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The Reaction of Benzoyloxy Radicals with Styrene—Implications Concerning the Structure of Polystyrene

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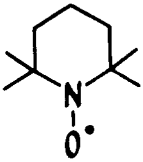
ABSTRACT

The selectivity of the reaction of benzoyloxy radicals with styrene has been examined. Analysis of the products formed when benzoyl peroxide is decomposed in styrene at 60°C in the presence of a radical trapping agent (2,2,6,6-tetramethylpiperidine-1-oxyl) shows that the reaction of benzoyloxy radicals with styrene proceeds with 80% "tail" addition, 5% "head" addition, and 15% aromatic substitution. Phenyl radicals (formed by decarboxylation of benzoyloxy radicals) also may add to either the double bond or the aromatic ring of styrene. The importance of the above-mentioned processes to the structure and properties of benzoyl-peroxide-initiated polystyrene is discussed.

INTRODUCTION

The reaction of free radicals with styrene is usually depicted [1, 2] as a selective process involving exclusive addition to the unsubstituted terminus of the double bond. While this is undoubtedly the dominant pathway involved in the initiation and propagation steps of styrene polymerization, it is also recognized [1-3] that polystyrene can contain a number of "weak links"–present either as end groups or as abnormal groups in the polymer chain–which may arise via some nonselectivity in free radical addition to styrene. These "weak links" are thought to be important in initiating the thermal degradation of polystyrene [3] and may have a significant influence on other properties of the polymer [4, 5]. Although some work has been directed into this area [1, 2, 6-8], there is as yet no definitive information on the nature of the "weak links."

Recently, Rizzardo and Solomon [9] have developed a new technique for examining the initiation step of radical polymerization. By using a stable nitroxide–for example, 2,2,6,6-tetramethylpiperidine-1-oxyl (1)–as a radical trapping agent, it is possible to inhibit completely the propagation step of vinyl polymerization, and products derived from the reaction of an initiating free radical and a single monomer unit can be isolated and characterized.



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The present paper is a preliminary report on the study of the interaction of benzoyloxy radicals with styrene using the above-mentioned technique.

EXPERIMENTAL

Solutions of the nitroxide (1) and benzoyl peroxide of the appropriate concentration (cf. Table 1) were degassed using the freeze-thaw technique and then heated in vacuo at 60°C in a constant temperature bath for 3-16 h. The solvent was then evaporated and the products were analyzed by HPLC using a Zorbax ODS column (6.2 mm × 25 cm) with ethanol/water as the eluent. The same column was used for preparative separations.

The nitroxide (1) was shown to be unreactive toward styrene by heating a solution of (1) in styrene at 60°C without added initiator. During 16 h no ($< 2\%$) change in nitroxide concentration [10] could be detected by UV or EPR spectroscopy.

In view of recent observations [11, 12] of the thermal instability of some alkoxyamine derivatives, a sample of 7a in benzene was heated to 60°C for 16 h. The starting material was recovered unchanged in quantitative yield.

TABLE 1. Relative Yields of Products from the Interaction of Benzoyloxy Radical with Styrene at 60°C[a]

[1][b] M	7a	8a	9a	10a	11a	$PhCO_2Ph$
0.237	79	5	6	2	7	0
0.043	80	5	5	2	7	0
0.042[c]	42	3	3	1	4	47
0.005	95	3	1	0.2	1	0

[a] The yield of 7a-11a and $PhCO_2Ph$ have been normalized to 100%.

[b] Initial concentration of the nitroxide (1); benzoyl peroxide concentration ~0.4× [1].

