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Initiation Mechanisms in Radical Polymerization: Reaction of *tert*-Alkyl Peroxypivalates with Methyl Methacrylate

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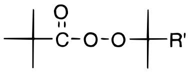
ABSTRACT: The reactions of *tert*-pentyl peroxypivalate (**1b**) and *tert*-hexyl peroxypivalate (**1c**) with methyl methacrylate (MMA) in the presence of the free radical scavenger 1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindol-2-yloxyl (**2**) have been studied at 60 °C. *tert*-Pentyloxyl radicals (**3b**) and *tert*-hexyloxyl radicals (**3c**) were formed in the thermolysis of **1b** and **1c**. The major reaction pathways of the alkoxyl radicals were β-scission and rearrangement (1,5-H shift) to generate alkyl radicals, which occurred to the extent of 83% (**3b**) and 90% (**3c**), respectively. The resulting alkyl radicals underwent selective addition to MMA. The overall ratios of addition to H-abstraction in the reactions of **3b** and of **3c** with MMA were 13:1 and 24:1, respectively. From the competitive addition/trap reactions of alkyl radicals, relative reactivities of alkyl radicals toward addition to MMA were in the ratio: Et$^\bullet$:n-Pr$^\bullet$:4-hydroxy-4-methylpentyl radical:Bu$^{t\bullet}$ = 0.39:0.48:0.51:1.00.

Introduction

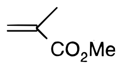
The use of alkoxyl radicals to initiate polymerization can involve significant hydrogen abstraction and, consequently, can lead to unsaturated end groups. Such end groups can have profound effects on the stability of the polymer toward thermal or photochemical degradation and on polymer properties such as molecular weight distribution and composition.[1−4] Previous work from our laboratories has shown that the extent of hydrogen abstraction generally increases with the steric bulk of the alkoxyl radical. Thus, the ratio of hydrogen abstraction from methyl methacrylate (MMA) versus addition to MMA increases from 1:11 to 1:7 to 1:2 for the series ethoxyl,[5] isopropoxyl,[6] and *tert*-butoxyl[7] radicals, respectively. This suggests that *tert*-alkoxyl radical initiation can lead to a considerable proportion of unsaturated end groups in the resulting poly(MMA). As part of an on-going study into the initiation process in free radical polymerization, we wished to investigate the use of *tert*-alkoxyl radicals of higher steric demand than *tert*-butoxyl. Such alkoxyl radicals were expected to undergo faster β-scission to produce alkyl radicals which are known to abstract from alkanes at much lower rates than alkoxyl radicals. For example, the absolute rate constants for hydrogen abstraction from toluene by *tert*-butoxyl radicals[8] and n-dodecyl radicals[9] have been reported to be 2.3×10^5 dm^3 mol^{-1} s^{-1} at 295 K and 3.6×10^2 dm^3 mol^{-1} s^{-1} at 368 K, respectively. In the case of the reaction of cyclohexyl radicals with MMA, only addition was observed.[10]

In this paper, the initiation mechanisms of *tert*-pentyl peroxypivalates (**1b**) and *tert*-hexyl peroxypivalates (**1c**), which are commercial initiators used in the radical polymerization of acrylates and methacrylates[11,12] as well as the *tert*-butyl analogue **1a**, with MMA have been studied by the nitroxide radical trapping technique. The technique, employing 1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindol-2-yloxyl (**2**) as a scavenger, has been used extensively to elucidate initiation mechanisms in free radical polymerization.[13]

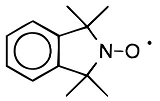


1a-c

a : R'=Me
b : R'=Et
c : R'=n-Pr



MMA



2 ≡ R$_2$NO$^\bullet$ (T)

tert-Alkoxyl radicals larger than *tert*-butoxyl radicals, i.e., *tert*-pentyloxyl radicals **3b** and *tert*-hexyloxyl radicals **3c**, formed in the thermolysis of the corresponding peroxypivalates (see Scheme 1) are known to be susceptible to β-scission to form a ketone and alkyl radicals at a significant rate in CCl$_4$.[14] The resulting alkyl radicals are poor in H-abstracting ability and they were expected to undergo selective addition to monomer as mentioned above. Kamath *et al.*[15] studied the polymerization of acrylic resins using *tert*-pentyl peroxides and they reported that the use of the peroxides resulted in polymers with narrower molecular weight distribution compared with the use of *tert*-butyl peroxide. This they suggested was due to the low degree of hydrogen abstraction by **3b** from both monomer and polymer molecules. However, the detailed reaction mechanisms of **3b** were not studied and there have been no reports regarding the initiation mechanisms of **3c**.

In previous work from this laboratory, we have shown[16] (i) that nitroxide **2** does not influence the thermal decomposition of **1**, (ii) that the peroxypivalate **1a** on thermolysis in MMA generates equimolar amounts of *tert*-butyl radicals and *tert*-alkoxyl radicals **3a** (Scheme 1), and (iii) that *tert*-butyl radicals undergo negligible H-abstraction from MMA; all abstraction products are formed exclusively from abstraction by the alkoxyl radicals.

