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Initiation mechanisms for radical polymerization of styrene and methyl methacrylate with highly substituted peroxypivalate initiators

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Abstract

The initiation mechanisms of 1,1,2-trimethylpropyl peroxypivalate **1a** and 1,1,2,2-tetramethylpropyl peroxypivalate **1b** in the radical polymerization of styrene and methyl methacrylate (MMA) have been studied using the nitroxide trapping technique. Thermolysis of **1** generated *t*-butyl and the corresponding *t*-alkoxyl radicals, i.e. 1,1,2-trimethylpropoxyl **2a** and 1,1,2,2-tetramethylpropoxyl radicals **2b**. Both *t*-alkoxyl radicals underwent very fast unimolecular processes (β-scission) essentially to the exclusion of intermolecular processes (addition and H-abstraction), in contrast to other *t*-alkoxyl radicals such as *t*-butoxyl radicals. The extent of β-scission of **2a** and **2b** to form alkyl radicals R· were 97.6 and 99.7% in styrene and 98.4 and 99.7% in MMA, respectively. Alkyl radicals formed in the reaction then underwent selective tail addition to monomers or were trapped by the nitroxide. From the relative yields of products arising from the competitive addition/trapping reactions of alkyl radicals, the absolute rate constants for the addition of isopropyl radicals to the two monomers at 60°C are estimated to be 4.7×10^5 l mol^{-1} s^{-1} to styrene and 1.3×10^6 l mol^{-1} s^{-1} to MMA, respectively.

Keywords: Initiation mechanism; Radical polymerization; Nitroxide trapping

1. Introduction

In our previous work [1–5], we have shown that the use of *t*-alkyl peroxypivalates **1** as initiators for the free radical polymerization of acrylic monomers can lead to a variety of initiator derived polymer end-groups including alkyl, *t*-alkoxyl and olefinic. The relative proportions of the different end groups can have a significant influence on the thermal and photo-degradative instability of the resultant polymer [6,7]. Scheme 1 shows the general initiation mechanism with methyl methacrylate (MMA) as monomer, and the variety of radicals derived from a peroxypivalate as initiator which can add to the monomer to eventually become end groups in the polymer. Addition [reaction (2)] and hydrogen abstraction reactions [reactions (3) and (4)] caused by *t*-alkoxyl radicals are particularly unwelcome as they lead to labile hydrogens (α position to ethereal oxygen and allylic) in the final polymer. Such hydrogens are susceptible to hydrogen abstraction under the conditions of oxidative degradation. Alkyl radicals are much more desirable than alkoxyl radicals as intermediates, since they undergo selective addition to monomer [reaction (7)] and then lead to stable (saturated) polymer end groups. Thus, the alkyl radical formation reactions of *t*-alkoxyl radicals, e.g. β-scission [reactions (5) and (6)], are very important in the initiation steps in the polymerization.

The extent of β-scission of *t*-alkoxyl radicals to form alkyl radicals has been shown to be markedly dependent on the nature of substituents α to oxygen. For *t*-alkoxyl radicals of general structure [$R(CH_3)_2CO\cdot$, **2**], it has been reported that the rate constant for β-scission increases in the series R = Me < Et < Pr^i < Bu^t in carbon tetrachloride [8,9]. However, there has been no systematic and quantitative study of the reaction carried out in monomers although β-scission strongly depends on solvent and it competes with intermolecular reactions with monomers, i.e. addition and hydrogen abstraction. In this paper, the initiation mechanisms for 1,1,2-trimethylpropoxyl **2a** (R = Pr^i in **2**) and 1,1,2,2-tetramethylpropoxyl radicals **2b** (R = Bu^t in **2**) with styrene and MMA have been investigated by the nitroxide radical trapping technique. These alkoxyl radicals