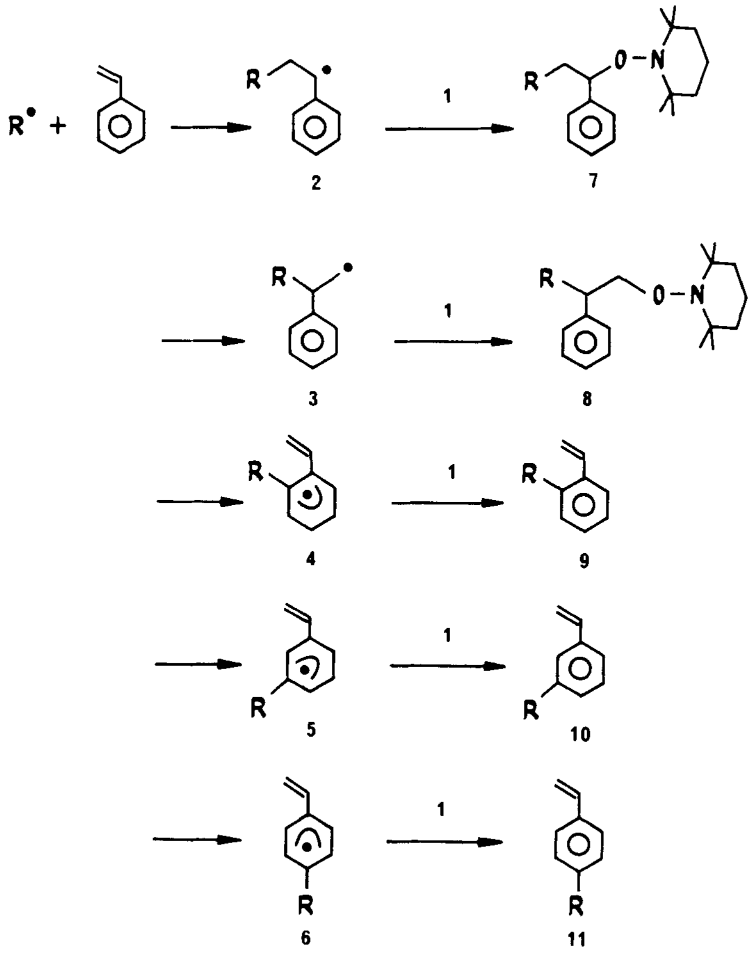
[c] 10% styrene in benzene.

The products 7a-11a and 7b formed from the decomposition of benzoyl peroxide in styrene at 60°C in the presence of the nitroxide (1) were each isolated by preparative HPLC and characterized by spectral and analytical data. Due to their low yield, the identity of the vinylbiphenyl derivatives (9b-11b) was established by GCMS and HPLC retention data. Authentic samples of 9a-11a and 10b were available commercially or were prepared according to the published procedure [13]. A sample of 7b was obtained from the reaction of tert-butoxy radicals (from tert-butylperoxalate) with 1,2-diphenylethane in the presence of the nitroxide (1). The benzoyloxy addition products (7a, 8a) were reduced to the corresponding hydroxybenzoates (13, 14) with zinc in acetic acid and compared with authentic specimens obtained from the reaction of benzoic acid with styrene oxide [14]. The absolute yield of these products (7-11) was quantitative (95 ± 5%) based on benzoyl peroxide after allowing for the formation of benzoic acid, phenyl benzoate, and biphenyl.

Full details of the synthesis of reference compounds and the characterization of products will be given in the near future.

RESULTS AND DISCUSSION

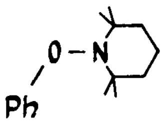
Benzoyl peroxide undergoes a facile reaction with nitroxide (1) in styrene or benzene at 60°C to afford benzoyloxy radicals [15]. The benzoyloxy radicals can react with styrene to give products according to Scheme 1 or decarboxylate to form phenyl radicals. The phenyl radicals may also react with styrene or are trapped by the nitroxide as the phenoxyamine (12). It has been reported [16] that the β-hydrogens of nitroxides are reactive toward abstraction by benzoyloxy



SCHEME 1. (a) R = $PhCO_2$; (b) R = Ph.

radicals. This process is not significant in the present experiments due to the much more favorable reaction of benzoyloxy radicals with solvent (i.e., styrene or benzene).

As shown in Table 1, the "tail" addition product (7a) accounts for only 80% of the benzoyloxy radical derived product with "head" addition (8a; 5%), the aromatic substitution products (9a-11a; 15%) accounting for the remainder. The ratio of these products (7a-11a) is invarient with nitroxide concentration ≥ 0.04 M (and styrene concentration), showing that each of the radicals 2a-6a is trapped efficiently under these conditions. It is also apparent from the



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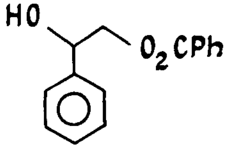

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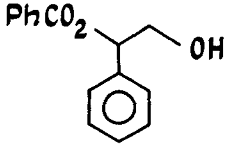

