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## Initiation Pathways in the Polymerization of Alkyl Methacrylates with tert-Butoxy Radicals

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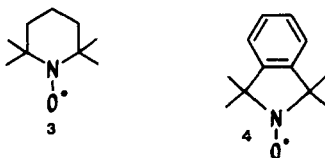
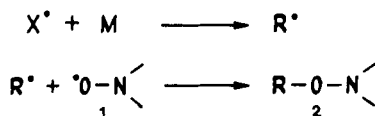
### ABSTRACT

Tert-butoxy radicals, derived from the thermal decomposition of di-tert-butyl peroxalate at 60°C, react with methyl, ethyl, and n-butyl methacrylate by double-bond addition and by hydrogen abstraction from the  $\alpha$ -methyl and ester alkyl functions. The proportion of each of these processes, as well as the fraction of tert-butoxy radicals that fragment to give methyl radicals, has been determined by analysis of the products that result on trapping the transient carbon-centered radicals with 1,1,3,3-tetramethylisindoline-2-oxyl.

### INTRODUCTION

Recently, we have described a new technique for investigating the mechanism of initiation of radical-induced polymerization and have demonstrated its value by defining the reactions of tert-butoxy radicals with methyl acrylate [1]. The method relies on the fast reaction of stable nitroxides (1) with carbon-centered radical species ( $R'$ ) ( $k = 10^6 - 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) [2-5] to inhibit the propagation step of vinyl polymerization ( $k = 10 - 10^4 \text{ M}^{-1} \text{ s}^{-1}$ ) so that information about the

interactions of the initiating radicals ( $X^\bullet$ ) and single monomer units ( $M$ ) can be obtained in the form of stable isolable products (alkoxyamines; 2).



This approach is not limited to the study of the reactions of monomers with radicals that do not themselves couple with nitroxide, e.g., oxygen-centered radicals. It also can be used to examine the behavior of carbon-centered radicals that are sufficiently reactive toward monomer to escape complete trapping by low concentrations of nitroxide, e.g., poorly stabilized alkyl radicals (see text).

In our earlier investigation [1] we employed the readily accessible 2,2,6,6-tetramethylpiperidine-1-oxyl (3) as the radical trapping agent. However, in order to resolve complex mixtures of alkoxyamines (2) by HPLC, it would be a distinct advantage if the trapping agent contained a detectable UV chromophore, since in many cases both the initiator and monomer derived fragments are transparent in the usable region of the UV. For this reason we have synthesized and made use of a new radical trap, namely 1,1,3,3-tetramethylisoindoline-2-oxyl (4), and have extended our studies of the tert-butoxy radical to its reaction with methyl, ethyl, and n-butyl methacrylate. The results that were obtained are described in this publication.

## EXPERIMENTAL

1,1,3,3-Tetramethylisoindoline-2-oxyl (4) (mp 128–129°C,  $\lambda_{\text{max}}$  435 nm in hexane) was prepared by oxidation of 1,1,2,3,3-pentamethylisoindoline [6] with hydrogen peroxide-sodium tungstate-Trilon B in acetone, a procedure used previously for the oxidation of other tertiary amines [7]. Di-tert-butyl peroxalate was prepared by the reaction of tert-butyl hydroperoxide with oxalyl chloride in the presence of pyridine [8]. All monomers were used immediately after purification by fractional distillation at reduced pressure.