Results

Reaction of *tert*-Pentyl Peroxypivalate (1b) with MMA. The thermal decomposition of **1b** (0.040 mol dm^{-3}) with MMA as a solvent in the presence of the trap **2** (0.040 mol dm^{-3}) was carried out *in vacuo* at 60 °C

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Scheme 1

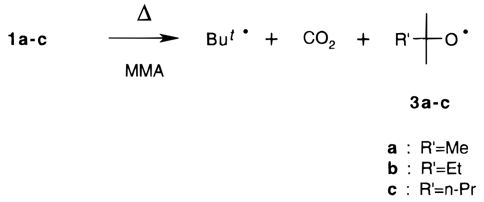
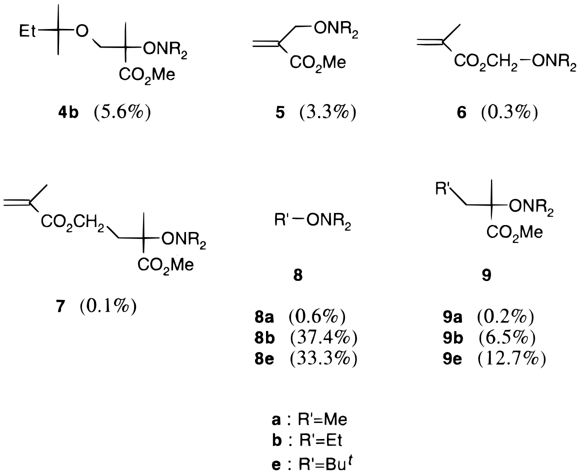


Chart 1

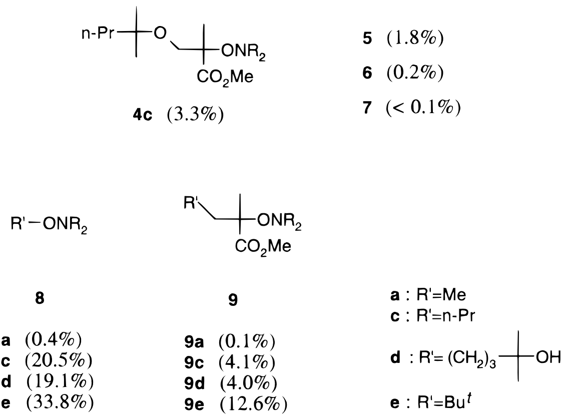


for 1 h. A relatively low concentration of **2** was used in order to study the (competitive) reaction of alkyl radicals with MMA (shown below). However, under the conditions of the reaction, **2** is still present in excess because of the low conversion (<15%) and the <100% efficiency of generation of radicals from **1**.[12] Alkoxyamines formed by trapping of the carbon-centered radicals derived from the initiators or of the radicals resulting from the reactions of initiator-radicals with MMA, were analyzed by high-performance liquid chromatography (HPLC), high-performance liquid chromatography/mass spectrometry (HPLC/MS), and nuclear magnetic resonance (NMR). Alkoxyamines **4b** and **5**−**9** were formed in the relative percentage yields as shown in Chart 1.

Alkoxyamine **4b** was derived from the addition of the *tert*-pentyloxyl radical **3b** to MMA (followed by trapping), and alkoxyamines **8** and **9** were the products derived from the corresponding alkyl radicals (Me•, Et•, and Bu^t•). Methyl and ethyl radicals were formed by β-scission of **3b**. These alkyl radicals and *tert*-butyl radicals, formed directly by the thermolysis of **1b**, were immediately trapped by **2** to form **8** or underwent competitive addition to MMA followed by trapping to give **9**. Alkoxyamines **5**−**7** are products formed by hydrogen abstraction from MMA, followed by trapping (**5** and **6**) or further monomer tail addition and trapping (**7**). We have previously shown that under these conditions, methyl and Bu^t radicals undergo negligible abstraction reactions with MMA. A separate reaction, in which propionyl peroxide was used as an exclusive source of ethyl radicals, was carried out in order to elucidate the reaction of ethyl radicals. The only products formed were alkoxyamines **8b** and **9b** (87:13), which indicated that ethyl radicals also underwent selective addition to MMA. This suggests that virtually all the abstraction products arose from *tert*-pentyloxyl radicals.

Reaction of *tert*-Hexyl Peroxypivalate (1c) with MMA. The thermal decomposition of **1c** (0.040 mol dm^{-3}) with MMA as a solvent in the presence of **2** (0.040 mol dm^{-3}) was carried out as described for **1b**. The corresponding products, that is, alkoxyamines **4c** (addition product), **5**−**7** (hydrogen abstraction products), **8a**,**c** and **9a**,**c** (alkyl radical derivatives formed via β-scission of **3c**), and **8e** and **9e** (*tert*-butyl radical derivatives) were formed (Chart 2). In addition, alkoxyamines **8d** and **9d** were detected in the reaction involving **3c**. These products were derived from 4-hydroxy-4-methylpentyl radicals **10** formed via a 1,5-hydrogen shift of **3c**. By analogy with the reactivity of ethyl radicals and other alkyl radicals[10,16] (cyclohexyl, methyl, and *tert*-butyl radicals), it is unlikely that MMA undergoes significant H-abstraction by *n*-propyl radicals or alkyl radicals **10** under these reaction conditions.

