Initiation Mechanisms for Radical Polymerization of Methyl Methacrylate with *tert*-Butyl Peroxypivalate

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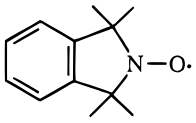
Abstract: The reaction of *tert*-butyl peroxypivalate (**2**) with methyl methacrylate (**3**) has been studied by the radical trapping technique employing 1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindol-2-yloxyl (**1**) as a scavenger. Thermolysis of **2** generated *tert*-butoxyl, *tert*-butyl, and methyl radicals in the ratios of 48:50:2 at 60 °C in **3**. Both alkyl radicals underwent selective tail addition to **3**. *tert*-Butyl radicals reacted about twice as fast as methyl radicals with **3**. The absolute rate constant for addition of *tert*-butyl radicals to **3** was estimated to be 2.3×10^6 M^{-1} s^{-1} at 60 °C. The overall ratio of addition to H abstraction in the reaction of **2** with **3** was 5:1.

Introduction

The initiation process in free radical polymerization plays an important role in determining polymer properties such as stability, molecular weight distribution, and composition.[1] In particular, initiator-derived end groups can have profound effects on the stability of the polymer toward thermal and/or photochemical degradation. The radical trapping technique developed by the CSIRO,[2] employing the nitroxide **1** as radical scavenger,



1 ≡ $R_2NO\cdot$ (T)

has been used extensively to elucidate initiation mechanisms in free radical polymerization. Most early work involved the reaction of oxygen-centered radicals, that is, *tert*-butoxyl,[2,3] benzoyloxyl,[4,5] isopropoxycarbonyloxyl,[5] cumyloxyl,[6] hydroxyl,[7] isopropoxyl,[8] and ethoxyl radicals[9] with monomer, since this technique is based on the fact that **1** reacts with carbon-centered radicals at almost diffusion-controlled rates[10] but not with oxygen-centered radicals.

However, there have been some observations of nitroxide trapped products arising from reactions of carbon-centered radicals (e.g., methyl radicals generated by β-scission of *tert*-butoxyl radicals, phenyl radicals[11] from decarboxylation of benzoyloxyl radicals, and solvent-derived carbon-centered radicals[12]), with monomer. More recently, we have reported the reaction of "second generation" carbon-centered radicals,[13] phosphorus-centered radicals,[14] and sulfur-centered radicals[15] with monomer followed by trapping by **1**. Thus we have shown that the radical trapping technique can also be used to study reactions of radicals other than oxygen-centered ones with monomer.

The work described in this paper is part of an ongoing investigation of the reaction of a combination of *tert*-alkoxyl radicals and alkyl radicals (generated by the thermolysis of *tert*-alkyl peroxypivalates) with monomers. This paper reports the results of a study of the reaction of *tert*-butyl peroxypivalate (**2**) with methyl methacrylate (**3**) in the presence of the nitroxide **1**. In the radical polymerization of acrylates and methacrylates, **2** is a widely used commercial initiator.[16] However, no reports

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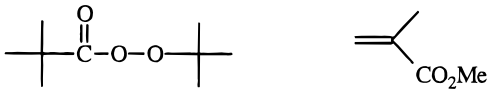
regarding the mechanism of initiation by **2** have been published.

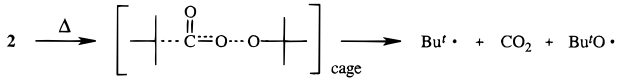


2 **3**

Results and Discussion

Initially the thermolysis of **2**, both in the presence and in the absence of **1**, was carried out in the absence of monomer in order to test for the possible induced decomposition of **2** by **1**. It has been reported that **1** catalyzed the decomposition of certain organic peroxides (e.g., diacylperoxides[5,17] and peroxydicarbonates[5]). The decomposition of **2** in cumene at 60 °C, measured by monitoring its disappearance by HPLC, satisfied first-order kinetics. The rate constant in the presence of **1**, 2.66×10^{-5} s^{-1}, was consistent with that in the absence of **1** ($k = 2.67 \times 10^{-5}$ s^{-1}) and also with the literature value, ($k = 2.70 \times 10^{-5}$ s^{-1}).[18] This clearly indicates that **1** does not influence the thermal decomposition of **2**. The initiator **2** is known to generate equimolar amounts of the two radicals via concerted two-bond scission in a solvent, such as cumene (Scheme 1).[18,19]

