Free Radical Initiation Mechanisms in the Polymerization of Methyl Methacrylate and Styrene with 1,1,3,3-Tetramethylbutyl Peroxypivalate: Addition of Neopentyl Radicals

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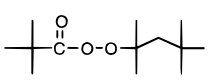
Received July 7, 1997[⊗]

Abstract: The reactions of 1,1,3,3-tetramethylbutyl (*tert*-octyl) peroxypivalate (**1**) with methyl methacrylate (MMA) and styrene 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*-Butyl and *tert*-octyloxyl radicals (**3**) were generated from the thermolysis of **1**. The predominant unimolecular reactions of **3**, that is, β-scission to form neopentyl radicals (**14b**) and a 1,5-H shift to form 4-hydroxy-2,2,4-trimethylpentyl radicals (**14c**), were observed in both monomer systems. The resulting alkyl radicals underwent selective addition to the two monomers. The relative reactivities of the alkyl radicals toward addition to the monomers were obtained from competitive addition/trapping reactions. The absolute rate constants for the addition of alkyl radicals **14b** and **14c** to the two monomers at 60 °C were estimated to be 9.5×10^5 and 2.6×10^5 M^{-1} s^{-1} to MMA and 4.5×10^5 and 0.7×10^5 M^{-1} s^{-1} to styrene, respectively. The low reactivities of **3** and **14c** toward addition to MMA and styrene were attributed to steric effects. Steric effects were also responsible for the low rate of the 1,5-H shift in **3**.

Introduction

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 commercially important vinyl and acrylic monomers. Previous papers have described the reactions of *tert*-butyl,[1,2] *tert*-pentyl,[2,3] and *tert*-hexyl[2−4] peroxypivalates with methyl methacrylate (MMA) and styrene; this paper reports the results of the reactions of 1,1,3,3-tetramethylbutyl (*tert*-octyl) peroxypivalate (**1**) with MMA and styrene. The radical trapping technique, employing 1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindol-2-yloxyl (**2**) as a radical scavenger, has been employed as



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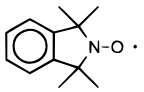

2 ≡ T

M

MMA (X=Me, Y=CO_2Me)
Styrene (S) (X=H, Y=Ph)

described previously.[1−5] *tert*-Octyl peroxyesters are known to be more reactive (their half-lives are shorter)[6,7] than *tert*-butyl, *tert*-pentyl, and *tert*-hexyl analogues, and they are widely used to initiate free radical polymerization of common monomers such as (meth)acrylates, styrene, vinyl chloride, and so on.[8,9] *tert*-Alkyl peroxypivalates are known to undergo a concerted two-bond scission.[10] In previous work,[1−4] we have shown (i) that the thermolysis of *tert*-alkyl peroxypivalates is not affected by the presence of **2** and it generates an equimolar amount of *tert*-butyl and *tert*-alkoxyl radicals in the monomer and (ii) that *tert*-butyl radicals are immediately trapped by **2** to form alkoxyamine **4** or undergo competitive (tail) addition to MMA (or S) followed by trapping to give alkoxyamine **5** (or **6**) (Scheme 1).

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⊗ Abstract published in *Advance ACS Abstracts,* October 15, 1997.

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(3) Nakamura, T.; Busfield, W. K.; Jenkins, I. D.; Rizzardo, E.; Thang, S. H.; Suyama, S. *Macromolecules* **1997**, *30*, 2843−2847.
(4) Nakamura, T.; Busfield, W. K.; Jenkins, I. D.; Rizzardo, E.; Thang, S. H.; Suyama, S. *Macromolecules* **1996**, *29*, 8975.
(5) (a) Rizzardo, E.; Solomon, D. H. *Polym. Bull.* **1979**, *1*, 529−534. (b) Moad, G.; Solomon, D. H. In *Comprehensive Polymer Science*; Eastmond, G. C., Ed.; Pergamon: London, 1989; Vol. 3, pp 116−117. (c) Bottle, S. E.; Busfield, W. K.; Heiland, K.; Jenkins, I. D.; Meutermans, W.; Monteiro, M. In *Progress in Pacific Polymer Science 3*; Ghiggino, K. P., Ed.; Springer-Verlag Berlin: Heidelberg, 1994; pp 85−97. (d) Busfield, W. K.; Grice, I. D.; Jenkins, I. D. *Aust. J. Chem.* **1995**, *48*, 625−634. (e) Moad, G.; Solomon, D. H. In *The Chemistry of Free Radical Polymerization*; Pergamon: London, 1995; pp 120−122 and references contained therein.
(6) The half-lives of **1**, *tert*-butyl, *tert*-pentyl, and *tert*-hexyl peroxypivalates at 60 °C in cumene have been reported to be 3.1, 6.5, 5.5, and 5.7 h, respectively. Komai, T.; Matsuyama, K.; Matsushima, M. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1641−1646.
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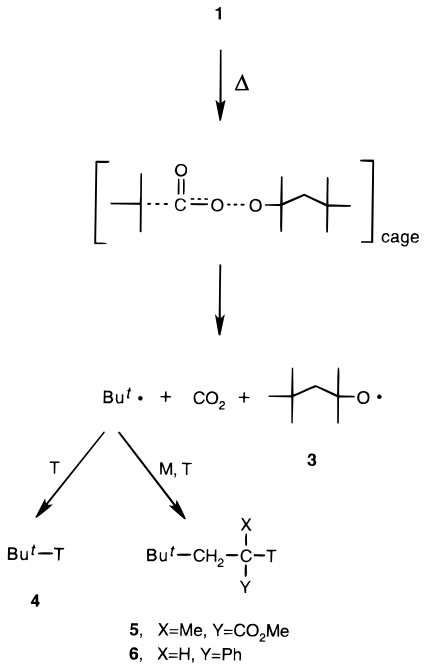
S0002-7863(97)02240-3 CCC: $14.00