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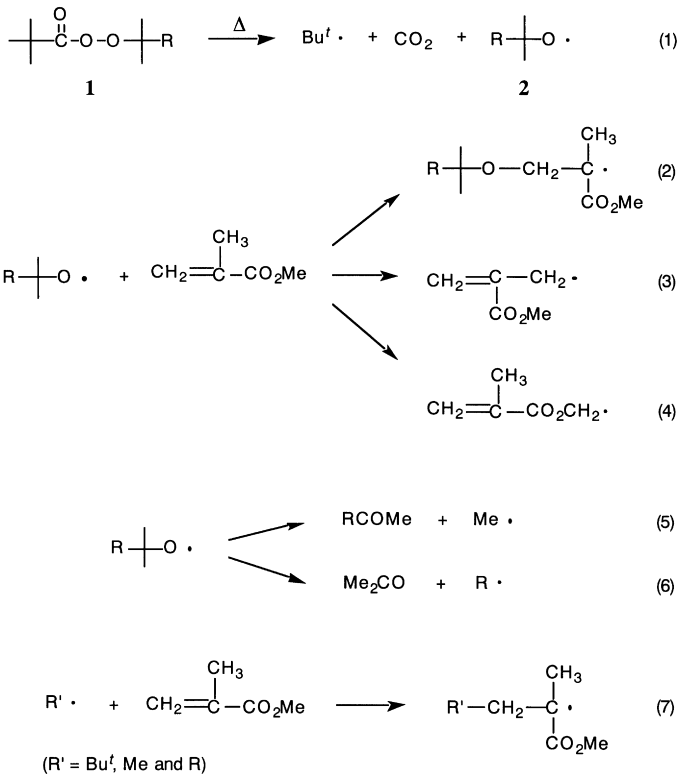
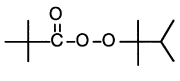
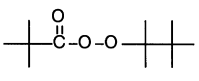


Scheme 1. General initiation mechanism of *t*-alkyl peroxypivalate with MMA.

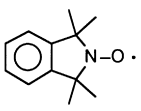
were generated from the thermolysis of the corresponding *t*-alkyl peroxypivalates, i.e. 1,1,2-trimethylpropyl peroxypivalate **1a** and 1,1,2,2-tetramethylpropyl peroxypivalate **1b**, which are used to initiate free radical polymerization (as is the *t*-butyl derivative) [10,11]. The technique used in this work relies on the high efficiency of 1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindol-2-yloxyl **T** in trapping carbon-centered radicals and the stability of the trapped products. It has been reported that **T** reacts with carbon-centered radicals at almost diffusion-controlled rates but not with oxygen-centered radicals [12]. We have previously shown [1–5] that the aminoxyl **T** does not affect the kinetics of the decomposition of *t*-alkyl peroxypivalates, and also that the initiator thermally decomposes to equimolar amounts of *t*-butyl and *t*-alkoxyl radicals under the conditions of trapping experiments.



1a



1b



T

M

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

2. Experimental

2.1. Materials

Styrene was purified by distillation. Methyl methacrylate was washed with 5% NaOH, dried over anhydrous Na_2SO_4 and distilled at atmospheric pressure. Both monomers were stored in a refrigerator (−20°C). 1,1,2-Trimethylpropyl peroxypivalate **1a** was prepared by the reaction of pivaloyl chloride with 1,1,2-trimethylpropyl hydroperoxide in alkaline solution. 1,1,2,2-Tetramethylpropyl peroxypivalate **1b** [13] and the nitroxide **T** [14] were prepared by the literature procedure. The half-lives of **1a** and **1b** at 60°C in cumene have been reported to be 3.7 [15] and 2.1 h [13], respectively.

2.2. Preparation of 1,1,2-trimethylpropyl hydroperoxide

1,1,2-Trimethylpropyl hydroperoxide was prepared by the reaction of the parent alcohol with H_2O_2 in the presence of H_2SO_4. Thus, 1,1,2-trimethylpropanol (20.4 g, 0.20 mol) was added dropwise with stirring at 5–10°C to a mixture of 50% H_2O_2 (57.1 g, 0.84 mol) and 98% H_2SO_4 (40.0 g, 0.40 mol). Stirring was continued for 2.5 h at 0–5°C. Hexane was added to the mixture and the organic layer was separated, washed with water, and dried over anhydrous Na_2SO_4 and $MgSO_4$. After evaporation of the solvent under vacuum, the product (19.0 g, 75.6% yield) was obtained. The purity was 94.1% (determined by iodometric titration using isopropyl alcohol and acetic acid as solvent, and

saturated sodium iodide as the source of iodide). δ_H ($CDCl_3$) 0.90 [d, 6H, $(CH_3)_2CH$, J = 6.8 Hz], 1.16 [s, 6H, $(CH_3)_2CO$], 1.99 [heptet, 1H, $(CH_3)_2CH$, J = 6.8 Hz], 6.62 (br s, 1H, OOH); δ_C ($CDCl_3$) 17.5 [$(CH_3)_2CH$], 20.8 [$(CH_3)_2CO$], 33.9 [$(CH_3)_2CH$], 85.6 [$(CH_3)_2CO$].

