoyloxy)-2-phenylethoxy]-2,2,6,6-tetramethylpiperidine (5 mg),[5] zinc dust (100 mg), and acetic acid (0.5 mL) was allowed to stand at room temperature for 16 h. Workup as described above gave the required compound (4 mg, 60%), which was shown to be free of its isomer (see above) by HPLC. The $^1$H NMR spectrum was identical with that reported previously.[13]

**2-[4-(Benzoyloxy)-1,4-diphenylbutoxy]-1,1,3,3-tetramethylisoindoline (22) and 2-[4-(Benzoyloxy)-1,3-diphenylbutoxy]-1,1,3,3-tetramethylisoindoline (23).** The compounds **22** and **23** were only partially resolved under the conditions used for preparative HPLC. However, it was possible to separate the mixture into two fractions containing **22** and the two diastereomers of **23** in the ratio 83:12:4 and 28:28:44, respectively. The assignment of structures is based on the $^1$H NMR (250 MHz), which showed the following: **22**, $\delta$ 4.8–5.0 (br, 1 H, $PhCO_2CH(Ph)CH_2$), 5.95–6.05 (m, 1 H, $CH_2CHON$), 8.1–8.2 (m, 2 H, benzoate *o*-hydrogens); **23** (first eluted diastereomer), $\delta$ 3.25–3.35 (m, 1 H, $CH_2CH(Ph)CH_2$), 4.35–4.45 (m, 2 H, $PhCO_2CH_2CH$), 4.50–4.60 (m, 1 H, $CH_2CHON$), 7.8–7.9 (m, 2 H, benzoate *o*-hydrogens); **23** (second eluted diastereomer), $\delta$ 2.7–2.8 (m, 1 H, $CH_2CH(Ph)CH_2$), 4.33 (t, $J$ = 7 Hz, 1 H, $CH_2CHON$), 4.49 (d, $J$ = 6 Hz, 2 H, $PhCO_2CH_2CH$), 7.9–8.0 (m, 2 H, benzoate *o*-hydrogens).

**(Benzoyloxy)styrenes (15–17).** *o*-(Benzoyloxy)styrene (**15**) and a mixture of *m*- and *p*-(benzoyloxy)styrenes (**16** and **17**) were isolated by preparative HPLC. These samples had the same spectral properties (NMR, CI/MS) as material prepared according to the following procedures.

*o*-(Benzoyloxy)styrene (**15**), contrary to a previous report,[14] was obtained from the reaction of *o*-vinylphenol[15] with benzoyl chloride in pyridine at room temperature and purified by chromatography on silica gel to give a colorless oil (60%): CI/MS *m/e* 225 (M + 1); high-resolution mass spectrum, *m/e* 224.083, $C_{15}H_{12}O_2$ requires 224.084; $^1$H NMR (250 MHz) $\delta$ 5.28 (dd, $J$ = 11, 1 Hz, 1 H), 5.76 (dd, $J$ = 17, 1 Hz, 1 H), 6.83 (dd, $J$ = 11, 17 Hz, 1 H), 7.1–7.6 (m, 7 H), 8.1–8.3 (m, 2 H).

Authentic *m*- and *p*-(benzoyloxy)styrenes were prepared according to the literature procedure.[15] Meta isomer (**16**): $^1$H NMR (250 MHz) $\delta$ 5.28 (dd, $J$ = 11, 1 Hz, 1 H), 5.74 (dd, $J$ = 17, 1 Hz, 1 H), 6.72 (dd, $J$ = 11, 17 Hz, 1 H), 7.1–7.6 (m, 7 H), 8.1–8.3 (m, 2 H). Para isomer (17): $^1$H NMR (250 MHz) $\delta$ 5.25 (dd, $J$ = 11, 1 Hz, 1 H), 5.71 (dd, $J$ = 17, 1 Hz, 1 H), 6.72 (dd, $J$ = 11, 17 Hz, 1 H), 7.1–7.6 (m, 7 H), 8.1–8.3 (m, 2 H).

**2-(1,2-Diphenylethoxy)-1,1,3,3-tetramethylisoindoline (7)**: mp 102–104 °C; CI/MS *m/e* 372 (M + 1); $^1$H NMR (100 MHz) $\delta$ 0.78 (s, 3 H), 1.21 (s, 3 H), 1.25 (s, 3 H), 1.45 (s, 3 H), 2.98 (dd, $J$ = 7, 13 Hz, 1 H), 3.54 (dd, $J$ = 7, 13 Hz, 1 H), 4.88 (t, $J$ = 7 Hz, 1 H), 6.9–7.4 (m, 14 H). Anal. ($C_{26}H_{29}NO$): C, H, N.