Scheme 1



Results

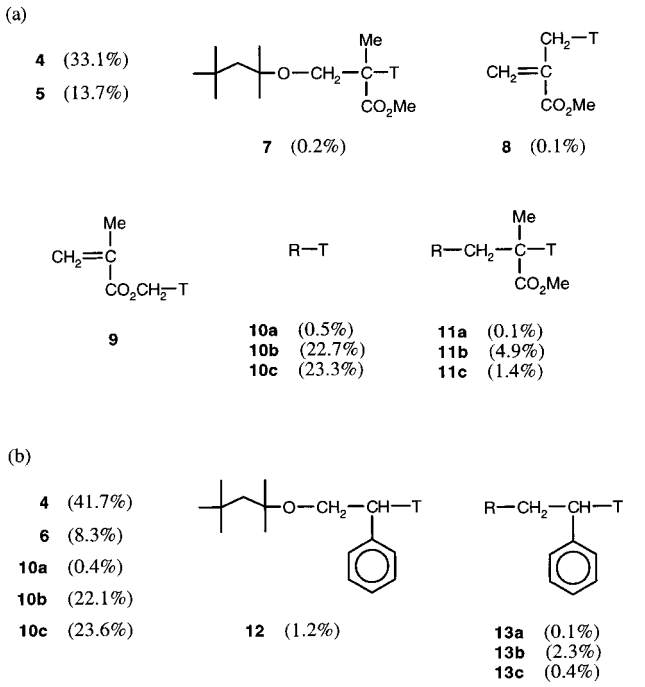
Following the thermolysis of **1** (0.040 M) in the presence of trap **2** (0.040 M) in neat monomer at 60 °C *in vacuo* for 1 h,[11] most of the excess monomer was removed at reduced pressure and the residue was then analyzed by reverse-phase HPLC, HPLC-MS, and NMR. Alkoxyamines (the reaction products) were formed in the relative percentage yields shown in Chart 1, while the various reactions of *tert*-octyloxyl radicals (**3**) in monomer are outlined in Scheme 2. Alkoxyamines **7**−**9** and **12** arise from the direct reaction of **3** with monomers followed by trapping. As expected, in the reaction with MMA, the hydrogen-abstraction product **8** was obtained as well as the addition product **7** (eqs 1 and 2). Another H-abstraction product **9** was also detected in a trace amount (<0.05%), which means this reaction pathway is not important in this system. With styrene, only the tail addition product **12** was formed. Thus, *tert*-octyloxyl radicals show the same high selectivity toward styrene as displayed by other *tert*-alkoxyl radicals.[2,12]

It can be seen from Chart 1 that the major products from the reaction of **3** in both monomer systems are alkoxyamines **10b**, **11b**, and **13b** derived from neopentyl radicals (**14b**) and alkoxyamines **10c**, **11c**, and **13c** derived from 4-hydroxy-2,2,4-trimethylpentyl radicals (**14c**). Methyl radical-derived compounds (**10a**, **11a**, and **13a**) were detected as minor products. These alkyl radicals are formed by the unimolecular reactions of **3**, that is, β-scission to produce **14a**,**b** (eqs 3 and 4) and intramolecular hydrogen abstraction (1,5-H shift) to produce **14c** (eq 5) and they undergo addition/trapping in an analogous fashion to *tert*-butyl radicals. Thus, the majority of alkyl radicals **14** are trapped by **2** to form **10** (eq 6) and the remainder undergo selective tail addition to monomers resulting in alkoxyamines **11** and **13** in MMA and styrene, respectively (eq 7).