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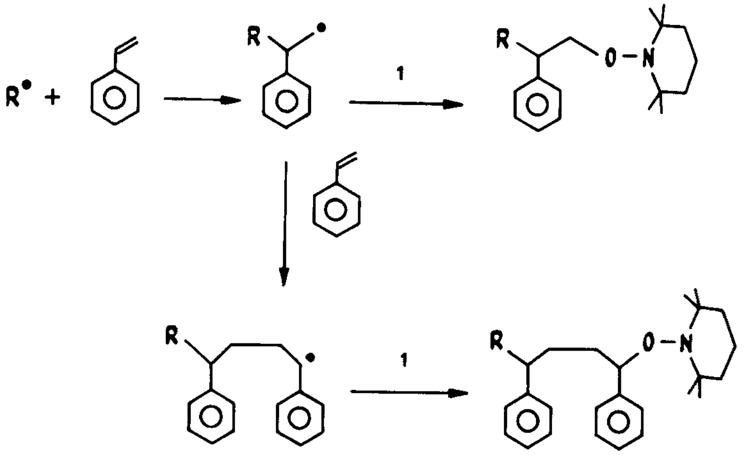
product distribution obtained from the reaction in 10% styrene in benzene that the aromatic ring of styrene has approximately the same reactivity as benzene toward benzoyloxy radicals (Table 1).

It is of interest to note that recently Sloane and Brudzynski [17] have shown that the gas phase reactions of hydroxyl radicals and oxygen atoms with styrene involve a significant amount of attack on the aromatic ring. In addition, homolytic aromatic substitution by hydroxyl radicals is suggested [18] to be a major process occurring during the pulse radiolysis of aqueous solutions of styrene. The reactions of hydroxyl radicals with styrene generated in a redox process are currently under investigation.

The trapping of cyclohexadienyl radicals by nitroxides occurs by oxidation (hydrogen atom abstraction or combination followed by elimination) to afford the corresponding aromatic compound and a hydroxylamine [19]. The latter compound may be oxidized by benzoyl peroxide to regenerate the nitroxide [20]. At low nitroxide concentrations (0.005 M) a lower yield of the aromatic substitution products (9a-11a) is observed. This result indicates that under these conditions the reversion of the benzoyloxycyclohexadienyl radicals (4a-6a) to benzoyloxy radicals and styrene is competitive with their oxidation by the nitroxide (1). This result is in accord with previous observations [21, 22] which show that the addition of benzoyloxy radicals to benzene and other aromatic substrates is a reversible process.

The addition of benzoyloxy radicals to olefins, unlike its reaction with aromatic substrates, is believed to be irreversible. The lower yield of 8a obtained at low nitroxide concentration (0.005 M; cf. Table 1) may be attributed to the ability of the radical 3a to undergo a "propagation" reaction in competition with combination with nitroxide (Scheme 2). Unstabilized alkyl radicals (e.g., methyl) have been observed to partition between olefin and nitroxide in this manner in experiments with other vinyl monomers including methyl acrylate [9], methyl methacrylate [23], and acrylonitrile [23]. Kinetic arguments also support this hypothesis. Rate constants for the combination of alkyl radicals with nitroxides have been found [24-26] to lie within the range 10^8-10^9 M^{-1} s^{-1} while the rate constant for the addition of the radical 3a to styrene should be ca. 10^5 $M^{-1}s^{-1}$; similar to that for 5-hexenyl ($k \sim 1.5 \times 10^5$ M^{-1} s^{-1} at 69°C) [27] and methyl ($k \sim 1 \times 10^5$ M^{-1} s^{-1} at 65°C) [28]. Thus, with a styrene concentration of 8.6 M and an initial nitroxide concentration of 0.005 M,

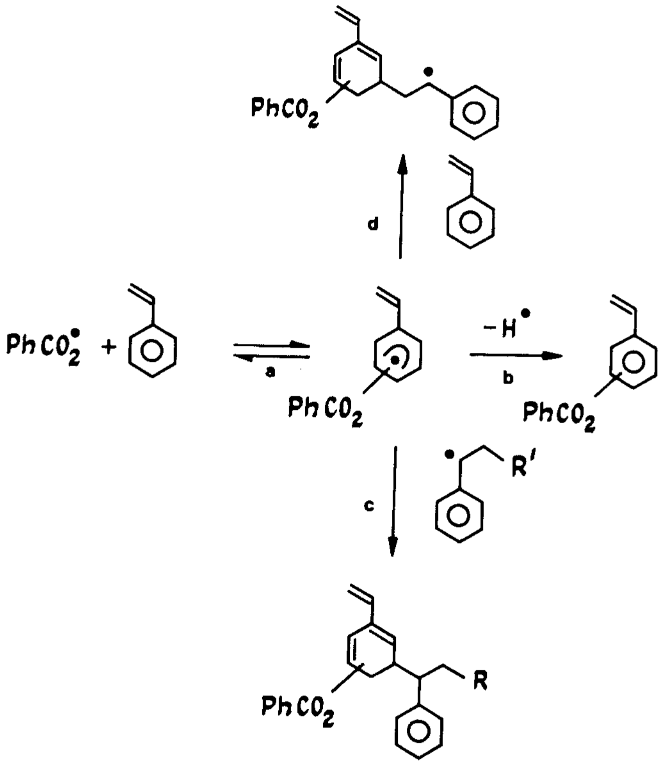


SCHEME 2. R = $PhCO_2$.