**Vinylbiphenyls 18–20.** *o*- and *m*-vinylbiphenyls were prepared according to the literature procedures.[16,17] *p*-Vinylbiphenyl was obtained commercially. These compounds were shown to cochromatograph with the corresponding products from the trapping experiments.

**Reaction of Triphenylmethylazobenzene and 1 in Styrene.** A solution of triphenylmethylazobenzene (344 mg) and 1 (401 mg) in styrene (50 mL) was heated at 60 °C for 2 h in vacuo. The styrene was removed under vacuum and the residue triturated with methanol to cause crystallization of a mixture (400 mg) of 8 and 24 (ca. 20:1), which was collected by filtration. The filtrate was evaporated and the residue recrystallized from methanol to give 7 (100 mg, 25%). Compound 11 was isolated by preparative HPLC, with methanol/water as the eluant. Pure 8 and 24 were obtained by chromatography on silica gel, with 10% chloroform/petroleum ether as the eluant.

**2-Phenoxy-1,1,3,3-tetramethylisoindoline (11)**: mp 93–95 °C; CI/MS *m/e* 268 (M + 1); high-resolution mass spectrum, *m/e* 267.161, $C_{18}H_{21}NO$ requires 267.162; $^1$H NMR (100 MHz) $\delta$ 1.45 (s, 12 H), 7.1–7.4 (m, 9 H).

This compound was also obtained from the decomposition of triphenylmethylazobenzene in benzene in the presence of 1.

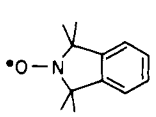
**2-(1,3,3,3-Tetraphenylpropoxy)-1,1,3,3-tetramethylisoindoline (8)**: mp 156–158 °C; CI/MS *m/e* 538 (M + 1); $^1$H NMR (250 MHz) $\delta$ 0.59 (s, 3 H), 1.21 (s, 3 H), 1.40 (s, 3 H), 1.42 (s, 3 H), 3.22 (dd, $J$ = 8.5, 14 Hz, 1 H), 3.83 (dd, $J$ = 3, 14 Hz, 1 H), 4.64 (dd, $J$ = 3, 8.5 Hz, 1 H), 6.9–7.4 (m, 24 H). Anal. ($C_{39}H_{39}NO$): C, H, N.

**1,1,1,2,3-Pentaphenylpropane (24).** This compound was isolated as a colorless oil: CI/MS *m/e* 425 (M + 1); $^1$H NMR (250 MHz) $\delta$ 3.35 (m, 1 H), 3.83 (br t, 1 H), 4.64 (m, 1 H), 6.9–7.4 (m, 25 H).

**Product Stability.** In view of recent reports regarding the instability of some alkoxyamine derivatives,[18,19] we have investigated the effect of heating representative compounds (6, 21, and 31) in vacuo at 60 °C for 24 h. No decomposition or isomerization was observed.

## Results

The radicals under investigation were generated from di-*tert*-butyl peroxalate (*tert*-butoxy, methyl), benzoyl peroxide (benzoyloxy, phenyl), and triphenylmethylazobenzene (phenyl, triphenylmethyl). The products from the decomposition of these initiators in styrene or in 50% styrene/acetone (v/v) at 60 °C in the presence of 1,1,3,3-tetramethylisoindolinyl-2-oxy (1)[7] were identified on the basis of NMR, mass spectra, and analytical data of samples isolated by preparative HPLC (see Experimental Section) and, where possible, by comparison with authentic samples.



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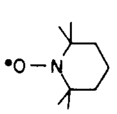
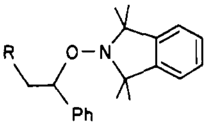


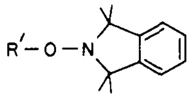
2

Nitroxide 1 was employed in the present work since this radical trapping agent has the advantage of affording alkoxyamine products with relatively high UV extinction coefficients, which renders their detection by HPLC easier. The isoindolinyl chromophore has a molar extinction of ca. 1100 at 270 nm. The nature of the styrene-derived products is the same irrespective of whether 1 or 2,2,6,6-tetramethylpiperidinyl-1-oxy (2)[5] is used.

