Advantage of Using *tert*-Hexyl Peroxypivalate as an Initiator for the Polymerization of Methyl Methacrylate

Tomoyuki Nakamura,[†,§] W. Ken Busfield,[†] Ian D. Jenkins,*[,†] Ezio Rizzardo,[‡] San H. Thang,[‡] and Shuji Suyama[§]

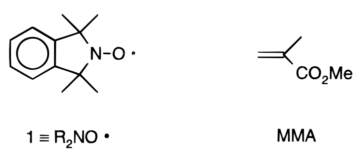
Faculty of Science and Technology, Griffith University, Nathan, Queensland 4111, Australia, Division of Chemicals and Polymers, CSIRO, Private Bag 10, Rosebank MDC, Clayton, Victoria 3169, Australia, and Fine Chemicals and Polymers Research Laboratory, NOF Corporation, Taketoyo-cho, Chita-gun, Aichi 470-23, Japan

Received July 26, 1996

Revised Manuscript Received October 21, 1996

Introduction

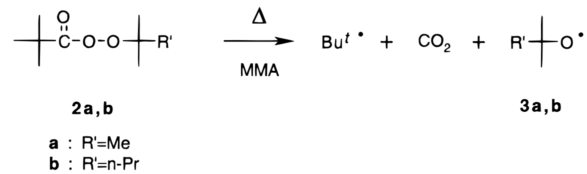
The initiation process in free radical polymerization plays an important role in determining polymer properties such as stability, molecular weight distribution, and composition. In particular, initiator-derived end groups can have profound effects on the stability of the polymer toward thermal and/or photochemical degradation.[1] The nitroxide radical trapping technique, employing 1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindol-2-yloxyl (**1**) as a



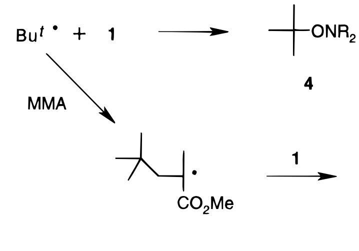
scavenger, has been used extensively to elucidate initiation mechanisms in free radical polymerization.[2] Griffiths *et al*. studied the reaction of *tert*-butoxyl radicals **3a** with methyl methacrylate (MMA) and reported that **3a** underwent not only addition to MMA but also hydrogen abstraction from MMA in significant proportion (33%).[3] This indicates that **3a** is a potent hydrogen abstractor and *tert*-butoxyl radical initiation introduces a considerable amount of unsaturated end groups in the poly(MMA), which will cause instability in the polymer.[4]

In this paper, the initiation mechanisms for *tert*-hexyloxyl radicals **3b**, with MMA have been studied. *tert*-Alkoxyl radicals having an alkyl group larger than a methyl group at the tertiary carbon are known to be susceptible to β-scission to form a ketone and alkyl radicals at a significant rate in carbon tetrachloride.[5] The resulting alkyl radicals have poor H-abstracting ability, and they will undergo selective addition to monomer.[6] However, there have been no reports regarding the detailed mechanisms of initiation by **3b**. *tert*-Alkyl peroxypivalates **2**, which are widely used commercial initiators in the radical polymerization of acrylates and methacrylates,[7] are a convenient source of *tert*-alkoxyl radicals. In previous work from this laboratory, we have shown[8] (i) that peroxypivalate **2a**, on thermolysis, generates equimolar amounts of *tert*-butyl radicals and *tert*-alkoxyl radicals in MMA (Scheme 1) and (ii) that *tert*-butyl radicals undergo negligible H

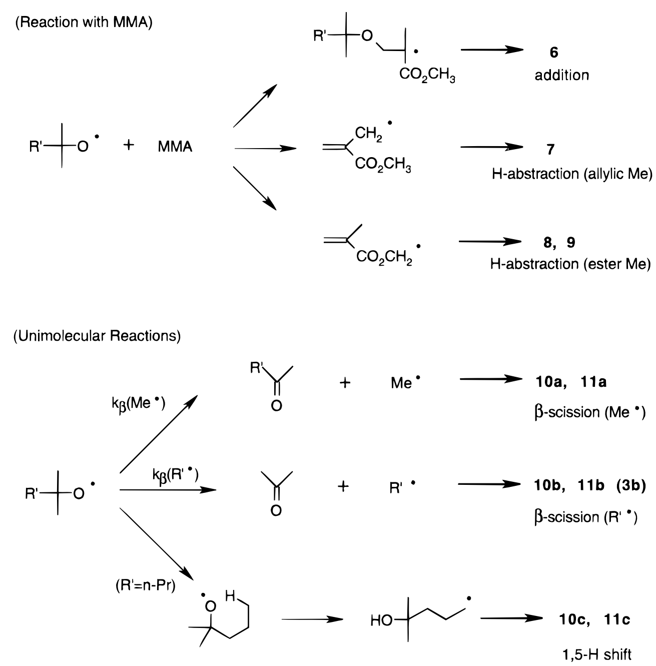
Scheme 1



Scheme 2



Scheme 3



abstraction from MMA; all abstraction products are formed exclusively from abstraction by the alkoxyl radicals.