2.3. Preparation of 1,1,2-trimethylpropyl peroxypivalate **1a**

Pivaloyl chloride (13.3 g, 0.11 mol) was added dropwise over a period of 10 min with stirring at 0–5°C to a mixture of 94.1% 1,1,2-trimethylpropyl hydroperoxide (12.6 g, 0.10 mol) and 30% KOH (29.9 g, 0.16 mol). Stirring was continued for 1 h at 0–5°C, and then cold water (20 g) was added to the mixture. The organic layer was washed with 5% NaOH, with a buffer solution containing Na_2SO_3, acetic acid and sodium acetate, and then washed with water, and dried over anhydrous Na_2SO_4 and $MgSO_4$ to give 18.0 g of viscous liquid in 89.0% yield. The purity was determined by the following titration method. Acetic acid (0.2 ml), isopropyl alcohol (20 ml), and saturated potassium iodide (2 ml) were added to a 0.2 M KOH–methanol solution containing the peroxide sample (0.2 g) at room temperature. The mixture was refluxed for 3 min. The liberated iodide was titrated with aqueous sodium thiosulfate solution. Thus, the purity of the peroxyester was determined as 93.5%. The structure of **1a** was consistent with its NMR and HPLC–MS. δ_H ($CDCl_3$) 0.89 [d, 6H, $(CH_3)_2CH$, J = 7.0 Hz], 1.16 [s, 6H, $(CH_3)_2CO$], 1.19 [s, 9H, $(CH_3)_3C$], 1.93 [heptet, 1H, $(CH_3)_2CH$, J = 7.0 Hz]; δ_C ($CDCl_3$) 17.4 [$(CH_3)_2CH$], 21.2 [$(CH_3)_2COO$], 27.2 [$(CH_3)_3C$], 34.6 [$(CH_3)_2CH$], 38.8 [$(CH_3)_3C$], 88.1 [$(CH_3)_2COO$], 174.9 (C=O); m/z 225 (M + Na), 203 $(M + H)^+$.

2.4. Trapping experiments

A solution of **1** (0.040 mol l^{-1}) and **T** (0.040 mol l^{-1}) in freshly distilled monomer was degassed by three successive freeze–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.

2.5. Analysis

Analytical HPLC was performed using 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 Instruments 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 re-injection of the solutions of known concentration to assess peak response ratio for the UV detector. The extinction coefficients of unisolated compounds were assumed to be the same as those of isolated products containing identical UV chromophores. 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 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 at 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 (200 MHz) spectrometer using deuterated chloroform as solvent. Chemical shifts for ^1H 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.

2.6. Products and new compounds

The HPLC-separated products were identified by electrospray mass spectrometry. Products **3** [1], **4** [4], **6** [1], **7** [16], **11** [1], **13**–**15** [1] were also identified by co-chromatography with authentic samples. New compounds **5**, **8**, **9** and **16** were isolated by preparative HPLC and characterized by NMR. Spectroscopic data of new compounds are listed below (J values are given in Hz; ring CH_3 refers to methyl substituents on the isoindole and primed numbers of carbon refer to monosubstituted phenyl ring). The tentative structures of **10**, **12** and **17** are based on their mass spectrum detected by HPLC–MS.

2.7. 2-[2-(1,1,2-Trimethylpropoxy)-1-phenylethoxy]-1,1,3,3-tetramethyl-2,3-dihydro-1H-isoindole **5**

δ_H ($CDCl_3$) 0.78, 1.26, 1.50 and 1.68 (4 × br s, 4 × 3H, 4 × ring CH_3), 0.89 [d, 6H, $(CH_3)_2CH$, J = 6.9], 1.07 [s, 3H, $(CH_3)_2CO$], 1.09 [s, 3H, $(CH_3)_2CO$], 1.80 [heptet, 1H, $(CH_3)_2CH$, J = 6.9], 3.40 (dd, 1H, CH_2, J = 4.4, 9.8), 3.80 (dd, 1H, CH_2, J = 8.1, 9.8), 4.85 (dd, 1H, CHON, J = 4.4, 8.1), 6.92–7.44 (m, 9H, ArH); δ_C ($CDCl_3$) 17.6 [$(CH_3)_2CH$], 21.9 [$(CH_3)_2CO$], 25.2, 29.4 and 29.6 (4 × ring CH_3), 35.9 [$(CH_3)_2CH$], 64.6 (CH_2), 88.5 (CHON), 121.4 and 121.7 (C-4, C-7), 127.0 (C-5, C-6), 127.7, 127.9 and 128.2 (C-2′, C-3′, C-4′); m/z 418 $(M + Na)^+$, 396 $(M + H)^+$.