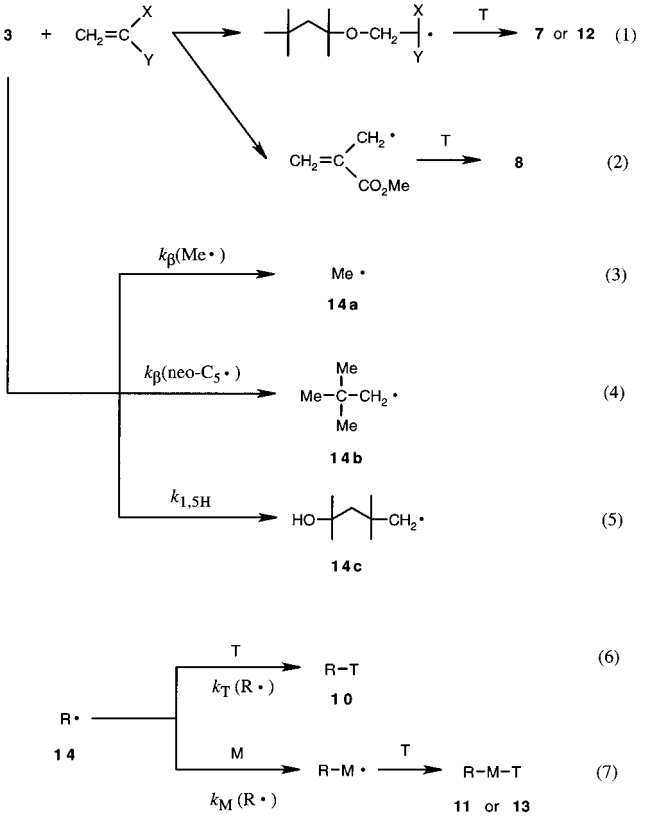
(11) A relatively low concentration of **2** was used to study the (competitive) reaction of alkyl radicals with monomers. However, under the conditions of the reaction, **2** is still present in excess because of the low conversion (ca. 20%) and the <100% efficiency of generation of radicals from **1**.[6]

(12) Moad, G.; Rizzardo, E.; Solomon, D. H. *Macromolecules* **1982**, *15*, 909−914.

Chart 1. Products in the Reactions of **1** with (a) MMA and (b) Styrene in the Presence of Nitroxide **2**



Scheme 2



Discussion

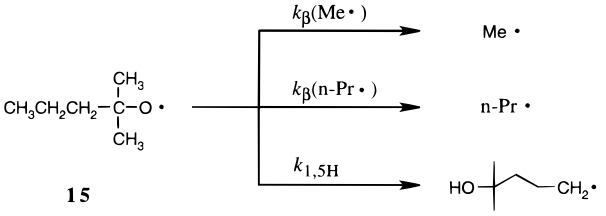
Table 1 shows the relative product yields for the reaction of **1** with MMA and styrene, which have been normalized so that the total yield of *tert*-octyloxyl radical-derived products (**7**−**11**

Table 1. Yields of All Products Relative to the Overall Yield of *tert*-Alkoxyl Radical-Derived Products in the Reaction of *tert*-Octyl Peroxypivalates (**1**) with MMA and Styrene in the Presence of Nitroxide **2** at 60 °C[a]

	relative product yields (%)									
	tert-butyl radical-derived products[b]		*tert*-octyloxyl radical-derived products[b]							
monomer	**4**	**5** (**6**)	**7** (**12**)	**8**	**10a**	**11a** (**13a**)	**10b**	**11b** (**13b**)	**10c**	**11c** (**13c**)
MMA	62.2	25.8	0.3	0.2	0.9	0.2	42.7	9.2	43.8	2.7
styrene	83.2	16.6	2.3		0.8	0.2	44.2	4.6	47.1	0.8

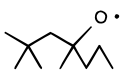
[a] $[\mathbf{1}]_0 = [\mathbf{2}]_0 = 0.040$ M; reaction time: 1.0 h. [b] Compounds in parentheses are the products in styrene.

Scheme 3



in MMA and **10**, **12**, and **13** in styrene) is 100%. It is apparent from Table 1, that the total yield of *tert*-butyl radical-derived products (**4** + **6**) is identical to that of *tert*-octyloxyl radical-derived products (100%) in styrene. This is consistent with the fact that peroxypivalates generate equimolar amounts of the two radicals, and with the efficient trapping of all radicals by the aminoxyl **2**. In the MMA system, however, the total yield of *tert*-butyl radical derivatives (**4** + **5**) was not equal to that of *tert*-octyloxyl radical derivatives. This is due to partial decomposition of the *tert*-butyl radical-addition product **5** under the conditions of the experiment.[1]