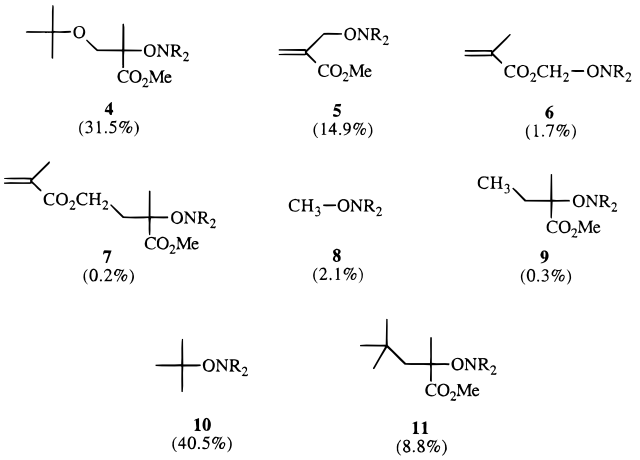
Scheme 1



Following the reaction of initiator **2** (0.040 M) with methyl methacrylate (**3**) as solvent in the presence of **1** (0.080 M) at 60 °C in vacuo, the reaction mixture was analyzed by HPLC and HPLC-MS. Alkoxyamines **4**−**11** (Chart 1) were formed in the relative percentage yields as shown. As expected, alkoxyamine **4** was the major product derived from *tert*-butoxyl radical addition to methyl methacrylate, **8** and **9** were minor products derived from methyl radical direct trapping and addition, respectively, and **10** and **11** were the products derived from competitive trapping and addition of *tert*-butyl radicals.

Products **5**, **6** and **7** are products formed by hydrogen abstraction from **3**, followed by trapping (**5** and **6**) or further monomer tail addition and trapping (**7**). In a separate experiment, diacetyl peroxide was used as initiator to provide an exclusive source of methyl radicals. The only products formed were alkoxyamines **8** (78%) and **9** (22%). Thus **3** undergoes negligible H-abstraction by methyl radicals. In a further separate experiment, di-*tert*-butyl peroxyoxalate was used as initiator to provide a major source of *tert*-butoxyl radicals. Products **4**−**9** were all observed; the ratios of the abstraction products to the main tail addition product **4** are compared with the corresponding products from the reaction with pivalate **2** in Table 1. The close similarity of the ratios suggests that all the abstraction products from the pivalate reaction arise from *tert*-butoxyl radicals and that *tert*-butyl radicals result in negligible abstraction from **3**. The reaction selectivity (preference for addition over abstraction) of both methyl and *tert*-butyl radicals is

Chart 1



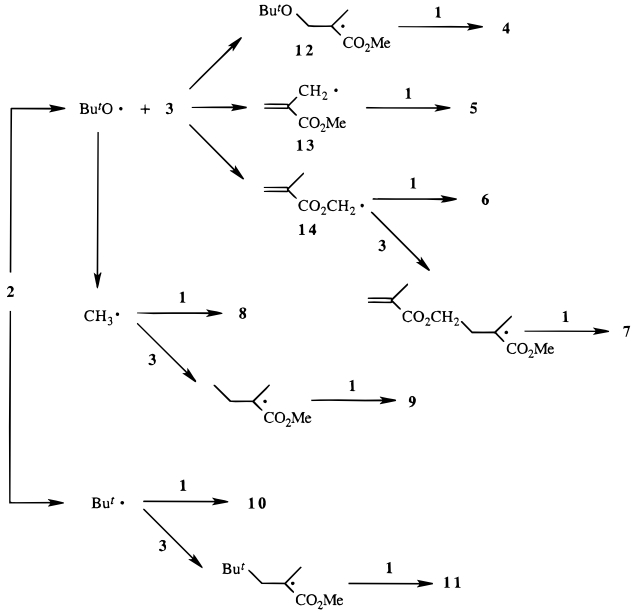
4 (31.5%) **5** (14.9%) **6** (1.7%)
7 (0.2%) **8** (2.1%) **9** (0.3%)
10 (40.5%) **11** (8.8%)