2.8. 2-Isopropoxy-1,1,3,3-tetramethyl-2,3-dihydro-1H-isoindole **8**

δ_H ($CDCl_3$) 1.28 [d, 6H, $(CH_3)_2CH$, $J = 6.2$], 1.38 and 1.54 (2 × br s, 2 × 6H, 4 × ring CH_3), 4.08 [heptet, 1H, $(CH_3)_2CH$], 7.11–7.16 (m, 2H, ArH), 7.21–7.28 (m, 2H, ArH); δ_C ($CDCl_3$) 22.2 [$(CH_3)_2CH$], 25.3 and 30.5 (2 × br s, 4 × ring CH_3), 67.3 (C-1, C-3), 75.5 [$(CH_3)_2CH$], 121.6 (C-4, C-7), 127.1 (C-5, C-6), 145.5 (C-3a, C-7a); *m/z* 256 $(M + Na)^+$, 234 $(M + H)^+$.

2.9. 2-(3-Methyl-1-phenylbutoxy)-1,1,3,3-tetramethyl-1,2-dihydro-1H-isoindole **9**

δ_H ($CDCl_3$) 0.68, 1.22, 1.45 and 1.64 (4 × br s, 4 × 3H, 4 × ring CH_3), 0.93 [d, 3H, $(CH_3)_2CH$, $J = 6.4$], 0.96 [d, 3H, $(CH_3)_2CH$, $J = 6.4$], 1.5 [m, 1H, $(CH_3)_2CH$], 1.74 (ddd, 1H, CH_2, $J = 5.0$, 9.1, 13.4), 2.01 (ddd, 1H, CH_2, $J = 5.9$, 8.7, 13.4), 4.73 (dd, 1H, CHON, $J = 5.9$, 9.1), 6.92–7.43 (m, 9H, ArH); δ_C ($CDCl_3$) 22.3 [$(CH_3)_2CH$], 23.6 [$(CH_3)_2CH$], 24.8 [$(CH_3)_2CH$], 25.3, 25.7, 29.1 and 30.3 (4 × br s, 4 × ring CH_3), 45.1 (CH_2), 66.9 and 68.0 (C-1, C-3), 86.6 (CHON), 121.4 and 121.7 (C-4, C-7), 127.0 and 127.1 (C-5, C-6), 127.5, 128.0 and 128.2 (C-2′, C-3′, C-4′), 143.9 (C-1′), 145.1 (C-3a, C-7a); *m/z* 360 $(M + Na)^+$, 338 $(M + H)^+$.

2.10. 2-[2-(1,1,2,2-Tetramethylpropoxy)-1-phenylethoxy]-1,1,3,3-tetramethyl-2,3-dihydro-1H-isoindole **10**

m/z 432 $(M + Na)^+$, 410 $(M + H)^+$.

2.11. Methyl 2-methyl-3-(1,1,2-trimethylpropoxy)-2-(1,1,3,3-tetramethyl-2,3-dihydro-1H-isoindol-2-yloxy)propanoate **12**

m/z 414 $(M + Na)^+$, 392 $(M + H)^+$.

2.12. Methyl 2,4-dimethyl-2-(1,1,3,3-tetramethyl-2,3-dihydro-1H-isoindol-2-yloxy)pentanoate **16**

δ_H ($CDCl_3$) 0.92 [d, 3H, $(CH_3)_2CH$, $J = 5.4$], 0.95 [d, 3H, $(CH_3)_2CH$, $J = 5.4$], 1.34, 1.35, 1.46, 1.47 and 1.57 (5 × s, 15H, 4 × ring CH_3 and 2-CH_3), 1.69–1.95 [m, 3H, $(CH_3)_2CH$ and CH_2], 3.76 (s, 3H, OCH_3), 7.07–7.13 (m, 2H, ArH), 7.20–7.26 (m, 2H, ArH); δ_C ($CDCl_3$) 21.3 [$(CH_3)_2CON$], 23.6, 24.5 and 24.6 [2 × $(CH_3)_2CH$ and $(CH_3)_2CH$], 25.0, 25.8, 29.4 and 29.8 (4 × ring CH_3), 49.5 (CH_2), 51.6 (OCH_3), 67.8 and 67.9 (C-1, C-3), 84.1 (CON), 121.5 and 121.6 (C-4, C-7), 127.1 and 127.3 (C-5, C-6), 144.7 and 145.6 (C-3a, C-7a), 175.5 (C=O); *m/z* 356 $(M + Na)^+$, 334 $(M + H)^+$.