Chart 2



Discussion

Reaction of *tert*-alkoxyl radicals with MMA. Table 1 shows the relative product yields for the reaction of **1b** and **1c** together with that of **1a**, which have been normalized so that the total yield of *tert*-alkoxyl radical derivatives is 100%. The various reactions of *tert*-alkoxyl radicals in MMA are outlined in Scheme 2, while the relative proportions are summarized in Table 2. Alkoxyl radicals **3b** and **3c** underwent three modes of direct reactions with MMA analogous to that of *tert*-butoxyl radicals, that is, addition, hydrogen abstraction from allylic methyl, and hydrogen abstraction from the ester methyl groups. Slightly lower ratios of addition versus H-abstraction for **3b** (1.5:1) and **3c** (1.6:1) compared with **3a** (1.9:1) were observed in the reaction with MMA. We have previously reported that this ratio decreases in the order hydroxyl > ethoxyl > isopropoxyl > *tert*-butoxyl.[5] The present data are consistent with this trend, the reduced addition rate being largely due to increased steric hindrance.

Unimolecular Reactions of *tert*-Alkoxyl Radicals in MMA. The extent of the direct reaction of **3b** or **3c** with MMA was greatly reduced by competing fast unimolecular reactions, that is, β-scission and 1,5-H shift. The β-scission of **3a** generated only methyl radicals, resulting in alkoxyamines **8a** and **9a**. On the other hand, *tert*-pentyloxyl radicals **3b** and *tert*-hexyloxyl radicals **3c** underwent alternative β-scission, generating ethyl radicals (to form **8b** and **9b**) and *n*-propyl radicals (to form **8c** and **9c**), respectively, as well as methyl radicals. The relative scission rates of alkyl radicals from *tert*-alkoxyl radicals **3b** and **3c** can be estimated from the ratios of (**8b** + **9b**) and (**8c** + **9c**) toward (**8a** + **9a**) as follows:

$$k_\beta(\mathrm{Me}^\bullet):k_\beta(\mathrm{Et}^\bullet) = 1:116 \text{ (for } \mathbf{3b}\text{)}$$

$$k_\beta(\mathrm{Me}^\bullet):k_\beta(n\text{-}\mathrm{Pr}^\bullet) = 1:102 \text{ (for } \mathbf{3c}\text{)}$$

Table 1. Yields of All Products Relative to the Total Yield of *tert*-Alkoxyl Radical Derived Products in the Reaction of *tert*-Alkyl Peroxypivalate (1) and Methyl Methacrylate in the Presence of Nitroxide (2) at 60 °C[a]

		relative product yields (%)													
		tert-alkoxyl radical derived products												*tert*-butyl radical derived products	
expt	initiator	**4**	**5**	**6**	**7**	**8a**	**9a**	**8b**	**9b**	**8c**	**9c**	**8d**	**9d**	**8e**	**9e**
1	**1b**	10.4	6.2	0.5	0.2	1.1	0.3	69.3	12.0					61.6	23.6
2	**1c**	6.2	3.4	0.4	0.1	0.7	0.2			38.3	7.6	35.6	7.6	63.0	23.6
ref[b]	**1a**	62.2	29.2	3.1	0.9	3.7	0.9							62.9	25.1

[a] $[\mathbf{1}]_0 = 0.040$ mol dm^{-3}, $[\mathbf{2}]_0 = 0.040$ mol dm^{-3}, reaction time 1.0 h. [b] See ref 16.

Scheme 2

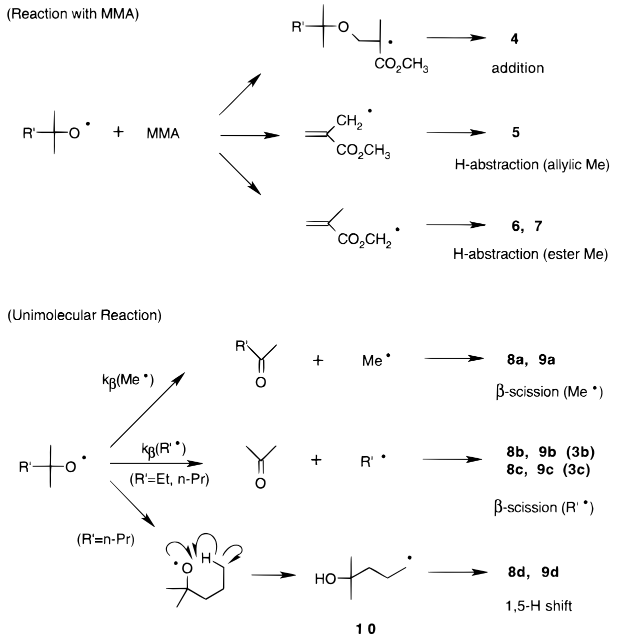
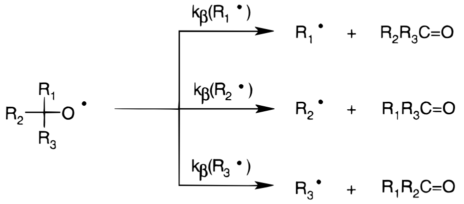