Table 1. Ratios of Abstraction Products to the Tail Addition Product of *tert*-Butoxyl Radicals and Methyl Methacrylate (4) for Two Initiators at 60 °C

	relative product yields					
initiator	**4**	**5**	**6**	**7**	**8**	**9**
DTBPO[a]	100	47.5	5.3	0.8	6.6	0.8
2[b]	100	47.1	5.4	0.7	6.7	0.8

[a] DTBPO = di-*tert*-butyl peroxyoxalate, $[DTBPO]_0 = 0.020$ M, $[\mathbf{1}]_0 = 0.088$ M, reaction time = 1.25h. [b] $[\mathbf{1}]_0 = 0.080$ M, $[\mathbf{2}]_0 = 0.040$ M, reaction time = 0.5h.

Scheme 2



therefore similar to that of cyclohexyl radicals reported by Giese et al.[20]

The range and yields of products can be adequately explained by Scheme 2. The yield of products derived from *tert*-butyl radicals (49.3%) was slightly less than that derived from *tert*-butoxyl radicals (50.7%) presumably due to partial product decomposition. A series of experiments was carried out for various times in order to test the stability of products in the reaction system. Product **11** was a prime suspect whereas the *tert*-butyl adduct **10** is expected to be stable under the reaction conditions.[10] A lower trap concentration was used to enhance the yield of **11**, which, according to Scheme 2, is formed from addition of *tert*-butyl radicals to methyl methacrylate in

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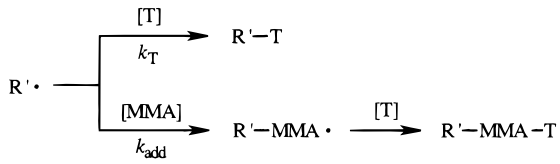
Table 2. Yields of All Products Relative to the Tail Addition Product of *tert*-Butoxyl Radicals and Methyl Methacrylate (4) at 60 °C[a]

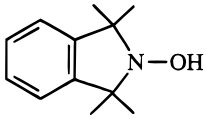
			relative product yields									
entry	$[T]_0$/M	reaction time/h	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**4**−**9**	**10** + **11**
1	0.040	0.5	100	47.1	5.0	1.3	5.9	1.5	104.2	46.6	160.8	150.8
2	0.040	1.0	100	46.9	5.0	1.4	6.0	1.4	101.1	40.4	160.7	141.5
3	0.040	2.0	100	47.2	5.0	1.5	6.0	1.6	98.1	28.9	161.3	127.0
4	0.040	3.0	100	47.7	5.0	1.6	6.0	1.6	90.6	22.3	161.9	112.9
5	0.040	5.0	100	48.5	4.7	1.8	5.9	2.0	84.9	11.9	162.9	96.8
6	0.060	0.5	100	47.0	5.3	0.9	6.5	1.1	118.0	35.7	160.8	153.7
7	0.080	0.5	100	47.1	5.4	0.7	6.7	0.8	128.3	28.0	160.7	156.3
8	0.120	0.5	100	47.1	5.6	0.5	6.9	0.6	136.7	20.3	160.8	157.0
9	0.160	0.5	100	47.2	5.8	0.3	7.1	0.4	142.6	15.3	160.8	157.9

[a] $[\mathbf{2}]_0 = 0.040$ M.