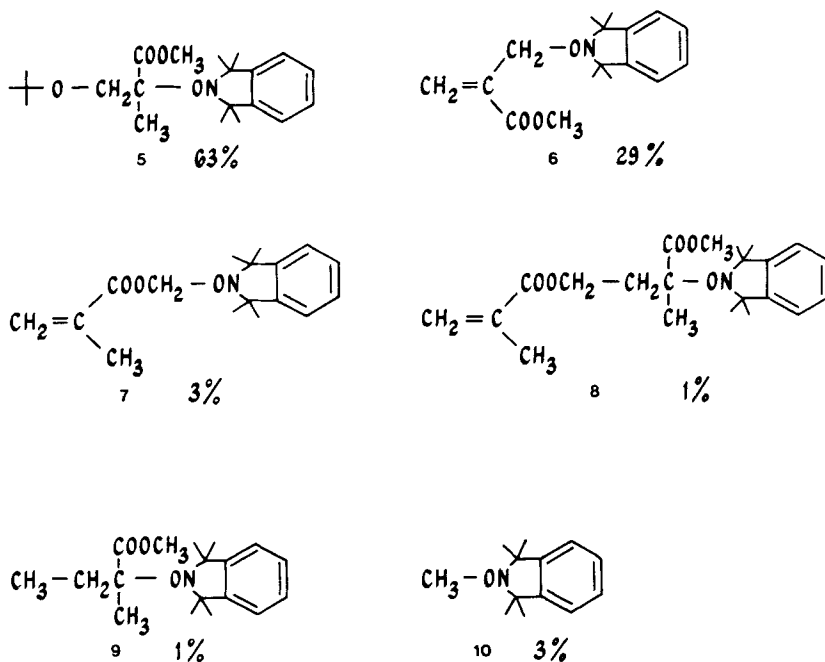


FIG. 1. Products from the reaction of tert-butoxy radicals with MMA in the presence of nitroxide 4 at 60°C.

Solutions of di-tert-butyl peroxalate (0.234 g, 1 mmol) and nitroxide 4 (0.418 g, 2.2 mmol) in monomer (50 mL) were degassed by repeated freezing and thawing on a vacuum line, sealed in vacuo, and heated at 60 ± 1°C for 1.25 h. The resulting solutions were analyzed on a Du Pont 850 HPLC instrument, using a Zorbax ODS column (6.2 mm × 25 cm) coupled to a Du Pont variable UV detector set at 270 nm and LDC 308 computing integrator. Ethanol-water mixtures were used as the eluents. Preparative isolations were performed on the same HPLC system after removal of the monomer at reduced pressure and each of the products was characterized by analytical and spectral data. UV spectroscopy (Cary 219) was used to confirm that nitroxide 4 did not react with any of the monomers at 60°C during several hours. It was also confirmed that products 5-10 had identical molar extinction coefficients at 270 nm so that the peak areas in the HPLC chromatogram reflected accurately the relative proportion of each in the mixture.

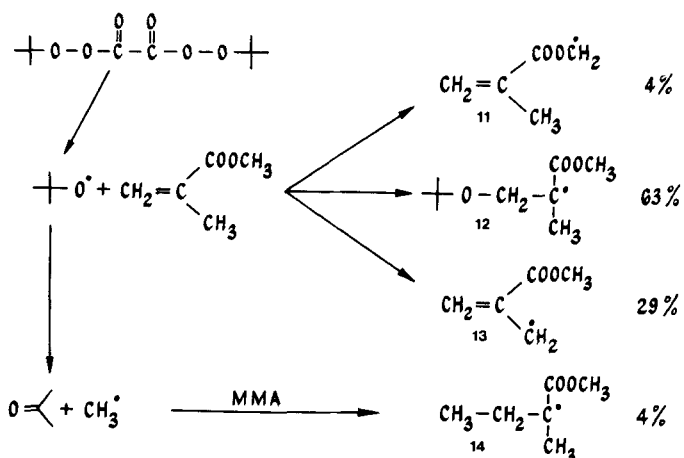


FIG. 2. The reactions of tert-butoxy radicals with MMA at 60°C.