Table 2. Proportion (%) of Reactions of *tert*-Alkoxyl Radicals ($R'(CH_3)_2CO^\bullet$) with MMA (60 °C)

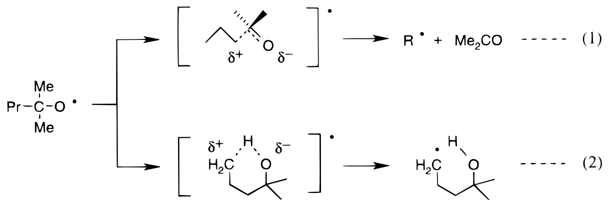
reaction mode	**3a** (R′ = Me)	**3b** (R′ = Et)	**3c** (R′ = *n*-Pr)
reactions with MMA			
addition	62.2	10.4	6.2
H-abstraction			
allylic Me	29.2	6.2	3.4
ester Me	4.0	0.7	0.5
unimolecular reactions			
β-scission			
to Me•	4.6	1.4	0.9
to R′•		81.3	45.9
1,5-H shift			43.1

Scheme 3

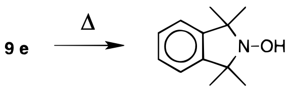


Thus, the scission rate of the alkoxyl radicals to produce ethyl or *n*-propyl radicals was over 100 times that to produce methyl radicals in MMA as solvent. Bacha and Kochi[14d] have studied the *β*-elimination of *tert*-alkoxyl radicals by carrying out the thermolysis of a series of *tert*-alkyl hypochlorites in CCl_4. The rate constant ratios for the *β*-elimination of radicals were determined from the competitive reactions as shown in Scheme 3. Their values[17] of $k_\beta(n\text{-Pr}^\bullet)/k_\beta(\text{Et}^\bullet)$ were 0.70 (R_1 = Me, R_2 = Et, R_3 = n-Pr), 0.83 ($R_1 = R_2$ = Et, R_3 = *n*-Pr), and 0.82 (R_1 = Et, R_2 = *n*-Pr, R_3 = *n*-Bu), which are close to the value determined in this work, 0.88.

Scheme 4



Scheme 5



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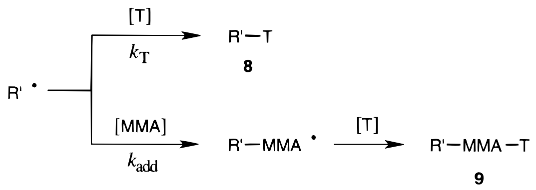
tert-Hexyloxyl radicals **3c** underwent a 1,5-H shift to form 4-hydroxy-4-methylpentyl radicals (**10**). From the ratio of the product yields [(**8c** + **9c**):(**8d** + **9d**) = 1:0.94], it can be seen that the reaction rate for the 1,5-H shift was comparable to the rate of *β*-scission to form *n*-propyl radicals. This contrasts with the behavior in CCl_4 solution reported by Walling and Padwa,[18] where the 1,5-H shift was observed as a minor pathway, i.e., $k_{1,5\text{H}}/k_\beta(n\text{-Pr}^\bullet) = 0.25$ at 40 °C. It has been pointed out, however, that free-radical chain reactions initiated by the photolysis of the *tert*-alkyl hypochlorite that these authors employed as an alkoxyl radical source showed some discrepancies[19] in comparison with the results obtained from other alkoxyl radical sources such as a peroxide decomposition. So, we reexamined the reaction of **3c** in CCl_4 using the nitroxide trapping technique. The thermolysis of **3a** in CCl_4 in the presence of **2** was carried out at 60 °C. This gave a value of $k_{1,5\text{H}}/k_\beta(n\text{-Pr}^\bullet) = 1.3$, much greater than the value reported by Walling and Padwa.[18] Thus, from the present results, a slight decrease in the ratio of $k_{1,5\text{H}}/k_\beta$ with increase in solvent polarity from CCl_4 to MMA was observed. This trend is consistent with increased stabilization of the transition state for *β*-scission by the more polar MMA (eq 1 in Scheme 4).[23] However, the relatively small change in $k_{1,5\text{H}}/k_\beta$ may indicate the possibility that polar solvents also stabilize the transition state for the 1,5-H shift (eq 2 in Scheme 4), although no significant solvent effect on intermolecular hydrogen abstraction has been reported.[23]

Thus, in contrast to **3a**, the unimolecular decomposition and rearrangement reactions to form alkyl radicals were predominant in the reactions of **3b** and of **3c** with MMA, occurring to the extent of 83% and 90%, respectively.