Scheme 3



competition with reaction with trap. Relative product yields are shown in Table 2. The results clearly indicate that product **11** is decomposing under the reaction conditions. A blank experiment was carried out in order to test the stability of **11**. Thermolysis of **11** in methyl methacrylate in the presence of **1** and in the absence of **2** indicated the rapid decomposition of **11** (75% of **11** was decomposed after 2 h at 60 °C) to form hydroxyamine **15**. This type of decomposition has been reported previously.[21] The fact that compound **15** was not detected in the reaction products of **2** with methyl methacrylate may be due to oxidation of **15** by **2**.[21b]



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Methyl, *tert*-butyl, and acyloxymethyl radicals **14** all underwent competitive addition/trapping reactions (Scheme 3). A series of experiments was carried out for various initial concentrations of **1** in order to investigate the reactions of these alkyl radicals. The product yields, relative to the yield of the major addition product **4** (taken as 100), are summarized in Table 2. As expected, the relative amounts of *tert*-butoxyl radical-derived products was basically independent of the initial concentration of T ($[T]_0$), that is, **4**:**5**:**6** + **7**:**8** + **9** = 100:47.1:6.1:7.6. On the other hand, *tert*-butyl radical-derived products were obtained in higher yield at higher $[T]_0$ since the yield of **11** (and therefore the amount of the decomposition of **11**) was reduced relative to the formation of **10**. The ratios of products derived from competitive reactions of methyl, *tert*-butyl, and acyloxymethyl radicals **14**, should be proportional to the ratio of the concentrations of T and MMA [see eq 1, where k_{add} and

$$\frac{k_{add}}{k_T} = \frac{(R'-MMA-T)}{(R'-T)}\frac{[T]}{[MMA]} \qquad (1)$$

k_T are the general rate constants for the reaction of radical R′ with MMA and T respectively and (R′−T) and (R′−MMA−T) are the yields of these compounds relative to the yield of **4**].

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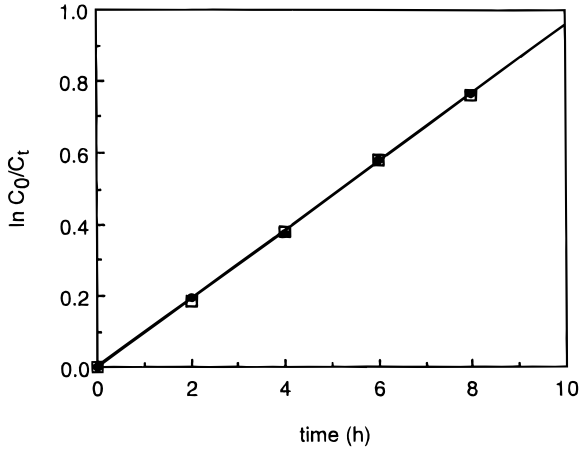

Figure 1. Thermolysis of **2** in cumene in the presence (●) and in the absence of **1** (□) at 60 °C.

The total yield of alkyl radicals, (R′•), is given by eq 2. As the conversion of pivalate is very low (half-life of **2** at 60 °C is ca. 7 h in cumene), the amounts of MMA and T consumed are very small, and these concentrations can be assumed to be constant and equal to the initial values ($[MMA]_0 = 9.1$ M at 60 °C[6] and $[T]_0$ as shown in Table 2). Therefore, according to eq 3 (derived from eqs 1 and 2), the plot of 1/(R′−T) vs $1/[T]_0$ should be linear with 1/(R′•) as the intercept.

$$(R'^{\bullet}) = (R'-T) + (R'-MMA-T) \qquad (2)$$

$$\frac{1}{(R'-T)} = \frac{k_{add}[MMA]_0}{k_T(R'^{\bullet})}\frac{1}{[T]_0} + \frac{1}{(R'^{\bullet})} \qquad (3)$$