*2.13. Methyl 2-methyl-3-(1,1,2,2-tetramethylpropoxy)-2-(1,1,3,3-tetramethyl-2,3-dihydro-1H-*isoindol-2-yloxy)propanoate **17**

m/z 428 $(M + Na)^+$, 406 $(M + H)^+$.

3. Results and discussion

Initially, the reactions of peroxypivalates with styrene were investigated. Thus, the thermolysis of **1** (0.040 mol l^{-1}) in styrene as a solvent in the presence of **T** (0.040 mol l^{-1}) was carried out in vacuo at 60°C for 1.0 h. A relatively low concentration of **T** was used in order to study the (competitive) reaction of alkyl radicals with monomer. However, under the conditions of the reaction, **T** is still present in excess because of the low conversion (ca. 17% for **1a** [15] and ca. 28% for **1b** [13]) and the $<$ 100% efficiency of generation of radicals from **1** [15]. Most of the excess monomer was removed at reduced pressure, before the products were isolated by HPLC and were identified by electrospray mass spectrometry (HPLC–MS). Products arising from the reactions of styrene with **1a** and **1b** and their relative percentage yields are shown in Fig. 1(a) and (b), respectively. Products **3**, **4**, **6** and **7** were identified also by co-chromatography with authentic samples. New compounds **5**, **8** and **9** were isolated by preparative HPLC and characterized by NMR.

Compounds **3** and **4** were the products derived from the competitive trapping and addition of *t*-butyl radicals to monomer before trapping. In the reaction of **2a** with styrene, product **5** was derived from the alkoxyl radical-addition to styrene and products **6**–**9** were derived from methyl and isopropyl radicals formed via β-scission of **2a**. It can be seen from Fig. 1(a) that the total yield of *t*-butyl radical-derived products (**3** and **4**) is equal to that of *t*-alkoxyl radical-derived products (**5**–**9**), which is consistent with the production of equimolar amounts of *t*-butyl and 1,1,2-trimethylpropoxyl radicals from **1a**, in agreement with previous findings [1–5]. The high total yield of isopropyl radical-derived products (**8** + **9**) clearly indicates that β-scission of **2a** predominates in the reaction of **2a** with styrene.

The products arising from the reaction of **1b** with styrene are dominated by the *t*-butyl radical-derived products, **3** and **4**, see Fig. 1(b). The total yield of the other products, **6**, **7** and **10**, was ca. 0.15%, which means the corresponding reaction pathways are not important in this system. Compound **10** was a very minor product and insufficient material was available for complete characterization by NMR. The tentative structure is based on the molecular weight by HPLC–MS and the structure of the corresponding product **5** in the reaction of **1a** with styrene.

Postulated reaction mechanisms for the reaction of **2a** and **2b** with styrene are shown in Scheme 2 and Scheme 3, respectively. It is apparent that the main reaction

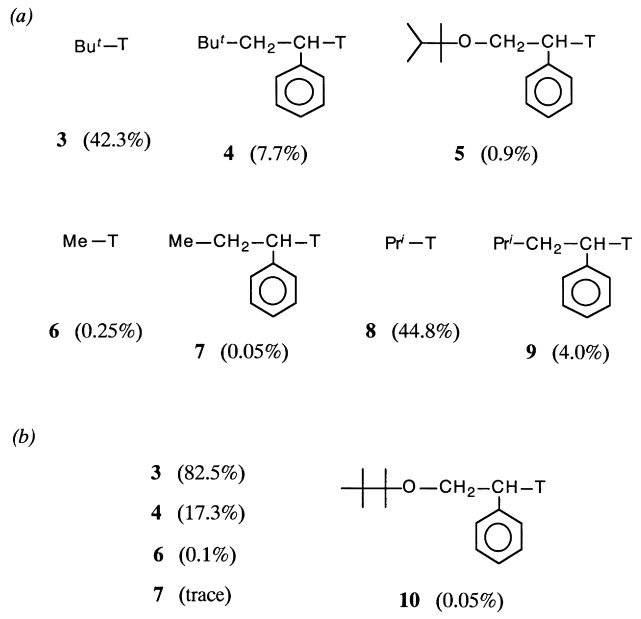
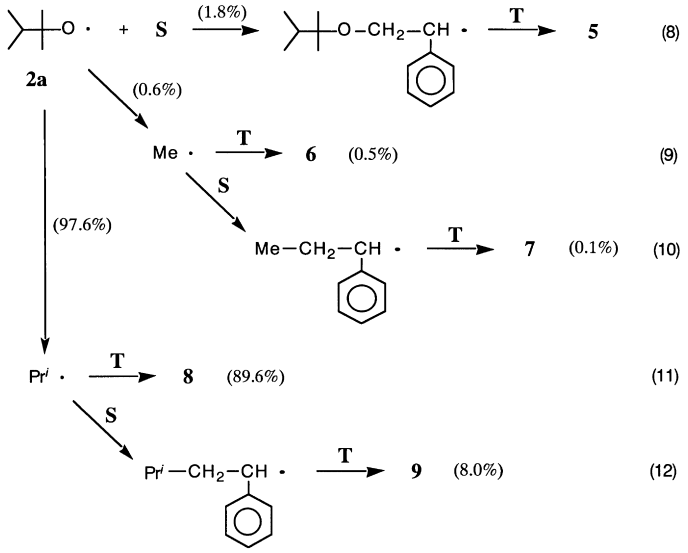