Reaction of Alkyl Radicals with MMA. The relative yields of *tert*-butyl radical derived products **8e** and **9e**, see Table 1, were almost independent of the substrate. Although the pivalates generate equimolar amounts of alkoxyl radicals and *tert*-butyl radicals in MMA, the total yield of *tert*-butyl radical derivatives (**8e** + **9e**) was not equal to that of alkoxyl radical derivatives (100%) due to partial decomposition of **9e** (Scheme 5), which has been shown to be converted slowly into

Scheme 6



nitroxide **2** via oxidation of hydroxyamine **11**.[16] Thus the theoretical yield of **9e** can be taken as (the total yield of *tert*-alkoxyl radical derived products (100%)) − (the yield of **8e**).

Alkyl radicals formed in the thermolysis of **1b** and **1c** underwent competitive addition/trapping reactions (Scheme 6).

The ratio of product yields **9**/**8** should be proportional to the ratio of k_{add}/k_T since the ratio of [T]/[MMA] is constant in an individual experiment, see eq 3, where k_{add} and k_T are the general rate constants for the reaction of alkyl radicals R′• with MMA and T, respectively. Thus, the values of k_{add}/k_T for ethyl, n-propyl,

$$\frac{k_{add}}{k_T} = \frac{(\mathbf{9})}{(\mathbf{8})} \frac{[\mathrm{T}]}{[\mathrm{MMA}]} \qquad (3)$$

4-hydroxy-4-methylpentyl (**10**), and *tert*-butyl radicals are in the ratios of the product yields **9b**/**8b**, **9c**/**8c**, **9d**/**8d**, and (100 − **8e**)/**8e**, respectively. The relative rate constants for tail addition of alkyl radicals (k_{add}) can be estimated by assuming that k_T for all primary alkyl radicals has the same value[24] of 1.3×10^9 dm^3 mol^{-1} s^{-1} and that the value[24] for *tert*-butyl radicals is 9.1×10^8 dm^3 mol^{-1} s^{-1}. The results in Table 1 give the following ratios:

$$k_{add}(\mathrm{Et}^\bullet):k_{add}(\mathrm{Bu}^{t\bullet}) = 0.39:1.0 \text{ (in experiment 1)}$$

$$k_{add}(n\text{-Pr}^\bullet):k_{add}(\mathbf{10}):k_{add}(\mathrm{Bu}^{t\bullet}) = 0.48:0.51:1.0 \text{ (in experiment 2)}$$

Thus, reactivities for primary alkyl radical addition to MMA are almost half of that for *tert*-butyl radicals. This trend is consistent with a literature report that the relative reactivity of alkyl radicals is in the general order *n*-alkyl < *sec*-alkyl < *tert*-alkyl radicals.[25] Absolute rate constants can be estimated by taking the value[16] of $k_{add}(\mathrm{Bu}^{t\bullet}) = 2.2 \times 10^6$ dm^3 mol^{-1} s^{-1} at 60 °C. The values for the addition of ethyl, *n*-propyl, and 4-hydroxy-4-methylpentyl radicals to MMA are *ca.* 8.6×10^5, 1.0×10^6, and 1.1×10^6 dm^3 mol^{-1} s^{-1}, respectively. These are very close to the reported value for methyl radical addition to MMA (1.0×10^6 dm^3 mol^{-1} s^{-1} at 60 °C).[16,26]

In conclusion, in contrast to **3a**, the main reacting species in the reactions of **3b** and of **3c** with MMA are not alkoxyl radicals but alkyl radicals formed by unimolecular decomposition and rearrangement reactions of the respective alkoxyl radicals. The alkyl radicals formed undergo selective addition to MMA and the relative reactivities of alkyl radicals toward addition to MMA were Et• (0.39):*n*-Pr• (0.48):4-hydroxy-4-methylpentyl radical (0.51):Bu$^{t\bullet}$ (1.0). The proportion of overall addition to MMA in the reaction with **3a**, **3b**, and **3c** is 67%, 93%, and 96%, respectively. This indicates that if **1b** or **1c** is used to initiate the polymerization of MMA, the proportion of unsaturated end groups derived from the initiation process should be much lower than if **1a** is used.

Experimental Section

General Methods. Analytical HPLC studies were carried out with a Shimadzu LC-9A liquid chromatograph fitted with either a Waters Nova-Pak C_{18} 6 μm 100 × 8 mm ODS analytical column or a Rainin Instrument Dynamax-60A 8 μm 250 × 4.6 mm C_{18} analytical column, connected to a Shimadzu UV spectrophotometric detector set at 270 nm and a CR-6A computing integrator.

Peak areas were determined by integration of HPLC chromatograms. Allowance for differing chromophores was made either by determining the extinction coefficients at 270 nm of the isolated products or by the reinjection of solutions of known concentration to assess peak response ratios for the UV detector. The adjusted peak areas were converted into relative product yields and normalized to 100%.