**Reactions with Di-*tert*-butyl Peroxalate.** *tert*-Butoxy radicals were generated from di-*tert*-butyl peroxalate.[12] Unlike benzoyl peroxide,[20] this initiator does not appear to undergo induced decomposition by nitroxides and the yield of the products 3, 4, and 9 is >98% based on initiator.



3 R = $(CH_3)_3CO$
4 R = $CH_3$
5 R = $CH_3COCH_2$
6 R = $PhCO_2$
7 R = Ph
8 R = $CPh_3$

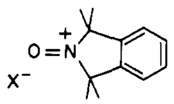


9 R′ = $CH_3$
10 R′ = $CH_3COCH_2$
11 R′ = Ph
12 R′ = H

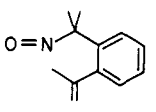
The addition product 3 accounts for 98.7% of *tert*-butoxy radicals formed from the decomposition of di-*tert*-butyl peroxalate in neat styrene at 60 °C. The remainder (1.3%) undergo fragmentation to methyl radicals. With 0.045 M 1, ca. 15% of these add to styrene to give 4 while the remaining 85% are trapped directly as the methoxyamine 9. *tert*-Butoxy radicals are extremely selective in their reaction with styrene, giving only addition to the less substituted end of the double bond (tail addition), which is in marked contrast to the behavior of benzoyloxy and phenyl radicals (see below). The reaction of methyl radicals with styrene also appears to be selective. However, the products 4 and 9 are formed only in small amounts and a separate study of methyl radical reactions is warranted.

The reaction of *tert*-butoxy radicals with styrene in acetone (50% v/v) with 0.046 M 1 has also been examined. In this case, in addition to an increased yield of methyl radical products (ca. 3%), the products 5 and 10, derived from *tert*-butoxy radicals abstracting hydrogen from acetone, are formed (ca. 4%).

**Reactions with Benzoyl Peroxide.** The mechanism of the induced decomposition of benzoyl peroxide by nitroxides has been discussed elsewhere.[20] Like the piperidine nitroxide (2), the isoindoline nitroxide (1) induces the decomposition of benzoyl peroxide, affording benzoyloxy radicals and benzoic acid. However, whereas 2 is quantitatively converted into a nitrone, which is unreactive under the reaction conditions,[20] the analogous transformation of 1 is not possible. Nitroxide 1 can be oxidized to the oxoammonium benzoate 13a which can then fragment to give the unsaturated nitroso compound 14 in a manner analogous to that proposed for the transformation of 2. Compound 14, however, cannot undergo further rearrangement and, therefore, may undergo typical nitroso compound reactions.[21] That is, it can react with monomer or trap radical species in competition with 1, leading ultimately to a very complex mixture of products. The product mixture is, however, simplified considerably if acetone is employed as cosolvent for the reaction. We have shown that acetone reacts extremely rapidly with the oxoammonium chloride 13b to give, quantitatively, the alkoxyamine 10, and the benzoate 13a may be expected to



13a X = $PhCO_2$
13b X = Cl



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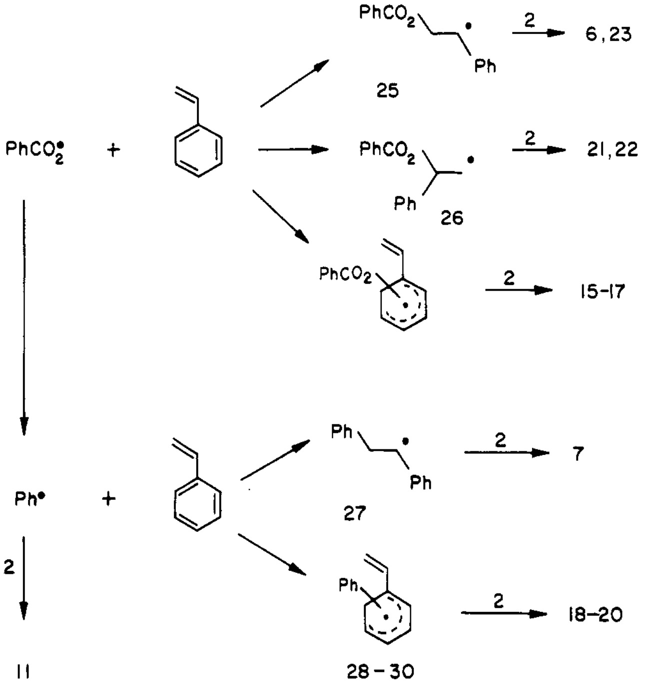
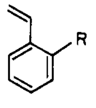
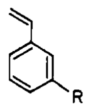
Scheme I
Reactions of Benzoyloxy and Phenyl Radicals with Styrene