Reaction of *tert*-Octyloxyl Radicals with Monomer. As mentioned above, *tert*-octyloxyl radicals (**3**) undergo three modes of unimolecular reactions (see Scheme 2) in a manner similar to that of *tert*-hexyloxyl radicals (**15**) (Scheme 3).[2−4] The ratios of the unimolecular reaction rates for **3** are in the ratios of the corresponding product yields, that is, k_β(Me•):k_β(neo-C_5•):$k_{1,5H}$ = 1:94:85 [(**10a** + **11a**)/2:(**10b** + **11b**):(**10c** + **11c**)] in MMA and 1:98:96 [(**10a** + **13a**)/2:(**10b** + **13b**):(**10c** + **13c**)] in styrene. Thus there appears to be no significant solvent effect on the unimolecular reactions of *tert*-octyloxyl radicals in MMA versus styrene. It is interesting that these ratios are almost the same as the values obtained from the corresponding reactions for *tert*-hexyloxyl radicals (**15**), i.e. k_β(Me•):k_β(*n*-Pr•):$k_{1,5H}$ = 1:102:96 (in MMA)[4] and 1:104:94 (in styrene).[2] Thus, the relative rate of neopentyl radical elimination from **3** (or of *n*-propyl radical elimination from **15**) is almost 100 times that of methyl radical elimination in both monomer systems. This is consistent with the results of Greene et al.,[13] who have reported that the elimination rates to produce neopentyl and *n*-propyl radicals in the β-scission of alkoxyl radical **16** are the same at 0 °C. Radicals **16** were obtained from the photolysis of the corresponding hypochlorite in $CFCl_3$.



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Surprisingly, if it is assumed that the absolute rate constant for k_β(neo-C_5•) in alkoxyl radicals **3** is equal to that for k_β(*n*-Pr•) in alkoxyl radicals **15**, the ratios of $k_{1,5H}$:k_β(neo-C_5•) for **3** and $k_{1,5H}$:k_β(*n*-Pr•) for **15** indicate that $k_{1,5H}$ for both alkoxyl radicals are also comparable, even though a 1,5-H shift in **3** has a 3-fold statistical advantage (*tert*-octyloxyl radicals have

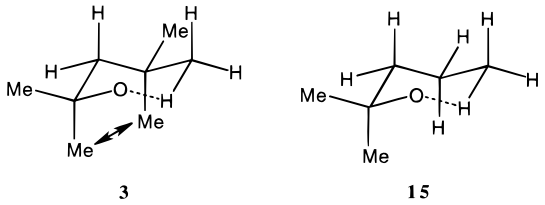
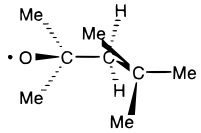


Figure 1. The transition states for intramolecular hydrogen abstraction in alkoxyl radicals **3** and **15**.

three times more δ-hydrogens than *tert*-hexyloxyl radicals do). We suggest that the relatively low rate for the 1,5-H shift observed in **3** is a result of the steric repulsion between the two methyl groups attached to the α- and γ-carbons (analogous to a 1,3-diaxial interaction)[14] in **3** (Figure 1), which may disfavor a chair conformation of the six-membered ring as the transition state for a 1,5-H shift.[15] It has been reported that a specific distance (2.5−2.7 Å) between the oxygen radical site and the δ-carbon is required for a 1,5-H shift and that the rate decreases if the distance exceeds 2.8 Å.[15a]

It can be seen that the proportion of direct addition of **3** to styrene (2.3%) is higher than that in MMA (0.5%), and this trend is the same as that observed in the reaction of other *tert*-alkoxyl radicals.[2] One possible reason is the differing electron density of the double bond of the two monomers. Alkoxyl radicals (which are electrophilic) react more rapidly with electron-rich monomers such as styrene than with electron-deficient monomers such as MMA. The proportions of addition for **3** are significantly lower than those observed with *tert*-hexyloxyl radicals (**15**) (10.1% in MMA and 32.3% in styrene). Since the rates of the unimolecular reactions for both alkoxyl radicals are comparable as discussed above, this result indicates that *tert*-octyloxyl radicals (**3**) are significantly less reactive than **15** toward addition to monomers. This is presumably due to the steric hindrance around the oxygen radical caused by the methyl groups on the γ-carbon. In the preferred conformer **17**,



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these γ-carbon methyl groups effectively shield the oxyl radical which is forced into an "endo" position (an "exo" oxyl radical would result in severe 1,3-diaxial-type interactions between the methyl groups on the α-carbon and those on the γ-carbon).

Reaction of Alkyl Radicals with Monomer. Alkyl radicals **14b** and **14c** and *tert*-butyl radicals underwent competitive addition/trapping to form the corresponding alkoxyamines in

(13) Greene, F. D.; Savitz, M. L.; Osterholtz, F. D.; Lau, H. H.; Smith, W. N.; Zanet, P. M. *J. Org. Chem.* **1963**, *28*, 55−64.

(14) The energy of the corresponding repulsion in such compounds as 2,2,4,4-tetramethylpentane, which is attributed to the repulsion between H atoms on 1,5-C atoms, has been estimated to be 1.5 kcal/mol (Benson, S. W. In *Thermochemical Kinetics*, 2nd ed.; Benson, S. W., Ed.; John Wiley: New York, 1976; p 31).