The reaction products were isolated using preparative reverse-phase HPLC on a Rainin Instrument Dynamax-60A 8 μm 250 × 21.4 mm C_{18} preparative column. Compounds were detected by a Soma UV detector S-310A fitted with a 1.0 mm preparative cell. Solvent flow rates were variable depending upon the methanol−water ratio and the back pressure which was kept less than 2500 psi by a Gilson 303 pump fitted with a 25 cm^3 min^{-1} preparative head and 803C manometric module.

NMR spectra were recorded on a Varian Gemini-200 (200MHz) spectrometer, using deuterated chloroform 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).

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

Materials. Methyl methacrylate was washed with 5% NaOH, dried over anhydrous Na_2SO_4 and distilled at atmospheric pressure, and then stored in a refrigerator (−20 °C). *tert*-Pentyl peroxypivalate (**1b**) and *tert*-hexyl peroxypivalate (**1c**) were prepared by the reaction of pivaloyl chloride with the corresponding alkyl hydroperoxide in alkaline solution.[12] Purity of peroxypivalates was determined by iodometric titration.[27] **1b** was 97.9% pure; ν_{max}(neat)/cm^{-1} 1768 vs (C=O); *m*/*z* 211 (M + Na)$^+$, **1c** was 96.8% pure; ν_{max}(neat)/cm^{-1} 1768 vs (C=O); *m*/*z* 225 (M + Na)$^+$. Propionyl peroxide (half-life at 60 °C = ca. 20 h (in toluene))[28] was prepared by the reaction of propionyl chloride with hydrogen peroxide in the presence of sodium hydroxide. Nitroxide **2** was prepared by the literature procedure.[29]

Trapping Experiments. Typical Procedure for Reaction of 1 with MMA in the Presence of 2. A solution of **1** and **2** in freshly distilled MMA 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 1.0 h. Excess 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. New compounds were isolated by preparative HPLC and characterized by the NMR data listed below. *J* values are given in Hz; ring CH_3 refers to methyl substituents on the isoindole.

Methyl 3-((1,1-dimethylpropyl)oxy)-2-methyl-2-(1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindol-2-yl)oxy)propanoate (4b). $\delta_{\mathbf{H}}(CDCl_3)$ 0.87 (3H, t, *J* = 7.2, CH_3CH_2), 1.14 [6H, s, $(CH_3)_2COCH_2$], 1.2−1.6 (17H, m, 4 × ring CH_3, 2-CH_3 and CH_3CH_2), 3.41 (1H, d, *J* = 8.0, OCH_2), 3.66 (1H, d, *J* = 8.0, OCH_2), 3.78 (3H, s, OCH_3), 7.1 (2H, m, 4-H, 7-H), 7.2 (2H, m, 5-H, 6-H); $\delta_{\mathbf{C}}(CDCl_3)$ 8.2 (CH_3CH_2), 18.8 (CH_3CON), 24.6, 25.2, 25.6, 29.5, and 29.7 [4 × s, 4 × ring CH_3 and $(CH_3)_2COCH_2$], 33.2 (CH_3CH_2), 51.7 (OCH_3), 66.7 (CH_2CON), 67.8 and 68.0 (C-1, C-3), 75.0 [$(CH_3)_2C$], 84.2 (CON), 121.6 (d, C-4, C-7), 127.2 (d, C-5, C-6), 144.9 (C-3a, C-7a), 174.0 (C=O); *m*/*z* 416 (M + K)$^+$, 400 (M + Na)$^+$, 378 (M + H)$^+$, 346 (M − OCH_3)$^+$.

Methyl 3-((1,1-dimethylbutyl)oxy)-2-methyl-2-((1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindol-2-yl)oxy)propanoate (4c). $\delta_{\mathbf{H}}(CDCl_3)$ 0.91 (3H, t, *J* = 6.8, CH_3CH_2), 1.13 and 1.14 [2 × 3H, 2 × s, $(CH_3)_2COCH_2$], 1.25−1.7 [19H, m, 4 ×

ring $\mathrm{CH_3}$, 2-$\mathrm{CH_3}$ and $\mathrm{CH_3(C}\mathit{H}_2)_2$], 3.41 (1H, d, $J = 8.1$, $\mathrm{OCH_2}$), 3.64 (1H, d, $J = 8.1$, $\mathrm{OCH_2}$), 3.76 (3H, s, $\mathrm{OCH_3}$), 7.1 (2H, m, 4-H, 7-H), 7.2 (2H, m, 5-H, 6-H); $\delta_\mathrm{C}(\mathrm{CDCl_3})$, 14.7 ($\mathit{C}\mathrm{H_3CH_2}$), 17.1 ($\mathrm{CH_3}\mathit{C}\mathrm{H_2}$), 18.8 ($\mathit{C}\mathrm{H_3CON}$), 25.1, 25.2, 25.3, 25.6, and 29.5 [4 × s, 4 × ring $\mathrm{CH_3}$ and $(\mathit{C}\mathrm{H_3})_2\mathrm{COCH_2}$], 43.3 ($\mathrm{CH_3CH_2}\mathit{C}\mathrm{H_2}$), 51.7 ($\mathrm{OCH_3}$), 66.7 ($\mathit{C}\mathrm{H_2CON}$), 67.8 and 68.0 (C-1, C-3), 74.9 [$(\mathrm{CH_3})_2\mathit{C}$], 84.2 (CON), 121.6 (d, C-4, C-7), 127.2 (d, C-5, C-6), 145.2 (C-3a, C-7a), 174.0 (C=O); *m/z* 430 $(\mathrm{M + K})^+$, 414 $(\mathrm{M + Na})^+$, 392 $(\mathrm{M + H})^+$.