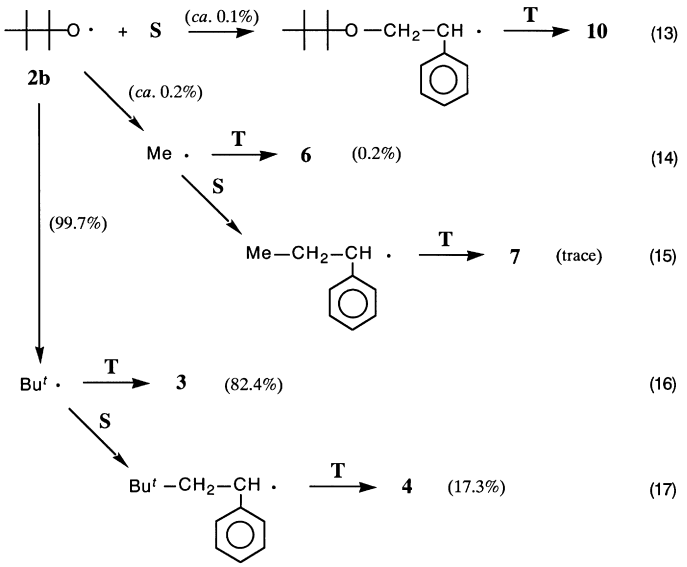
Fig. 1. Products derived from the reaction of *t*-alkyl peroxypivalates (a) **1a** and (b) **1b** with styrene in the presence of **T** at 60°C.

pathway for both *t*-alkoxyl radicals is β-scission to form alkyl radicals R·. The extents of the reaction were 97.6% (R· = Pr^i· for **2a**) and 99.7% (R· = Bu^t· for **2b**). The ratio of the rate constants for alkyl radical elimination to methyl radical elimination, k_β(R·)/k_β(Me·), can be calculated from the product ratios (**8** + **9**)/[(**6** + **7**)/2] for **2a** and (**3** + **4**)/[(**6** + **7**)/2] for **2b**. The ratios are about 330 for **2a** and 1000 for **2b**. These values are well in excess of those we have previously measured for some other *t*-alkoxyl radicals such as R = Et, n-Pr and neo-pentyl in R(CH$_3$)$_2$CO·, i.e. 131 (R = Et), 117 (R = n-Pr) and 98 (R = neo-C$_5$H$_{11}$) for reactions in styrene [4,5]. This is qualitatively consistent with the result observed in carbon tetrachloride as a solvent and in the presence of cyclohexane [8].

Next, the reactions of **1a** and **1b** with MMA as substrate monomer and solvent were studied in a similar manner to the styrene systems. The reaction products are shown in Fig. 2 with their relative percentage yields. Products **11**, **13**–**15** have been identified and characterized previously [1]. A new compound **16** was isolated by preparative HPLC and characterized by HPLC–MS and NMR. However, insufficient quantities of the alkoxyl radical addition products (**12** and **17**) were available for complete characterization and the structures are based on the molecular weight measured by HPLC–MS. As can be seen in Fig. 2(a), the total yield of *t*-butyl radical-derived products (**3** + **11**) is not equal to that of *t*-alkoxyl radical-derived products. This is due to the known instability of **11** [1]. Assuming that (theoretical yield of **11**) = (total yield of **2a** derivatives) − (yield of **3**), it can be estimated that ca. 27% of **11** was decomposed under the conditions of the experiment. The reactions of *t*-alkoxyl radicals with MMA are summarized in Table 1, in which the proportions of reactions have been normalized so that the total yield of *t*-alkoxyl radical derivatives is 100% and in the case of **2b** the decomposition conversion of product **11** has been assumed to be 27%. *t*-Alkoxyl radicals **2a** (R = Pr^i) and **2b** (R = Bu^t) underwent the direct reactions with MMA [reactions (2)–(4) in Scheme 1], i.e. addition to MMA (to form **12** and **17**) and hydrogen abstraction from MMA (to form **13** and **14**), to a much smaller extent than other *t*-alkoxyl radicals. In fact they accounted for only ca. 0.5% for **2a** and < 0.1% for **2b** of the total reactions. β-Scission, in which alkyl radicals R· were generated as almost the only reacting species accounted for the remaining bulk of reaction. Thus, *t*-alkyl peroxypivalates **1a** and **1b** can be used as initiators to provide a virtually exclusive source of the alkyl radicals in both styrene and MMA.