the rates of both reactions (the reaction of 3a with styrene and with nitroxide) should be of the same order of magnitude. On the other hand, the rate constant for addition of the benzylic radicals 2a and 2b to styrene should be similar to that for polystyryl radical (k ~2 × 10^2 M^{-1} s^{-1} at 60°C) [28]. It is not surprising, therefore, that the addition of these radicals (2a, 2b) to styrene cannot compete with the trapping reaction even at low nitroxide concentration (0.005 M).

The low yield of the phenyl radical derived products (7b-11b) and problems associated with determining the phenoxyamine (12) render their quantitation difficult. Nevertheless, it is possible to state that ca. 5% of benzoyloxy radicals decarboxylate to give phenyl radicals. Radiochemical studies [29, 30] show that a similar number of phenyl vs benzoyloxy end groups are present in benzoyl-peroxide-initiated polystyrene. Phenyl radicals, like benzoyloxy radicals, add to the aromatic ring of styrene albeit to a lesser extent (ca. 1% relative to double bond addition). The reactions of phenyl radicals with styrene are currently being studied using alternate initiators.

In a preliminary experiment aimed at ascertaining the significance of the aromatic substitution reaction under polymerization conditions (i.e., in the absence of nitroxide), benzoyl peroxide (1% w/v) was decomposed in 10% styrene in benzene at 80°C. The reaction was stopped after ca. 50% conversion (based on the yield of isolated polymer) and ca. 20% utilization of initiator (based on the known [31] decomposition rate of benzoyl peroxide). The low molecular weight material from the polymerization was analyzed by GCMS to show a ca. 1% yield (based on benzoyl peroxide consumed) of aromatic substitution products comprising benzoyloxystyrenes (7a-11a), vinylbiphenyls (9b-11b), phenyl benzoate, and biphenyl in the ratio



SCHEME 3.

3:7:27:63. The high ratio of phenyl radical vs benzoyloxy radical derived products observed in this experiment as compared to that in the presence of nitroxide can be ascribed to the fact that while aromatic substitution by benzoyloxy radical is readily reversible, that by phenyl radical is essentially irreversible [21, 22]. It is notable that the yield of 9a-11a relative to phenyl benzoate is, within the limits of experimental error, the same as that observed in the presence of nitroxide (cf. Table 1), allowing for the fact that some of 9a-11a may have been incorporated into the polymer.

The four most likely reaction pathways available to a vinylcyclohexadienyl radical in the absence of nitroxide are summarized in Scheme 3. These are: (a) reversion to styrene and the initiating radical, (b) oxidation to a substituted styrene derivative, (c) reaction with another radical species by combination, and (d) initiation of polymerization by addition to styrene. Processes (a) and (b) are established by the experiments described in this report. It will be noted that, in the absence of nitroxide, the most likely oxidants for participation in Process (b) are radical species—namely the initiating radicals and polystyryl radical—and possibly benzoyl peroxide. Thus Process (b), in addition to affording a substituted styrene derivative that can be incorporated into a polymer chain, can terminate a polymer chain by hydrogen atom transfer. Available data on the reactivity of cyclohexadienyl radicals [21, 22, 32-34] suggest that Processes (c) and (d) have a lower probability. Nevertheless, even if these processes occur only to a small extent they are of significance in that they lead to the formation of a highly reactive vinylcyclohexadienyl end group. The unsaturated end group would be reactive toward free radicals and could be involved in a chain branching reaction particularly if the polymerization is taken to high conversion. In the finished polymer the cyclohexadienyl group would be immediately susceptible to autoxidation [35]. Finally it should be noted that any aromatic solvent used for the polymerization can be involved in processes analogous to those described above and in Scheme 3.

It will be evident from the preceding discussion that benzoyl-peroxide-initiated polystyrene will incorporate a number of "abnormal" groups arising via nonselectivity in the initiation process. In this context it is of interest to note that polystyrene formed using benzoyl peroxide is recognized [5] to have a number of adverse properties which are not found in polystyrene produced with alternate initiators. The present findings may provide an explanation for these observations.

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