The linear relationships, shown in Figure 2, provide strong support for the validity of the experimental data and for Scheme 2. The intercepts give the total yield of radicals based on the yields of the directly trapped radical products, R′−T, and is independent of the yields of the products R′−MMA−T. This eliminates the problem of the decomposition of **11**. The total yield of *tert*-butyl radicals is 162.9 (relative to **4** as 100), in very close agreement with the total yield of products from *tert*-butoxyl radicals (see Table 2). This shows that **2** generates equimolar amounts of the two radicals in monomer as well as in cumene.[18,19] The yields of other alkyl radicals relative to alkoxyamine **4** were also confirmed [methyl (6.1) and acyloxymethyl radical **14** (7.6) respectively]. Assuming that *tert*-butyl radicals (the yield of **11**) = (the total yield of *tert*-butoxyl radical-derived products) − (the yield of **10**), the ratios of k_{add}/k_T for methyl, *tert*-butyl, and acrylate radicals are obtained from the linear (R′−MMA−T)/(R′−T) vs $1/[T]_0$ plot according to eq 1 (shown in Figure 2).

The resulting values were 1.1×10^{-3}, 2.4×10^{-3}, and 1.2×10^{-3}, respectively, and if k_T is assumed to have the same

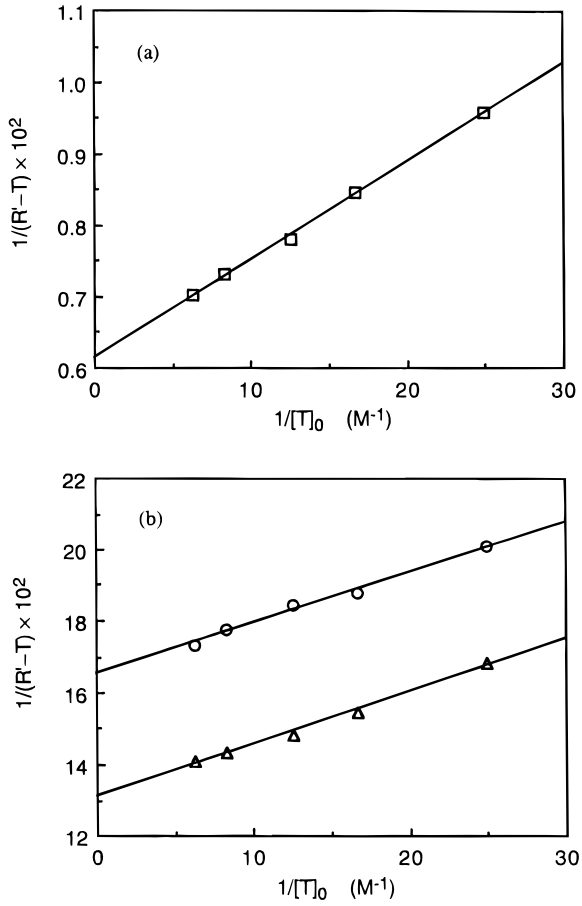

Figure 2. $1/(R'-T)$ vs $1/[T]_0$ plots for alkyl radicals. (a) *tert*-Butyl radicals (□). (b) Methyl radicals (△) and acyloxymethyl radicals **14** (○).

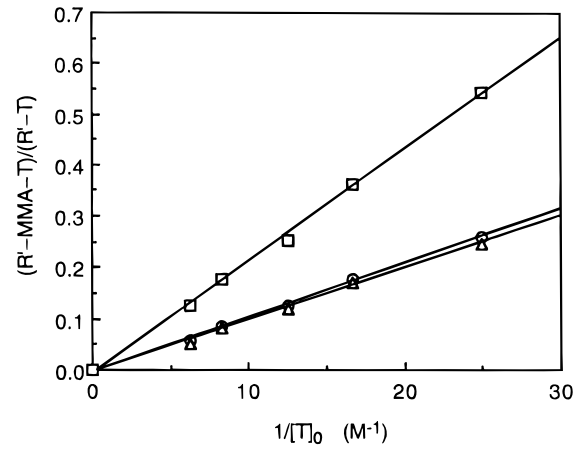

Figure 3. $(R'-MMA-T)/(R'-T)$ vs $1/[T]_0$ plots for alkyl radicals. *tert*-Butyl radicals (□), methyl radicals (△), and acyloxymethyl radicals **14** (○).