Scheme 2. Reactions of *t*-alkoxyl radicals **2a** with styrene at 60°C.



Scheme 3. Reactions of *t*-alkoxyl radicals **2b** with styrene at 60°C.

3.1. The reactions of alkyl radicals with monomer

Alkyl radicals formed in the reaction underwent a competitive addition/trapping reaction [for example, reactions (12) and (11) for isopropyl radicals]. As discussed in our previous papers [1–5], the ratios of the competitive reaction products should be proportional to the relative reactivity of the alkyl radicals to monomer and **T** in an individual experiment (in which the ratio of [monomer]/[**T**] is constant). Therefore, the relative reactivity of isopropyl and *t*-butyl radicals toward styrene can be calculated from the corresponding product yields in the reaction of **1a** as follows:

$$\left[\frac{k_S(Pr^{i}\cdot)}{k_T(Pr^{i}\cdot)} : \frac{k_S(Bu^{t}\cdot)}{k_T(Bu^{t}\cdot)} = \frac{(\boldsymbol{9})}{(\boldsymbol{8})} : \frac{(\boldsymbol{4})}{(\boldsymbol{3})}\right]$$

where $k_S(R\cdot)$ and $k_T(R\cdot)$ are the general rate constants for the reaction of alkyl radicals R· with styrene and **T**, respectively. The value of $k_T(Bu^{t}\cdot)$ has been reported to be 9.1×10^8 l mol^{-1} s^{-1} [17]. If $k_T(Pr^{i}\cdot)$ is assumed to be 1.2×10^9 l mol^{-1} s^{-1} (the rate constant for trapping by **T** of cyclopentyl radicals [17]), the ratio of $k_S(Pr^{i}\cdot)/k_S(Bu^{t}\cdot)$ is estimated to be 0.65. A similar calculation for the reaction of **2a** with MMA gave a value of $k_{MMA}(Pr^{i}\cdot)/k_{MMA}(Bu^{t}\cdot) = 0.60$. The absolute rate constants for the addition of isopropyl radicals to styrene and MMA, estimated by taking the previous reported values of $k_S(Bu^{t}\cdot)$ [4] and $k_{MMA}(Bu^{t}\cdot)$ [1] ($= 7.2 \times 10^5$ and 2.2×10^6 l mol^{-1} s^{-1} at 60°C), are 4.7×10^5 and 1.3×10^6 l mol^{-1} s^{-1}, respectively. Therefore the rate constant for isopropyl radicals toward addition to MMA observed here is between that for *t*-butyl and ethyl radicals [$k_{MMA}(Et\cdot) = 8.6 \times 10^5$ l mol^{-1} s^{-1} [3]]. Thus the more nucleophilic alkyl radicals are more reactive toward addition to MMA, which is consistent with a literature report that the relative reactivity of alkyl radicals in addition reactions to electron-deficient monomers such as diethyl vinylphosphate [18] and acrylonitrile [19] is in the general order n-alkyl < *sec*-alkyl < *t*-alkyl radicals. This can be understood in terms of polar factors. It is interesting that the reactivity of isopropyl radicals toward styrene is not significantly higher than that of ethyl radicals [$k_S(Et\cdot) = 4.6 \times 10^5$ l mol^{-1} s^{-1} [4]]. This also can be described using frontier orbital theory. That is, one possible reason is that the energy difference between the SOMO of the alkyl radical and the LUMO of the monomer is small in MMA (electron-deficient monomer), so that variation of the nucleophilicity of the alkyl radical exerts a large effect. In comparison, the SOMO–LUMO energy difference is larger

Table 1
Proportion (%) of reactions of *t*-alkoxyl radicals [$R(CH_3)_2CO\cdot$] with styrene and MMA at 60°C

R	Reactions with styrene			Reactions with MMA				
	Addition	β-Scission		Addition	H-Abstraction		β-scission	
		To Me·	To R·		Allylic Me	Ester Me	To Me·	To R·
Me[a]	98.6	1.4	–	62.2	29.2	4.0	4.6	–
Et[a]	46.7	0.8	52.5	10.4	6.2	0.7	1.4	81.3
Pr^i	1.8	0.6	97.6	0.3	0.2	Trace	1.1	98.4
Bu^t	ca. 0.2	ca. 0.2	99.7	Trace	Trace	Trace	0.3	99.7

[a]From Refs. [3,4].