(15) (a) Wilt, J. W. In *Free Radicals*; Kochi, J. K., Ed.; John Wiley: New York, 1973; Vol. 1, pp 386−387. (b) Reference 5e, p 23.

Table 2. Absolute Rate Constants for Alkyl Radical Addition to MMA and Styrene (60 °C)

alkyl radicals	rate constant × 10^{-5} (M^{-1} s^{-1}) k_{MMA}	k_S	ref
neo-C_5H_{11} (**14b**)	9.5	4.5	this work
14b	2.6	0.7	this work
C_2H_5	8.6	4.6	2, 3
n-C_3H_7	10	5.3	2, 3
$HOCMe_2(CH_2)_2CH_2$	11	4.9	2, 3
t-C_4H_9	22	7.2	1, 2

significant yields as shown in Table 1 and eqs 6 and 7 in Scheme 2, where k_M and k_T are the general rate constants for the reaction of alkyl radicals with monomer and T, respectively. Since the reaction is only run to very low conversion, the ratio of [T]/[M] is constant in an individual experiment and therefore, the ratio of product yields (R−M−T)/(R−T) should be proportional to the ratio of k_M/k_T (see eq 8). Therefore, the reactivity for those

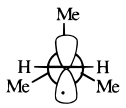
$$\frac{k_M}{k_T} = \frac{(R-M-T)}{(R-T)}\frac{[T]}{[M]} \qquad (8)$$

alkyl radicals toward monomers has been evaluated by a simple comparison of the reaction product yields. Thus, the values of k_M/k_T for neopentyl (**14b**), 4-hydroxy-2,2,4-trimethylpentyl (**14c**), and *tert*-butyl radicals are in the ratios of the product yields **11b**/**10b**, **11c**/**10c**, and **5**/**4** in MMA and **13b**/**10b**, **13c**/**10c**, and **6**/**4** in styrene, respectively. Here, the theoretical yield of **5** can be taken as (the total yield of *tert*-octyloxyl radical-derived products) − (the yield of **4**), since alkoxyamine **5** partially decomposed during the reaction as mentioned above. On the other hand, no significant decomposition of MMA-derived products **11b**,**c** was observed in a separate experiment (ca. 2% decomposition was observed for each compound after 1 h at 60 °C in MMA and in the presence of **2**). The relative rate constants for tail addition of alkyl radicals (k_M) can be estimated by assuming that k_T for alkyl radicals **14b**,**c** has the same value[16,17] of 1.1×10^9 dm^3 mol^{-1} s^{-1} and that the value[16] for *tert*-butyl radicals is 9.1×10^8 dm^3 mol^{-1} s^{-1}. The results in Table 1 give the following ratios:

$$k_{MMA}(\text{neo-}C_5^{\bullet}):k_{MMA}(\mathbf{14c}):k_{MMA}(Bu^{t\bullet}) = 0.43:0.12:1.0$$

$$k_S(\text{neo-}C_5^{\bullet}):k_S(\mathbf{14c}):k_S(Bu^{t\bullet}) = 0.63:0.10:1.0.$$

Absolute rate constants can be estimated by taking the reported value[1,2] of $k_{MMA}(Bu^{t\bullet})$ and $k_S(Bu^{t\bullet})$ as shown in Table 2. It can be seen from Table 2 that the reactivity of neopentyl radicals toward addition to monomers is almost the same as that for other primary alkyl radicals such as ethyl and *n*-propyl radicals. On the other hand, a significantly lower reactivity for alkyl radicals **14c** is observed in both monomer systems. This can also be understood in terms of steric factors as discussed for *tert*-octyloxyl radicals. Thus, comparing the Newman projections **18** and **19** for the neopentyl radical and **14c**, respectively, it is clear that the steric bulkiness around the radical carbon caused by the 2-hydroxy-2-methylpropyl groups may hinder the approach of alkyl radicals **14c** to monomer. The steric effects described here for the alkyl radical **14c** and the alkoxy radical **3** are similar to those observed by Giese,[18] who showed that



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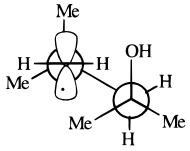

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substitution of a CH_3 group by a $C(CH_3)_3$ group in *tert*-radicals decreased the rate of addition to fumarate esters.