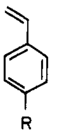


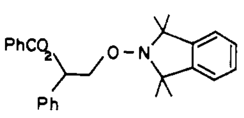
react similarly. Indeed, the reaction of benzoyl peroxide with nitroxide in neat acetone is extremely clean, affording benzoic acid, **10**, benzene, and the phenoxyamine **11** as the only products.

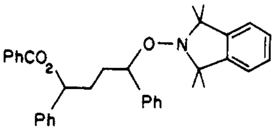
The interaction of benzoyloxy radicals with styrene in the presence of nitroxide **1** is summarized in Scheme I and the relative yields of products are given in Table I. The following observations clearly demonstrate that the reactions leading to these compounds are not influenced by the mode of generation of benzoyloxy radicals or by the presence of a nitroxide trapping agent: (a) the proportion of head (including head addition propagated) vs. tail addition is constant[22] with varying nitroxide concentration; (b) the products of benzoyloxy radical adding to styrene propagate to an extent consistent with available rate data;[5] (c) the amount of head vs. tail addition determined by the trapping technique is in accord with that determined by direct NMR analysis of polystyrene prepared using $^{13}$C-labeled peroxide;[23] (d) at high concentrations of nitroxide **2**[5] the proportion of aromatic substitution products **15–17** is constant with varying nitroxide concentration (see later discussion); (e) the relative yield of phenyl radical products is independent of the nitroxide concentration used—the proportion of phenyl vs. benzoyloxy plus phenyl radical products found (6.9%) is in excellent agreement with the data of Bevington et al.,[24,25] who used a radiochemical technique to show that ca. 7% of benzoyloxy radicals undergo decarboxylation in 50% styrene/benzene or styrene/dioxane (v/v) at 60 °C; (f) the nature and relative amounts of phenyl radical products are the same whether benzoyl peroxide or triphenylmethylazobenzene is used as the phenyl radical source (see below).

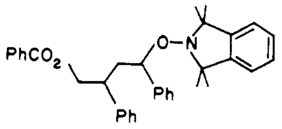

15 R = $PhCO_2$
18 R = Ph

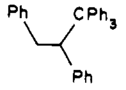

16 R = $PhCO_2$
19 R = Ph


17 R = $PhCO_2$
20 R = Ph


21


22

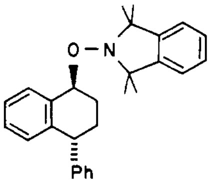

23

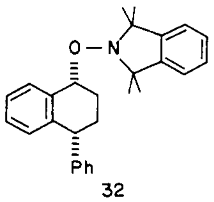

24

**Reactions with Triphenylmethylazobenzene.** The interaction of phenyl radicals with styrene was investigated by examining the decomposition of triphenylmethylazobenzene in styrene in the presence of **1** (0.045 M). Under these conditions phenyl radicals partition 96:4 between reacting with styrene and being trapped directly as the phenoxyamine **11**. The yield of **11** is small, indicating a high rate of reaction of phenyl radicals with styrene or a relatively low rate of trapping of phenyl radicals. Phenyl radicals react with styrene to give a mixture of tail addition (99%) and aromatic substitution products (1%). The latter comprises *o*-, *m*-, and *p*-vinylbiphenyls (**18–20**) in the ratio 10:3:14.

In addition to the above-mentioned compounds, products from triphenylmethyl radicals are formed. These include tetraphenylmethane, triphenylmethane, products from triphenylmethyl radical adding to styrene and being trapped by nitroxide **8** and from phenyl radical adding to styrene and being trapped by triphenylmethyl radical (less than 10% of **27** are trapped as **24**), and other minor products($\leq$1% of total). The formation of "nitroxide-trapped" triphenylmethyl radical is reversible under the reaction conditions;[19] consequently, it is not surprising that triphenylmethyl radical is available to compete with the nitroxide as a trapping agent. There is no evidence in our experiments that triphenylmethyl or phenyl radicals abstract hydrogen from the nitroxide **1** as has been reported under other conditions.[19,26] The triphenylmethane formed during the reaction probably results from the reaction of triphenylmethyl radicals with the phenylcyclohexadienyl radicals **28–30** or with the hydroxylamine **12**, which can be formed from the reaction of the nitroxide **1** with **28–30**.