2-Ethoxy-1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindole (8b). $\delta_\mathrm{H}(\mathrm{CDCl_3})$ 1.27 (3H, t, $J = 7.1$, $\mathrm{CH_3}$), 1.45 (12H, br s, 4 × ring $\mathrm{CH_3}$), 3.99 (2H, q, $J = 7.1$, $\mathrm{CH_2}$), 7.1 (2H, m, 4-H, 7-H), 7.2 (2H, m, 5-H, 6-H); $\delta_\mathrm{C}(\mathrm{CDCl_3})$ 14.6 ($\mathrm{CH_3}$), 24−32 (br hump, 4 × ring $\mathrm{CH_3}$), 67.1 (C-1, C-3), 72.6 ($\mathrm{CH_2}$), 121.5 (C-4, C-7), 127.1 (C-5, C-6), 145.3 (C-3a, C-7a); *m/z* 220 $(\mathrm{M + H})^+$.

2-Propoxy-1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindole (8c). $\delta_\mathrm{H}(\mathrm{CDCl_3})$ 1.03 (3H, t, $J = 7.5$, $\mathrm{CH_3}$), 1.45 (12H, br s, 4 × ring $\mathrm{CH_3}$), 1.68 (2H, m, $\mathrm{CH_3C}\mathit{H}_2$), 3.91 (2H, t, $J = 6.6$, $\mathrm{CH_2O}$), 7.1 (2H, m, 4-H, 7-H), 7.2 (2H, m, 5-H, 6-H); $\delta_\mathrm{C}(\mathrm{CDCl_3})$ 11.1 ($\mathrm{CH_3}$), 22.5 ($\mathrm{CH_3}\mathit{C}\mathrm{H_2}$), 24−31 (br hump, 4 × ring $\mathrm{CH_3}$), 67.2 (C-1, C-3), 79.1 ($\mathrm{CH_2ON}$), 121.5 (C-4, C-7), 127.1 (C-5, C-6), 145.4 (C-3a, C-7a); *m/z* 256 $(\mathrm{M + Na})^+$, 234 $(\mathrm{M + H})^+$.

2-((4-Hydroxy-4-methylpentyl)oxy)-1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindole (8d). $\delta_\mathrm{H}(\mathrm{CDCl_3})$ 1.27 [6H, s, $(\mathrm{C}\mathit{H}_3)_2$-COH], 1.44 (12H, br s, 4 × ring $\mathrm{CH_3}$), 1.55−1.85 [5H, m, $(\mathrm{C}\mathit{H}_2)_2\mathrm{COH}$ and OH], 3.96 (2H, t, $J = 6.1$, $\mathrm{CH_2O}$), 7.1 (2H, m, 4-H, 7-H), 7.2 (2H, m, 5-H, 6-H); $\delta_\mathrm{C}(\mathrm{CDCl_3})$ 24.3 ($\mathit{C}\mathrm{H_2CH_2O}$), 24−31 (br hump, 4 × ring $\mathrm{CH_3}$), 29.3 [$(\mathit{C}\mathrm{H_3})_2\mathrm{C}$], 40.8 [$\mathit{C}\mathrm{H_2}$-$(\mathrm{CH_2})_2\mathrm{O}$], 67.2 (C-1, C-3), 70.8 [$(\mathrm{CH_3})_2\mathit{C}$], 78.0 ($\mathrm{CH_2ON}$), 121.5 (C-4, C-7), 127.2 (C-5, C-6), 145.2 (C-3a, C-7a); *m/z* 330 $(\mathrm{M + K})^+$, 314 $(\mathrm{M + Na})^+$, 292 $(\mathrm{M + H})^+$.