In summary, this work has shown that in the reaction of *tert*-octyl peroxypivalate **1** with MMA and styrene, *tert*-octyloxyl radicals (**3**) undergo unimolecular reactions (β-scission and 1,5-H shift) almost exclusively (>97%) rather than direct addition to the monomer. This low reactivity toward addition can be attributed to the decreased reactivity of **3** as a result of steric hindrance by the neopentyl group. After the unimolecular reactions, the resulting alkyl radicals undergo selective tail addition to both monomers. The rate constants for alkyl radical addition were estimated to be neo-$C_5^{\bullet}$ (9.5×10^5) and **14c** (2.6×10^5) to MMA and neo-$C_5^{\bullet}$ (4.5×10^5) and **14c** (0.7×10^5 dm^3 mol^{-1} s^{-1}) to styrene, respectively. The reactivities of neopentyl radicals toward addition to both monomers are comparable with those of other primary alkyl radicals such as ethyl and *n*-propyl radicals, whereas the reactivity of the sterically more hindered 4-hydroxy-2,2,4-trimethylpentyl radicals is significantly lower. The extent of the direct reaction of **3** with MMA and styrene is 0.5% and 2.3%, respectively, and hydrogen abstraction from MMA by **3** is observed as a very minor reaction path (0.2%). This proportion is the lowest among the corresponding values observed in the study of *tert*-butoxyl (33.2%),[1] *tert*-pentyloxyl (6.9%),[3] and *tert*-hexyloxyl radicals (3.9%).[3] This indicates that the use of **1** as an initiator for the polymerization of MMA can minimise the proportion of unsaturated end groups derived from the initiation process.

Experimental Section

Materials. Methyl methacrylate was washed with 5% NaOH, dried over anhydrous Na_2SO_4, and distilled at atmospheric pressure. Styrene was purified by distillation. Both monomers were stored in a refrigerator (−20 °C). *tert*-Octyl peroxypivalate (**1**) was prepared by the reaction of pivaloyl chloride with 1,1,3,3-tetramethylbutyl hydroperoxide in alkaline solution,[6] and the purity was determined by iodometric titration.[19] **1** was 95.5% pure; *m/z* 253 $(M + Na)^+$, 269 $(M + K)^+$. Nitroxide **2** was prepared by the literature procedure.[20]

Trapping Experiments. A solution of **1** (0.040 M) and **2** (0.040 M) in freshly distilled monomer was degassed by three successive freezing−pump−thaw cycles to 10^{-4} mmHg). The reaction vessel was then sealed under vacuum and heated at 60 ± 0.1 °C for 1.0 h. The majority (ca. 90%) of excess monomer was then removed 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. Products **4**,[1] **5**,[1] **6**,[2] **8**,[21] **9**,[21] **10a**,[22] **11a**,[23] and **13a**[12] were also identified by cochromatography with authentic samples. New compounds were isolated by preparative HPLC and characterized by NMR.

Product Analysis. Analytical HPLC studies were carried out with a Shimadzu LC-9A liquid chromatograph fitted with either a Waters Nova-Pak C_{18} 6 mm, 100 × 8 mm ODS analytical column or a Rainin Instruments Dynamax-60A 8 mm 250 × 4.6 mm C_{18} analytical column,

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(17) If the trapping rate of **14c** is slower than that of **14b** (due to steric effects), the ratio of $k_M(\mathbf{14c}):k_M(Bu^{t\bullet})$ becomes higher correspondingly.

(18) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 753−764.

(19) Komai, T.; Matsuyama, K.; Matsushima, M. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1641−1646.

(20) Griffith, P. G.; Moad, G.; Rizzardo, E.; Solomon, D. H. *Aust. J. Chem.* **1983**, *36*, 397−401.

(21) Grant, R. D.; Rizzardo, E.; Solomon, D. H. *J. Chem. Soc., Perkin Trans. 2* **1985**, 379−384.

(22) Rizzardo, E.; Serelis, A. K.; Solomon, D. H. *Aust. J. Chem.* **1982**, *35*, 2013−2024.

(23) Griffiths, P. G.; Rizzardo, E.; Solomon, D. H. *J. Macromol. Sci., Chem.* **1982**, *17*, 45−50.

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 Instruments Dynamax-60A 8μm 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.

New compounds were isolated by preparative HPLC and characterized by the NMR data listed below (*J* values are given in hertz; ring CH_3 refers to methyl substituents on the isoindole, and primed numbers of carbon refer to the monosubstituted phenyl ring).

Methyl 2-Methyl-2-((1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindol-2-yl)oxy)-3-((2,4,4-trimethylpent-2-yl)oxy)propanoate (7): $\delta_H(CDCl_3)$ 0.97 [s, 9H, (C*H*$_3$)$_3$C], 1.13 and 1.14 [2 × s, 2 × 3H, (CH$_3$)$_2$CO], 1.37 (s, 6H, ring CH$_3$ and CH$_3$CON), 1.39 (s, 3H, ring CH$_3$), 1.49 (s, 5H, ring CH$_3$ and CH$_2$CO), 1.60 (s, 3H, ring CH$_3$), 3.41 (d, 1H, *J* 8.1, OCH$_2$), 3.65 (d, 1H, *J* 8.1, OCH$_2$), 3.77 (s, 3H, OCH$_3$), 7.06−7.14 (m, 2H ArH), 7.20−7.27 (m, 2H ArH); *m/z* 442 (M + Na)$^+$, 420 (M + H)$^+$.