**Thermal Initiation.** Accompanying the products from the reaction of initiator-derived radicals with styrene are the compounds **31** and **32**, which derive from the thermal reaction of styrene.[27] However, the yield of these products is insignificant except in cases where the reaction is carried out over an extended period. For example, in the experiments described in Table I the combined yields of **31** and **32** are ca. 0.1, 0.5, and 1.0% relative to the total benzoyloxy radical products with 0.05, 0.01, and 0.005 M **1**, respectively.


31


32

## Discussion

On the basis of our data we can derive Table II, which summarizes the processes that characterize the reactions of *tert*-butoxy, benzoyloxy, and phenyl radicals with styrene and the types of functionality that are thereby in-

Table II
Initiator-Derived Functional Groups in Polystyrene

| group | origin |
|---|---|
| (i) Using Benzoyl Peroxide | |
| primary benzoyloxy | tail addition |
| secondary benzoyloxy | head addition |
| secondary benzoyloxy | transfer to benzoyl peroxide |
| secondary benzoyloxy | primary radical termination |
| primary phenyl | tail addition |
| aromatic benzoyloxy | aromatic substitution of styrene |
| aromatic benzoyloxy | aromatic substitution of polystyrene |
| aromatic phenyl | aromatic substitution of styrene |
| aromatic phenyl | aromatic substitution of polystyrene |
| aliphatic benzoyloxy | abstraction from backbone followed by transfer to initiator or primary radical termination |
| (ii) Using *tert*-Butyl Peroxalate | |
| primary *tert*-butoxy[a] | tail addition |
| primary methyl[a] | tail addition |

[a] There is no evidence of primary radical termination or transfer in the case of *tert*-butyl peroxalate, though, in the absence of any relevant studies, the possibility should not be excluded.

troduced into polystyrene. The extent of each process is a function of the radical involved, with selectivity increasing in the series benzoyloxy < phenyl < *tert*-butoxy. Let us consider some of these reactions in more detail.

**Aromatic Substitution.** Aromatic substitution by *tert*-butoxy radicals is not competitive with addition to the double bond of styrene. The low reactivity of aromatic substrates toward *tert*-butoxy radicals is consistent with previous observations. The only example of a reaction that may involve aromatic substitution by *tert*-butoxy radical was reported by Brokenshare and Ingold,[28] who observed an unstated yield of *tert*-butoxybenzene among the products of decomposition of *tert*-butyl hyponitrite in benzene at 30 °C.

The yield of (benzoyloxy)styrenes **15**–**17** will be dependent on the competition between the reversion of the initially formed cyclohexadienyl radicals to starting materials and their oxidation. In the presence of a nitroxide, cyclohexadienyl radicals are readily oxidized. The isoindoline nitroxide (**1**) appears to be a poorer oxidant than the piperidine nitroxide (**2**). This is indicated by the dependence of the yield of **15**–**17** on nitroxide concentration (see Table I). When nitroxide **2** is employed, the yield of **15**–**17** (14% of benzoyloxy radical derived products) remains essentially constant when nitroxide concentrations above 0.02 M are used. The reaction has been studied by using concentrations of **2** in the range 0.002–0.2 M.[5]

The addition of phenyl radicals to the styrene aromatic ring is shown by the consistency in the ratio of vinylbiphenyls to the product of double-bond addition (**18** + **19** + **20**:**7**; see Table I) to be irreversible even when low nitroxide concentrations are used. The amount of vinylbiphenyl formed is, therefore, a direct reflection of the reactivity of styrene toward aromatic substitution by phenyl radicals.

**Head Addition.** Head addition to styrene by benzoyloxy radicals is remarkable in that it results in the formation of the primary alkyl radical **26** in preference to the resonance-stabilized secondary benzylic radical **25**. In contrast, the reaction of *tert*-butoxy or phenyl radicals with the styrene double bond proceeds exclusively by tail addition.