value for any carbon-centered radical,[22] the relative reactivities of the three radicals toward tail addition can be estimated as follows:

$$k_{add}(CH_3^{\bullet}):k_{add}(Bu^{t\bullet}):k_{add}(\mathbf{14}) = 1.0:2.2:1.1$$

Thus *tert*-butyl radicals add to methyl methacrylate about twice as fast as do methyl radicals.[23] On the other hand, **14** shows about the same reactivity as methyl radicals. Probably the increased steric bulk of **14** (relative to methyl radicals) is compensated by an increased nucleophilicity resulting from the α-oxygen atom. Caronna et al.[24] have reported that the relative reactivity of alkyl radicals in addition reactions to diethyl vinyl phosphonate is in the general order methyl < *n*-alkyl < *sec*-alkyl < *tert*-alkyl radicals. Also Baban et al.[25] reported that isopropyl radicals react with acrylonitrile and methyl acrylate about 7 times faster than *n*-heptyl radicals at 0 °C. From these results, Giese[26] concluded that for relatively small alkyl substituents on the carbon-centered radical, polar effects, which increase the nucleophilicity of the radical with an increasing number of alkyl groups at the radical center, are apparently more important than substituent effects on the stability of the radicals. The absolute rate constant for addition of *tert*-butyl radicals to methyl methacrylate, $k_{add}(Bu^{t\bullet})$, was also estimated to be ca. 2.2×10^6 M^{-1} s^{-1} using the value[10] of $k_T = 9.1 \times 10^8$ M^{-1} s^{-1}. This is consistent with a literature report[27] that the addition of *tert*-butyl radicals to methyl methacrylate occurs >7.6 times faster than the corresponding addition to styrene ($k = 2.3 \times 10^5$ M^{-1} s^{-1} at 60 °C).[28] Furthermore, the resulting value, $k_{add}(CH_3^{\bullet}) = 1.0 \times 10^6$ M^{-1} s^{-1} at 60 °C, agrees with the value recently reported by Zytowski et al.,[29] $k_{add}(CH_3^{\bullet}) = 4.9 \times 10^5$ M^{-1} s^{-1} at 24 °C and $E_a = 16.0$ kJ mol^{-1}.

In conclusion, in the reaction of **2** with **3**, *tert*-butyl radicals and methyl radicals generated from the thermolysis of **2** underwent selective tail addition to **3**, while *tert*-butoxyl radicals were responsible for all of the H-abstraction products. The rate constant for addition of *tert*-butyl radicals to **3** was about twice that for addition of methyl radicals and it was estimated to be 2.2×10^6 M^{-1} s^{-1} at 60 °C. About 83% of initiator-derived free radicals, that is, *tert*-butoxyl (31%), *tert*-butyl (50%), and methyl radicals (2%), underwent addition to **3**.

Experimental Section

HPLC was performed using Shimadzu LC-9A liquid chromatograph fitted with a Waters Nova-Pak C_{18}, ODS column, connected to a Shimadzu UV spectrophotometric detector set at 270 nm and a CR-6A computing integrator. Peak areas from HPLC chromatograms were converted directly into percent molar yields of products. Alkoxyamine compounds containing 1 mol equiv of the radical trapping moiety as UV chromophore have been shown to have almost identical molar extinction coefficients at 270 nm.[6]

NMR spectra were recorded on a Varian Gemini-200 (200MHz) spectrometer, using deuterated chloroform or methanol as solvent. Chemical shifts for ^{1}H NMR spectra are relative to residual C**H**Cl_3 (δ 7.24 ppm) and for ^{13}C NMR spectra are relative to the central peak of the triplet resonance due to $CDCl_3$ (δ 77.0 ppm) or the central peak of seven-line multiplet resonance due to CD_3OD (δ 49.0 ppm).

HPLC-electrospray mass spectra were obtained with a Single Quadrupole VG Platform II mass spectrometer, coupled to a MassLynx data system.