2-((2,2-Dimethylpropyl)oxy)-1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindole (10b): $\delta_H(CDCl_3)$ 1.01 [s, 9H, (CH$_3$)$_3$], 1.44 (br s, 12H, 4 × ring CH$_3$), 3.62 (s, 2H, CH$_2$), 7.07−7.12 (m, 2H ArH), 7.20−7.26 (m, 2H ArH); $\delta_C(CDCl_3)$ 24−32 (br hump, ring CH$_3$), 27.2 [(*C*H$_3$)$_3$C], 32.3 [(CH$_3$)$_3$*C*], 67.4 (C-1, C-3), 87.6 (CH$_2$), 121.5 (C-4, C-7), 127.2 (C-5, C-6), 145.6 (C-3a, C-7a); *m/z* 284 (M + Na)$^+$, 262 (M + H)$^+$.

2-((4-Hydroxy-2,2,4-trimethylpentyl)oxy)-1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindole (10c): $\delta_H(CDCl_3)$ 1.15 [s, 6H, (C*H*$_3$)$_2$CCH$_2$ON], 1.33 [s, 6H, (C*H*$_3$)$_2$COH], 1.48 (br s, 12H, 4 × ring CH$_3$), 1.67 (s, 2H, C*H*$_2$COH), 3.29 (br s, 1H, OH), 3.87 (s, 2H, CH$_2$ON), 7.06−7.14 (m, 2H ArH), 7.20−7.27 (m, 2H ArH); $\delta_C(CDCl_3)$ 25−30 (br hump, ring CH$_3$), 27.8 [(*C*H$_3$)$_2$CCH$_2$ON], 31.9 [(*C*H$_3$)$_2$COH], 35.8 [(CH$_3$)$_2$*C*CH$_2$ON], 53.3 (*C*H$_2$COH), 67.5 (C-1, C-3), 71.3 (COH), 87.7 (CH$_2$ON), 121.4 (C-4, C-7), 127.3 (C-5, C-6), 145.0 (C-3a, C-7a); *m/z* 342 (M + Na)$^+$, 320 (M + H)$^+$.

Methyl 2-((1,1,3,3-Tetramethyl-2,3-dihydro-1*H*-isoindol-2-yl)-oxy)-2,5,5-trimethylhexanoate (11b): $\delta_H(CDCl_3)$ 0.92 [s, 9H, (CH$_3$)$_3$C], 1.1−1.3 [m, 2H, (CH$_3$)$_3$CC*H*$_2$], 1.35, 1.37, 1.46, 1.48 and 1.54 (5 × s, 5 × 3H, 4 × ring CH$_3$ and CH$_3$CON), 1.6−2.0 (m, 2H, CH$_2$CON), 3.78 (s, 3H, OCH$_3$), 7.08−7.16 (m, 2H ArH), 7.20−7.27 (m, 2H ArH); $\delta_C(CDCl_3)$ 20.6 (*C*H$_3$CON), 25.1, 25.7, 29.5 and 29.7 (4 × ring CH$_3$), 29.3 [(*C*H$_3$)$_3$C], 30.2 [(CH$_3$)$_3$*C*], 35.6 (*C*H$_2$CON), 38.0 (*C*H$_2$CH$_2$CON), 51.7 (OCH$_3$), 67.8 and 67.9 (C-1, C-3), 84.5 (CON), 121.5 and 121.6 (C-4, C-7), 127.2 and 127.3 (C-5, C-6), 144.8 and 145.5 (C-3a, C-7a), 175.3 (C═O); *m/z* 384 (M + Na)$^+$, 362 (M + H)$^+$.

Methyl 7-Hydroxy-2,5,5,7-tetramethyl-2-((1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindol-2-yl)oxy)octanoate (11c): $\delta_H(CDCl_3)$ 1.04 [s, 6H, (C*H*$_3$)$_2$CCH$_2$COH], 1.2−1.3 (m, 2H, C*H*$_2$CH$_2$CON), 1.30 [s, 6H, (C*H*$_3$)$_2$-COH], 1.34, 1.36, 1.44, 1.46 and 1.53 (5 × s, 5 × 3H, 4 × ring CH$_3$ and CH$_3$CON), 1.52 (s, 2H, CH$_2$OH), 1.6−2.0 (m, 2H, CH$_2$CON), 3.76 (s, 3H, OCH$_3$), 7.06−7.14 (m, 2H ArH), 7.21−7.26 (m, 2H ArH); $\delta_C(CDCl_3)$ 20.6 (*C*H$_3$CON), 25.0, 25.7, 29.5 and 29.7 (4 × ring CH$_3$), 28.6 [(*C*H$_3$)$_2$COH], 31.9 and 32.1 [(*C*H$_3$)$_2$CCH$_2$COH], 33.7 [(CH$_3$)$_2$*C*CH$_2$-COH], 35.0 (*C*H$_2$CON), 38.4 (*C*H$_2$CH$_2$CON), 51.7 (OCH$_3$), 53.1 (*C*H$_2$-COH), 67.8 and 67.9 (C-1, C-3), 72.4 [(CH$_3$)$_2$COH], 84.5 (CON), 121.5 and 121.6 (C-4, C-7), 127.2 and 127.3 (C-5, C-6), 144.7 and 145.4 (C-3a, C-7a), 175.3 (C═O); *m/z* 442 (M + Na)$^+$, 420 (M + H)$^+$.