Results and Discussion

The thermal decomposition of *tert*-hexyl peroxypivalate (**2b**) (0.040 mol dm^{-3}) in MMA as solvent in the presence of **1** (0.040 mol dm^{-3}) was carried out *in vacuo* at 60 °C for 1 h. Alkoxyamines formed by trapping of the carbon-centered radicals derived from the initiator or of the radicals resulting from the reactions of initiator radicals with MMA, were analyzed by HPLC, HPLC−MS, and NMR. *tert*-Butyl radicals formed by the thermolysis of **2b** were immediately trapped by **1** to form **4** or underwent competitive addition to MMA followed by trapping to give **5** (Scheme 2).

On the other hand, a variety of products were formed by the reaction of *tert*-hexyloxyl radicals with MMA, as shown in Scheme 3. Yields (shown in Table 1) have been normalized so that the total yield of *tert*-alkoxyl radical-derived products is 100%. Alkoxyamines **6** and **7**−**9** were derived from *tert*-alkoxyl radical addition to

* Corresponding author. Tel: (07) 3875 7476. Fax: (07) 3875 7656. E-mail: I.D.Jenkins@sct.gu.edu.au.

† Griffith University.

‡ CSIRO.

§ NOF Corp.

S0024-9297(96)01112-6 CCC: $12.00

Table 1. Normalized Yields (%) of Products from the Reaction of *tert*-Alkoxyl Radicals (R′(CH₃)₂CO•) with MMA at 60 °C[a]

product	**3a**[b] (R′ = Me)	**3b** (R′ = *n*-Pr)
6	62.2	6.2
7	29.2	3.4
8	3.1	0.4
9	0.9	0.1
10a	3.7	0.7
11a	0.9	0.2
10b		38.3
11b		7.6
10c		35.6
11c		7.5

[a] $[\mathbf{1}]_0 = 0.040$ mol dm^{-3}, $[\mathbf{2}]_0 = 0.040$ mol dm^{-3}. Reaction time = 1.0 h. [b] Reference 8.

Chart 1

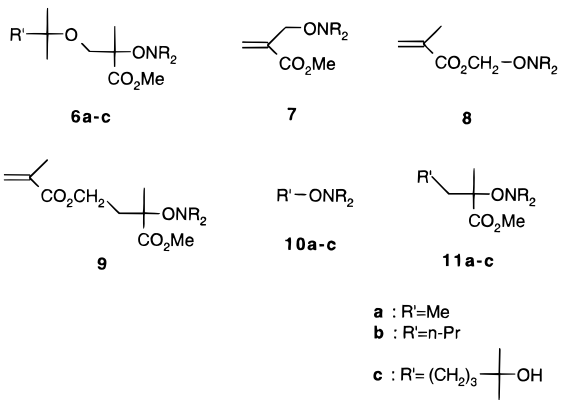


Table 2. Proportion (%) of Reactions of *tert*-Alkoxyl Radicals (R′(CH₃)₂CO•) with MMA at 60 °C

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

MMA and hydrogen abstraction from MMA, respectively (it is unlikely that any of the alkyl radicals undergo significant H abstraction from MMA under these reaction conditions, as shown in our work[8] on peroxypivalate **2a**). Alkoxyamines **10** and **11** were derived from the alkyl radicals formed by rearrangement and/or β-scission of the *tert*-alkoxyl radicals. β-Scission of **3a** generated only methyl radicals, resulting in alkoxylamines **10a** and **11a**. On the other hand, *tert*-hexyloxyl radicals **3b** underwent alternative β-scission, generating *n*-propyl radicals (to form **10b** and **11b**), as well as β-scission to generate methyl radicals. Furthermore, products **10c** and **11c** were detected in the reaction involving **3b**. These products were derived from 4-hydroxy-4-methylpentyl radicals formed via a 1,5-hydrogen shift of **3b**. This type of rearrangement is known in carbon tetrachloride,[9] but it has not previously been reported in a monomer such as MMA. The relative proportions of the various *tert*-alkoxyl radical-derived products are summarized in Table 2. Slightly lower ratios of addition versus H abstraction for **3b** compared with **3a** were observed in the reaction with MMA; these were 65:35 (**3a**) and 61:39 (**3b**). We have previously reported that this ratio decreases in the order hydroxyl > ethoxyl > isopropoxyl > *tert*-butoxyl.[10] The present data are consistent with this trend, the reduced addition rate being largely due to increased steric hindrance.