(22) Though the rate constants for nitroxide trapping of alkyl radicals by **1** were reported to be almost diffusion controlled (ca. 1×10^9 M^{-1} s^{-1}),[10] the values depend on the structure of the radicals trapped (e.g., steric protection of the radical center and resonance stability of the radical). Therefore, rate constants for radicals, **12** and **13** are likely to be lower than 10^9 M^{-1} s^{-1} (Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.*, **1992**, *114*, 4992−4996).

(23) If the trapping rate of methyl radicals is faster than that of *tert*-butyl radicals (9.1×10^8 M^{-1} s^{-1} at 18 °C),[10] this ratio becomes smaller correspondingly.

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Materials. Methyl methacrylate **3** was washed with 5% NaOH, dried over anhydrous Na_2SO_4, and distilled at atmospheric pressure. Cumene was washed with concentrated H_2SO_4, dried over anhydrous Na_2SO_4, and distilled at reduced pressure. Both solvents were stored in a refrigerator (−20 °C). *tert*-Butyl peroxypivalate (**2**) was prepared by the reaction of pivaloyl chloride with *tert*-butyl hydroperoxide in alkaline solution. **2** was 99.7% pure (iodometric titration[30]); ν_{max}(neat)/cm^{-1} 1769vs (C═O); *m*/*z* 197 (M + Na)$^+$, 175 (M + H)$^+$. Acetyl peroxide was prepared by the reaction of acetic anhydride with hydrogen peroxide in the presence of sodium carbonate.[31] Di-*tert*-butyl peroxyoxalate,[32] nitroxide **1**,[33] and hydroxyamine **15**[8] were prepared by literature procedures.

Kinetic Experiment. *Thermolysis of **2** in the Presence of **1** in Cumene*. Cumene solutions (5 mL) containing **2** (0.05 M) and **1** (0.11 M) were placed in glass ampules, which were purged with nitrogen, sealed, and immersed in a constant temperature bath regulated at 60 °C. At successive time intervals, ampules were removed from the bath. The concentration of peroxide in each solution was measured by HPLC (at 250 nm). The reaction was followed up to 50% decomposition and exhibited first-order kinetics.

Trapping Experiments. *Typical Procedure for Reaction of **2** with **3** in the presence of **1***. A solution of **2** and **1** in freshly distilled **3** was degassed by repeated freezing and thawing (three cycles) on a vacuum line (<10^{-4} mmHg). The reaction vessel was then sealed under vacuum and heated at 60 ± 0.1 °C for 0.5 h. Excess of monomer was then removed by distillation under reduced pressure prior to analysis by reverse phase HPLC with methanol/water mixtures as the eluent. The HPLC separated products were identified by electrospray mass spectrometry. The new compound (alkoxyamine **11**) and some known compounds (**4**, **9**, and **10**) were isolated by preparative HPLC and characterized by the NMR data listed below (NMR data not previously reported).

*Methyl 3-tert-butoxy-2-methyl-2-(1,1,3,3-tetramethyl-2,3-dihydro-1H-isoindol-2-yloxy)propanoate[3a] (**4**).* ^{1}H NMR ($CDCl_3$) δ 7.26−7.19 (2H), 7.12−7.06 (2H), 3.77 (s, 3H), 3.67 (d, J = 8.2 Hz, 1H), 3.45 (d, J = 8.2 Hz, 1H), 1.58 (s, 3H), 1.49 (s, 3H), 1.40 (s, 3H), 1.36 (s, 6H), 1.19 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 174.0, 145.2, 145.0, 127.2, 121.6, 84.2, 73.1, 68.1, 67.9, 67.0, 51.7, 29.5, 27.5, 25.6, 25.3, 18.8; *m*/*z* 386 (M + Na)$^+$, 364 (M + H)$^+$.

*Methyl 2-[(1,1,3,3-tetramethyl-2,3-dihydro-1H-isoindol-2-yloxy)-methyl]propenoate[7] (**5**).* *m*/*z* 312 (M + Na)$^+$, 290 (M + H)$^+$, 258 (M − MeO)$^+$.