## RESULTS AND DISCUSSION

The decomposition of di-tert-butyl peroxalate in methyl methacrylate (MMA) in the presence of a slight excess of 1,1,3,3-tetramethylisindoline-2-oxyl (4) at 60°C gave rise to a mixture of the six alkoxyamines (5-10) shown in Fig. 1. These products can be clearly translated into the series of reaction pathways outlined in Fig. 2 for the initiation of MMA polymerization by tert-butoxy radicals. The expected product (5), derived from tert-butoxy radical addition to monomer and coupling of the resulting radical (12) with nitroxide, accounts for only 63% of the total. Of major significance to the polymer chemist is the extent of hydrogen abstraction from monomer. Hydrogen abstraction from the allylic position of MMA gives rise to radical 13 which in the presence of nitroxide 4 manifests itself as product 6 (in 29% yield). This implies that a poly(methyl methacrylate) obtained via tert-butoxy radical initiation will most likely contain a large proportion of unsaturated end groups and these are well known to be deleterious to the stability of the polymer [9]. Radical 13 could become incorporated into the polymer either by initiation or termination of chains. The proposition that an allylic radical such as 13 could initiate polymer chains is not unreasonable in view of the known copolymerization of butadiene with MMA [10].

Of equal significance is the formation of radical 11 by hydrogen abstraction from the ester methyl group. Although this is a minor

process (4%) in the case of MMA,\* it has important implications in a consideration of the structure of the final polymer since it suggests that hydrogen abstraction could also take place from the ester alkyl groups of poly(methyl methacrylate) during MMA polymerizations initiated by tert-butoxy radicals. This would result in chain branching of the polymer, especially in polymerizations carried to high conversion.

A recent investigation [ 11] has confirmed the ability of tert-butoxy radicals to abstract hydrogen atoms from poly(alkyl methacrylate) albeit at a lower rate than from monomeric model compounds. These results, however, have only limited applicability since they cannot be readily applied to a polymerizing system where both polymer and monomer are present simultaneously. The question of most interest is whether hydrogen abstraction from polymer can compete with the overall reaction of tert-butoxy radicals with monomer and thus lead to chain branching. Experiments designed to test this possibility are now underway in our laboratories.

Radical 11 is sufficiently reactive toward MMA to partition between coupling with the nitroxide to give product 7, and addition to monomer to yield ultimately the trapped product 8 (Fig. 1). Formation of 8 clearly demonstrates the ability of radical 11 to initiate MMA polymerization. The incorporation of radicals of types 11 and 13 as end groups in polymer chains raises the possibility of chain branching by way of copolymerization of monomer with preformed polymer. This process could be of considerable importance in the polymerization of n-butyl methacrylate with tert-butoxy radicals where more than 50% of the initiation, at 60°C, could be induced by unsaturated entities.

In each of the experiments with the alkyl methacrylates we have identified products of the methyl radical which is formed by fragmentation of the tert-butoxy radical [ 12]. The methyl radical, like radical 11, partitions between monomer and nitroxide and with MMA, for example, gives rise to products 9 and 10. The proportion of methyl radical products remains essentially constant (3-4%) for the series methyl, ethyl, and n-butyl methacrylate, indicating a similarity in the rates of reaction of these monomers with the tert-butoxy radical. By way of contrast, the reaction of tert-butoxy radicals with acrylonitrile yields a much larger proportion (19%) of methyl radical products while with styrene as the substrate, methyl radical products are produced only in trace amounts. This clearly places the reactivity

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\*For ethyl methacrylate, 15% of the reaction products have been shown to result from hydrogen abstraction at the ethyl group, while for n-butyl methacrylate, 40% of the trapped radicals are as yet not fully characterized but appear to arise predominantly, if not exclusively, by hydrogen abstraction from the n-butyl group. The various reaction pathways of these monomers with the tert-butoxy radical will be described in more detail in a subsequent full paper.

of these monomers toward the electrophilic tert-butoxy radical in the order styrene > alkyl methacrylate > acrylonitrile and may reflect inter alia the decreasing nucleophilicity of the monomers [13].

In conclusion, it is evident from the results of this investigation that a single free-radical initiator is capable of inducing vinyl polymerization by a multitude of pathways, each of which introduces a different end group into the polymer chain. Since these end groups are chemically distinct from the repeating unit of the polymer backbone, it follows that they have the potential of modifying the properties and working life of the final product, keeping in mind that polymer degradation (thermal, photochemical, oxidative, etc.) is often a chain or autocatalytic process that begins at the most susceptible link in the polymer chain.

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