The extent of the direct reaction of **3b** with MMA was greatly reduced by competing fast unimolecular reactions, that is, β-scission and a 1,5-H shift. Also, the product yields indicate that the rate of the 1,5-H shift reaction of **3b** was comparable to the β-scission rate [(**10c** + **11c**):(**10b** + **11b**)]. Thus, unimolecular decomposition and rearrangement reactions to form alkyl radicals are predominant in the reaction of **3b** with MMA, occurring to the extent of about 90%. This means that, overall, the ratio of addition to abstraction is very high (from Table 2, addition:abstraction = 96.1:3.9, or about 24:1).

It is concluded that, in contrast to **3a**, the main reacting species in the reaction of **3b** with MMA are not alkoxyl radicals but alkyl radicals formed by β-scission and rearrangement of the *tert*-hexyloxyl radicals. The alkyl radicals formed will undergo selective addition to MMA;[11] therefore, the proportion of overall addition to MMA in the reaction with **3a** and **3b** is 67% and 96%, respectively. This indicates that if **3b** was used to initiate the polymerization of MMA, the proportion of unsaturated end groups derived from the initiation process should be much lower than if **3a** was used.

Acknowledgment. Financial assistance from NOF Corp., Griffith University, and the Australian Research Council is gratefully acknowledged.

References and Notes

(1) (a) Moad, G.; Solomon, D. H. *Aust. J. Chem.* **1990**, *43*, 215. (b) Krstina, J.; Moad, G.; Solomon, D. H. *Eur. Polym. J.* **1989**, *25*, 767.

(2) (a) Moad, G.; Solomon, D. H. In *Comprehensive Polymer Science*; Eastmond, G. C., Ed.; Pergamon: London, 1989; Vol. 3, pp 116−117. (b) Busfield, W. K.; Grice, I. D.; Jenkins, I. D. *Aust. J. Chem.* **1995**, *48*, 625 and references contained therein.

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

(4) (a) Cacioli, P.; Moad, G.; Rizzardo, E.; Serelis, A. K.; Solomon, D. H. *Polym. Bull.* **1984**, *11*, 325. (b) Meisters, A.; Moad, G.; Rizzardo, E.; Solomon, D. H. *Polym. Bull.* **1988**, *20*, 499.

(5) (a) Kochi, J. K. *J. Am. Chem. Soc.* **1962**, *84*, 1193. (b) Walling, C.; Padwa, A. *J. Am. Chem. Soc.* **1963**, *85*, 1593. (c) Greene, F. D.; Savitz, M. L.; Osterholtz, F. D.; Lau, H. H.; Smith, W. N.; Zanet, P. M. *J. Org. Chem.* **1963**, *28*, 55. (d) Bacha, J. D.; Kochi, J. K. *J. Org. Chem.* **1965**, *30*, 3272.

(6) Giese, B.; Meixner, J. *Chem. Ber.* **1981**, *114*, 2138.

(7) (a) Sheppard, C. S. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Klingsberg, A., Piccininni, R. M., Salvatore, A., Baldwin, T., Eds.; Wiley-Interscience: New York, 1988; Vol. 11, pp 1−21. (b) Suyama, S.; Nakamura, T.; Ishigaki, H. Jpn. Kokai Tokkyo Koho 841417; *Chem. Abstr.* **1996**, *124*, 346158.

(8) Nakamura, T.; Busfield, W. K.; Jenkins, I. D.; Rizzardo, E.; Thang, S. H.; Suyama, S. *J. Am. Chem. Soc.*, in press.

(9) (a) Walling, C.; Padwa, A. *J. Am. Chem. Soc.* **1961**, *83*, 2207. (b) Walling, C.; Padwa, A. *J. Am. Chem. Soc.* **1963**, *85*, 1597.

(10) Busfield, W. K.; Jenkins, I. D.; Thang, S. H.; Rizzardo, E.; Solomon, D. H. *Eur. Polym. J.* **1993**, *29*, 397.

(11) The selective addition for particular alkyl radicals (cyclohexyl,[6] methyl[8] and *tert*-butyl[8]) to MMA has been reported. The detailed pattern of reaction of ethyl and *n*-propyl radicals with MMA is currently being investigated.

MA9611127