*(1,1,3,3-Tetramethyl-2,3-dihydro-1H-isoindol-2-yloxy)methyl 2-Methylpropenoate[7] (**6**).* *m*/*z* 312 (M + Na)$^+$, 290 (M + H)$^+$.

*3-Methoxycarbonyl-3-(1,1,3,3-tetramethyl-2,3-dihydro-1H-isoindol-2-yloxy)butyl 2-methylpropenoate[3a] (**7**).* *m*/*z* 412 (M + Na)$^+$, 390 (M + H)$^+$.

*2-Methoxy-1,1,3,3-tetramethyl-2,3-dihydro-1H-isoindole[6,34] (**8**).* *m*/*z* 206 (M + H)$^+$.

*Methyl 2-Methyl-2-(1,1,3,3-tetramethyl-2,3-dihydro-1H-isoindol-2-yloxy)butanoate[3a] (**9**).* ^{1}H NMR ($CDCl_3$) δ 7.26−7.19 (2H), 7.13−7.06 (2H), 3.77 (s, 3H), 2.20−1.72 (m, 2H), 1.53 (s, 3H), 1.47 (s, 3H), 1.44 (s, 3H), 1.36 (s, 3H), 1.34 (s, 3H), 0.95 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 175.3, 145.5, 144.8, 127.3, 127.2, 121.6, 121.5, 84.7, 67.9, 67.8, 51.7, 33.3, 29.7, 29.5, 25.7, 25.0, 20.0, 8.9; *m*/*z* 328 (M + Na)$^+$, 306 (M + H)$^+$.

*2-tert-Butoxy-1,1,3,3-tetramethyl-2,3-dihydro-1H-isoindole[7] (**10**).* ^{1}H NMR ($CDCl_3$) δ 7.27−7.20 (2H), 7.15−7.09 (2H), 1.51 (s, 6H), 1.34 (s, 6H), 1.32 (s, 9H); ^{13}C-NMR (CD_3OD) δ 146.7, 128.2, 122.7, 77.5, 69.2, 31.3, 29.8, 26.2; *m*/*z* 248 (M+H)$^+$.

*Methyl 2,4,4-Trimethyl-2-(1,1,3,3-tetramethyl-2,3-dihydro-1H-isoindol-2-yloxy)pentanoate (**11**).* ^{1}H NMR ($CDCl_3$) δ 7.26−7.19 (2H), 7.12−7.06 (2H), 3.75 (s, 3H), 2.08 (d, J = 14Hz, 1H), 1.76 (d, J = 14 Hz, 1H), 1.62 (s, 3H), 1.46 (s, 3H), 1.45 (s, 3H), 1.35 (s, 3H), 1.32 (s, 3H), 0.98 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 175.6, 144.6, 127.3, 127.1, 121.7, 121.5, 83.8, 67.7, 53.9, 51.5, 30.8, 30.5, 29.8, 29.3, 29.2, 26.1, 25.0, 22.5; *m*/*z* 370 (M + Na)$^+$, 348 (M + H)$^+$. Note that compound **11** was unstable and partially decomposed during the running of the ^{13}C NMR spectrum.

Reaction of Methyl Radicals with 3 in the Presence of 1. A solution of diacetyl peroxide (0.20 M) with **3** in the presence of **1** (0.050 M) was reacted at 60 °C for 3 h in the same manner as above.

Reaction of *tert*-Butoxyl Radicals with 3 in the Presence of 1. The reaction of di-*tert*-butyl peroxyoxalate (0.020 M) and **3** in the presence of **1** (0.088 M) was carried out at 60 °C for 1.25 h in the same manner as above.

Thermolysis of 11 in the Presence of 1. A MMA solution of **11** (0.030 M) and **1** (0.040 M) was heated at 60 °C for 2 h in the same manner as above. The resulting solution was concentrated and followed by HPLC analysis (alkoxyamine **10** was used as an internal standard).

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