It has been stated[4] that the rate and orientation of addition of free radicals to olefins is controlled by "a complex interplay of steric, polar, and bond strength terms". The difference in selectivity between the two oxygen-centered radicals can be rationalized in terms of steric factors.[3] *tert*-Butoxy has a significantly greater steric bulk than benzoyloxy radical and thus might be expected to show a greater preference for addition to the less hindered end of the double bond. Details of other factors influencing the addition reaction will follow from the investigation of the interaction of these radicals with other monomers. This study is currently in progress.

**Implications.** Reactivity ratios for copolymerization of (benzoyloxy)styrene and styrene have not been reported. However, the following reactivity ratios appear in the literature for *p*-acetoxystyrene and styrene:[29] $r_1 = 1.18$; $r_2 = 0.88$. The reactivity ratios for *p*-vinylbiphenyl and styrene[30] are $r_1 = 1.40 \pm 0.1$ and $r_2 = 0.89 \pm 0.1$. Therefore, both the (benzoyloxy)styrenes and vinylbiphenyls produced during the polymerization can be expected to undergo copolymerization with styrene.

The actual amount of (benzoyloxy)styrenes formed during a polymerization experiment will be a function of the reaction conditions and the competition between the reversion of the intermediate cyclohexadienyl radicals to starting material and their oxidation to products. The likely oxidants for the cyclohexadienyl radicals are other radicals (i.e., the growing polymer radical, the primary radicals, and other cyclohexadienyl radicals). However, these species are present only in low concentration; therefore, the reversion of the (benzoyloxy)cyclohexadienyl radical to benzoyloxy radical and aromatic substrate will be significant, and the amount of (benzoyloxy)styrenes formed will usually be less than observed in the presence of a nitroxide. The yield of (benzoyloxy)styrenes could be enhanced by additives or impurities:[31–35] for example, transition-metal salts,[31] oxygen,[32] and nitrogen compounds.[33] Benzoyl peroxide is a poor oxidant for cyclohexadienyl radicals.[33]

On the other hand, since aromatic substitution by phenyl radicals is irreversible, we should anticipate the incorporation into polystyrene of an amount of biphenyl groups which is at least 1% of the number of chains initiated by phenyl radicals (assuming 100% conversion). Note that while phenylcylcohexadienyl radicals react with nitroxide to give exclusively the vinylbiphenyls **18**–**20**, they may react with other radical species either by disproportionation or by coupling.[33–35]

Aromatic substitution of styrene monomer is not, however, the only route by which aryl benzoate and biphenyl groups may be incorporated into polystyrene. We have shown that toward benzoyloxy and phenyl radicals the aromatic ring of styrene has similar reactivity to that of benzene.[5] The aromatic rings attached to the polystyrene backbone can also be expected to undergo aromatic substitution. This process should become increasingly important as the polymerization is carried to higher conversions. Indeed, in these circumstances benzoyloxy and phenyl radicals may well interact with polymer rather than residual monomer.[36]

The influence of the functionality introduced (Table II) into the polystyrene on polymer properties should be considered. For example, the effects on photochemical and thermal degradation.

It is known that poly[*p*-(benzoyloxy)styrene][37] and copolymers of styrene and *p*-(benzoyloxy)styrene[38] are photoreactive. The major process involved is a photo-Fries rearrangement,[37] which results in the conversion of aryl benzoate groups into *o*-hydroxybenzophenones.[39] This reaction is, however, not clean and is accompanied by a side reaction that gives phenol groups and free benzoyl radicals.[37] Phenolic residues may also be formed from hydrolytic degradation of aryl benzoate units in the polymer. The presence of the above-mentioned functionality could well influence the resistance of the polymer to yellowing and may also have other effects.

The presence of benzoate end groups and the amount of head addition of benzoyloxy radicals to styrene may influence the thermal stability of polystyrene. On the basis of the known ease with which many low molecular weight esters undergo pyrolytic elimination,[40] primary and secondary benzoate end groups of polystyrene can be anticipated to have relatively short half-lives at temperatures in excess of 300 °C. Therefore, in thermal analysis experiments, which for polystyrene involve the use of temperatures in the range 300–400 °C,[41–44] one will be dealing with a polymer having a significant fraction of unsaturated end groups. This is important inasmuch as the presence of terminal unsaturation is thought to be an important factor in determining the rate of thermal degradation of polystyrene and other polymers.[42–44] Unfortunately, there are no quantitative data available to support these claims. It is, nevertheless, possible to speculate that the above may provide an explanation for the relative instability of benzoyl peroxide initiated vs. thermally initiated polystyrene as seen by thermal gravimetric analysis.[41,42]

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