2-(1-Phenyl-2-((2,4,4-trimethylpent-2-yl)oxy)ethoxy)-1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindole (12): $\delta_H(CDCl_3)$ 0.80 (s, 3H, ring CH$_3$), 0.97 [s, 9H, (CH$_3$)$_3$], 1.21 and 1.25 [2 × s, 2 × 3H, (CH$_3$)$_2$CO], 1.25 (s, 3H, ring CH$_3$), 1.49 (s, 5H, ring CH$_3$ and CH$_2$CO), 1.68 (s, 3H, ring CH$_3$), 3.44 (dd, *J* 4.8, 9.7, 1H, C*H*$_2$CHON), 3.83 (dd, *J* 7.8, 9.7, 1H, C*H*$_2$CHON), 4.83 (dd, *J* 4.8, 7.8, 1H, CHON), 6.94−7.44 (m, 9H, ArH); *m/z* 446 (M + Na)$^+$, 424 (M + H)$^+$.

2-(((4,4-Dimethyl-1-phenyl)pentyl)oxy)-1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindole (13b): $\delta_H(CDCl_3)$ 0.73 (s, 3H, ring CH$_3$), 0.88 [s, 9H, (CH$_3$)$_3$], 1.2−1.4 [m, 2H, (CH$_3$)$_3$CC*H*$_2$], 1.24, 1.46, 1.64 (3 × s, 3 × 3H, 3 × ring CH$_3$), 1.66−1.87 (m, 1H, C*H*$_2$CHON), 2.04−2.24 (m, 1H, C*H*$_2$CHON), 4.61 (dd, *J* 5.9, 8.3, 1H, CHON), 6.92−7.40 (m, 9H, ArH); $\delta_C(CDCl_3)$ 25.3, 25.7, 29.3, 30.2 and 30.3 [4 × ring CH$_3$ and (CH$_3$)$_3$*C*], 29.4 [(*C*H$_3$)$_3$C], 31.0 (*C*H$_2$CHON), 40.3 (*C*H$_2$CH$_2$-CHON), 67.0 and 68.0 (C-1, C-3), 89.0 (CHON), 121.4 and 121.9 (C-4, C-7), 127.0 and 127.1 (C-5, C-6), 127.4, 128.0 and 128.1 (C-2′, C-3′, C-4′), 143.9 (C-1′), 145.2 and 145.5 (C-3a, C-7a); *m/z* 388 (M + Na)$^+$, 366 (M + H)$^+$.

2-(((6-Hydroxy-4,4,6-trimethyl-1-phenyl)heptyl)oxy)-1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindole (13c): $\delta_H(CDCl_3)$ 0.73 (s, 3H, ring CH$_3$), 1.01 [s, 6H, (C*H*$_3$)$_2$CCH$_2$COH], 1.2−1.4 (m, 2H, *C*H$_2$CH$_2$-CHON), 1.23 (s, 3H, ring CH$_3$), 1.25 and 1.26 [2 × s, 2 × 3H, (C*H*$_3$)$_2$-OH], 1.46 (s, 3H, ring CH$_3$), 1.50 and 1.51 (2 × s, 2 × 1H, C*H*$_2$COH), 1.63 (s, 3H, ring CH$_3$), 1.66−1.87 (m, 1H, C*H*$_2$CHON), 2.02−2.27 (m, 1H, C*H*$_2$CHON), 2.80 (s, 1H, OH), 4.60 (dd, *J* 6.0, 8.1, 1H, CHON), 6.94−7.42 (m, 9H, ArH); *m/z* 446 (M + Na)$^+$, 424 (M + H)$^+$.

Thermolysis of 11b,c in the Presence of 2. A MMA solution of **11b** (0.01 M), **11c** (0.01 M), **4** (internal standard, 0.01 M) and **2** (0.01 M) was heated at 60 °C for 1 h in the same manner as above. The resulting solution was concentrated and followed by HPLC analysis.

Acknowledgment. We thank NOF Corp., Griffith University, and the Australian Research Council for financial assistance.

JA972240T