Methyl 2-Methyl-2-((1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindol-2-yl)oxy)pentanoate (9b). $\delta_\mathrm{H}(\mathrm{CDCl_3})$ 0.97 (3H, t, $J = 7.3$, $\mathrm{C}\mathit{H}_3\mathrm{CH_2}$), 1.2−1.6 (17H, m, 4 × ring $\mathrm{CH_3}$, 2-$\mathrm{CH_3}$ and $\mathrm{CH_3C}\mathit{H}_2$), 1.68−1.96 (2H, m, $\mathrm{CH_2CON}$), 3.78 (3H, s, $\mathrm{OCH_3}$), 7.1 (2H, m, 4-H, 7-H), 7.2 (2H, m, 5-H, 6-H); $\delta_\mathrm{C}(\mathrm{CDCl_3})$ 14.5 ($\mathit{C}\mathrm{H_3CH_2}$), 17.8 ($\mathrm{CH_3}\mathit{C}\mathrm{H_2}$), 20.5 ($\mathit{C}\mathrm{H_3CON}$), 25.0, 25.7, 29.5, and 29.7 (4 × s, 4 × ring $\mathrm{CH_3}$), 42.8 ($\mathit{C}\mathrm{H_2CON}$), 51.7 ($\mathrm{OCH_3}$), 67.8 and 67.9 (C-1, C-3), 84.2 (CON), 121.5 (d, C-4, C-7), 127.2 (d, C-5, C-6), 144.8 and 145.5 (C-3a, C-7a), 175.4 (C=O); *m/z* 342 $(\mathrm{M + Na})^+$, 320 $(\mathrm{M + H})^+$.

Methyl 2-methyl-2-((1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindol-2-yl)oxy)hexanoate (9c). $\delta_\mathrm{H}(\mathrm{CDCl_3})$ 0.93 (3H, t, $J = 6.7$, $\mathrm{C}\mathit{H}_3\mathrm{CH_2}$), 1.2−1.6 [19H, m, 4 × ring $\mathrm{CH_3}$, 2-$\mathrm{CH_3}$, and $\mathrm{CH_3(C}\mathit{H}_2)_2$] , 1.7−2.0 (2H, m, $\mathrm{CH_2CON}$), 3.77 (3H, s, $\mathrm{OCH_3}$), 7.1 (2H, m, 4-H, 7-H), 7.2 (2H, m, 5-H, 6-H); $\delta_\mathrm{C}(\mathrm{CDCl_3})$ 14.1 ($\mathit{C}\mathrm{H_3CH_2}$), 20.5 ($\mathit{C}\mathrm{H_3CON}$), 23.1 ($\mathrm{CH_3}\mathit{C}\mathrm{H_2}$), 25.0, 25.7, 29.5, and 29.7 (4 × s, 4 × ring $\mathrm{CH_3}$), 26.6 ($\mathit{C}\mathrm{H_2CH_2CON}$), 40.3 ($\mathit{C}\mathrm{H_2CON}$), 51.7 ($\mathrm{OCH_3}$), 67.7 and 67.8 (C-1, C-3), 84.3 (CON), 121.6 (d, C-4, C-7), 127.2 (d, C-5, C-6), 144.8 and 145.5 (C-3a, C-7a), 175.4 (C=O); *m/z* 356 $(\mathrm{M + Na})^+$, 334 $(\mathrm{M + H})^+$.

Methyl 7-Hydroxy-2,7-dimethyl-2-((1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindol-2-yl)oxy)octanoate (9d). $\delta_\mathrm{H}(\mathrm{CDCl_3})$ 1.22 [6H, s, $(\mathrm{C}\mathit{H}_3)_2\mathrm{COH}$], 1.25−1.55 [21H, m, 4 × ring $\mathrm{CH_3}$, 2-$\mathrm{CH_3}$ and $(\mathrm{C}\mathit{H}_2)_3\mathrm{COH}$], 1.75−1.95 (2H, m, $\mathrm{C}\mathit{H}_2\mathrm{CON}$), 2.18 (1H, s, OH), 3.76 (3H, s, $\mathrm{OCH_3}$), 7.1 (2H, m, 4-H, 7-H), 7.2 (2H, m, 5-H, 6-H); $\delta_\mathrm{C}(\mathrm{CDCl_3})$ 20.5 ($\mathit{C}\mathrm{H_3CON}$), 24.7, 24.9 [$\mathit{C}\mathrm{H_2(CH_2)_2}$-CON and $\mathit{C}\mathrm{H_2CH_2CON}$)], 25.0, 25.7, 29.5, and 29.7 (4 × ring $\mathrm{CH_3}$), 29.3 [$(\mathit{C}\mathrm{H_3})_2\mathrm{COH}$], 40.5 ($\mathit{C}\mathrm{H_2CON}$), 43.8 ($\mathit{C}\mathrm{H_2COH}$), 51.7 ($\mathrm{OCH_3}$), 67.8, 67.9 (C-1, C-3), 71.0 [$(\mathrm{CH_3})_2\mathit{C}\mathrm{OH}$], 84.2 (CON), 121.5 (d, C-4, C-7), 127.2 (d, C-5, C-6), 144.7, 145.4 (C-3a, C-7a), 175.3 (C=O); *m/z* 430 $(\mathrm{M + K})^+$, 414 $(\mathrm{M + Na})^+$, 392 $(\mathrm{M + H})^+$.

Reaction of Ethyl Radicals with MMA in the Presence of 2. A solution of propionyl peroxide (0.050 mol $\mathrm{dm^{-3}}$) with MMA in the presence of **2** (0.050 mol $\mathrm{dm^{-3}}$) was reacted at 60 °C for 2 h in the same manner as above.

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