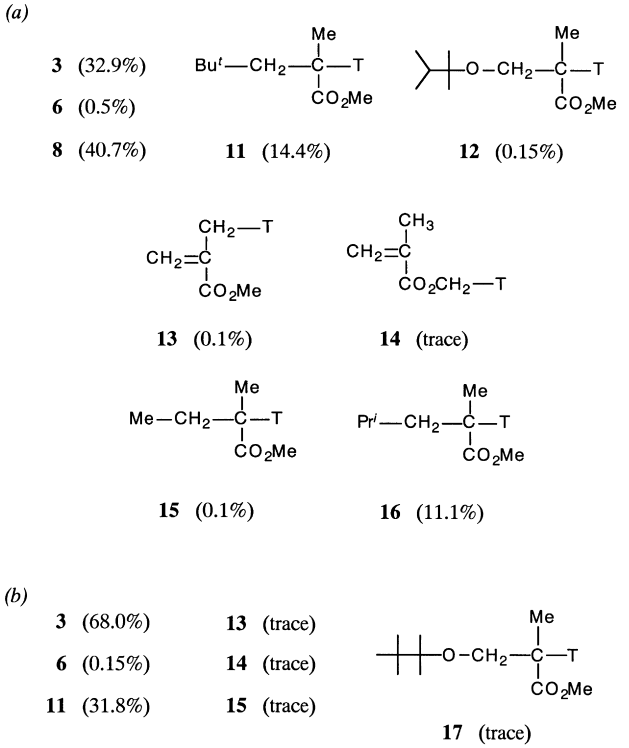


Fig. 2. Products derived from the reaction of *t*-alkyl peroxypivalates (a) **1a** and (b) **1b** with MMA in the presence of **T** at 60°C.

in the styrene (electron-rich monomer) system, and hence the same variation of the nucleophilicity has less influence on the rate of addition [20,21]. MMA exhibits, thus, not only a higher reactivity toward alkyl radical addition but also a higher selectivity than does styrene.

4. Conclusion

In this study, we have shown that *t*-alkoxyl radicals **2a** and **2b** undergo extremely fast β-scission to form alkyl radicals in monomers such as styrene and MMA, which almost eliminates the direct reactions of alkoxyl radicals with the monomers. Alkoxyl radical initiation reactions, i.e. addition and H-abstraction, which lead to labile hydrogens (α position to ethereal oxygen and allylic) in the final polymer, are thereby minimized. Alkyl radicals are much more desirable than alkoxyl radicals as intermediates, since they lead to stable (saturated) polymer end groups via selective tail addition to monomers. For example, Walling and Mintz [22] have reported that the relative rates for H-abstraction by *t*-butoxyl radicals from cyclohexane, tetrahydropyran and cyclohexane are 1:4:18 (per equivalent hydrogen) at 273 K. We have also reported that a hydrogen α to oxygen in tetrahydropyran is 8.7 times as reactive as a cyclohexyl hydrogen towards abstraction by *t*-butoxyl radicals at 60°C [23,24].

Thus *t*-alkyl peroxypivalates **1a** and **1b** can be used as initiators to provide an almost exclusive source of alkyl radicals as reacting species, and the predominant ($\geq$ 99.5%) initiation-derived end group in polymerization systems would be R–CH_2–CXY– (R = Pr^i and/or Bu^t). Therefore it can be concluded that if **1a** and **1b** were used to initiate the polymerization of monomers such as styrene and MMA, the proportion of stable polymer end groups derived from the initiation process should be much higher than if *t*-butyl peroxypivalate (R = Me in **1**) was used.

From the relative yields of products arising from the competitive addition/trapping reactions of alkyl radicals, the absolute rate constants for isopropyl radical addition reactions are estimated to be 4.7×10^5 l mol^{-1} s^{-1} to styrene and 1.3×10^6 l mol^{-1} s^{-1} to MMA. These values are significantly lower than those for *t*-butyl radical addition reactions to styrene and MMA.

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