

Kinetics of Bulk Styrene Polymerization Initiated by 2,2-Bis(*t*-butyldioxy)alkanes

Yasumasa WATANABE, Hideyo ISHIGAKI, and Shuji SUYAMA*

Chemicals and Explosives Research Laboratory, Nippon Oil & Fats Co.,
Takeotoyo-cho, Chita-gun, Aichi 470-23, Japan

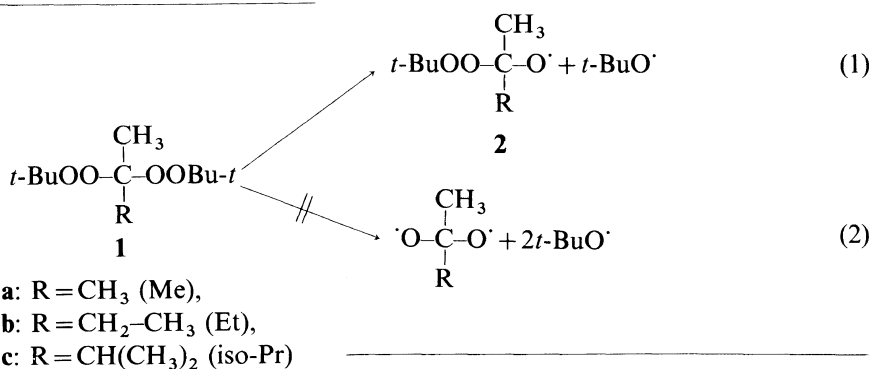
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ABSTRACT: Bulk styrene polymerizations initiated by 2,2-bis(*t*-butyldioxy)propane, 2,2-bis(*t*-butyldioxy)butane, and 2,2-bis(*t*-butyldioxy)-3-methylbutane have been examined. The polymerization rate simulation based on the decomposition mechanism of initiators is presented, and compared with experimental data. It is shown that the radicals generated from the initiators effectively initiate the polymerization of styrene. We discuss the radical species actually initiating the polymerization of styrene from these initiators.

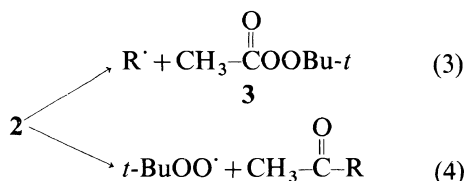
KEY WORDS Styrene / Peroxide Initiator / Radical Polymerization / Polymerization Kinetics / Initiator Efficiency / Simulation /

gem-Bis(*t*-alkyldioxy)alkanes which possess two dioxy groups on the same carbon atom are used as effective free radical initiators for styrene polymerization. However, little attention has been paid to the decomposition mechanism¹⁻³ and behavior in styrene polymerization^{4,5} because of the complicated decomposition.

We⁶⁻⁸ recently started to elucidate the decomposition mechanism of 2,2-bis(*t*-butyldioxy)alkanes (**1**) and showed that the initial decomposition occurs by one bond O—O fission (eq 1) rather than synchronous two bond O—O fission (eq 2). The resulting alkoxy radical **2** with α -*t*-butyldioxy group undergoes facile



β -scission reactions (eq 3 and 4) even in the presence of hydrogen donor (*e.g.*, cumene) or vinyl monomer (*e.g.*, styrene).



* To whom all correspondence should be addressed.

In this paper, we report the polymerization of styrene initiated by **1** focusing on polymerization kinetics.

EXPERIMENTAL

Measurements

GLC analysis was performed with a Shimadzu GC-9A gas chromatograph with a flame ionization detector using a 15 m flexible fused silica capillary column (0.53 mm in diameter) coated with silicone OV-1. A Shimadzu chromatopac C-R6A integrator was used for quantitative analysis. GPC analysis was accomplished on a Shimadzu RID-6A using THF as the eluent. Two columns, a Shodex KF-80M (60 cm) and a Shimadzu HSG-10S (60 cm), were connected in series. The calibration curve was made using standard samples of polystyrene.

Materials

2,2-Bis(*t*-butyldioxy)alkanes were prepared by methods previously described.⁷ The purities of peroxides were over 97.0% by iodometric titration or GLC analysis. Styrene was washed with 2% aqueous sodium hydroxide and water, dried over anhydrous MgSO₄, and distilled under reduced pressure. Cumene was purified by distillation after washing with concentrated sulfuric acid.

Polymerization and Thermolysis

Bulk polymerizations of styrene were carried out in a sealed glass ampoule purged with nitrogen in the presence of initiators **1** (2 mM) at 110°C. After polymerization for a given time, the conversion of styrene and the molecular weight of polystyrene were determined by GLC and GPC analyses, respectively.

Thermolyses of **1** and **3** (0.1 M, respectively) were carried out in cumene under the same conditions as for polymerization. Decomposition rate constants of **1** and **3** were determined by following the disappearance of **1** and **3** by GLC analysis and iodometric titration, respec-

tively.

RESULTS AND DISCUSSION

Polymerization

The bulk polymerization of styrene initiated by **1** was carried out at 110°C. The monomer conversion vs. time curves are shown in Figure 1. The weight-average molecular weight (M_w) of polystyrene obtained by each initiator was *ca.* 5×10^5 at high monomer conversion (*e.g.*, *ca.* 90% conversion). As can be seen from Figure 1, the polymerization rate increased in the order **1a** < **1b** < **1c**, which is consistent with the decomposition rate of initiators (see k_1 in Table I).

Kinetic Modeling

In comparison with relatively simple peroxides such as benzoyl peroxide or di-*t*-butyl peroxide possessing only one dioxy bond in a molecule, kinetic treatment for polymerization of **1** is quite difficult because of the complicated decomposition. But we attempted to derive a kinetic model for styrene polymerization initiated by **1** based on the following decomposition equations established by studies on

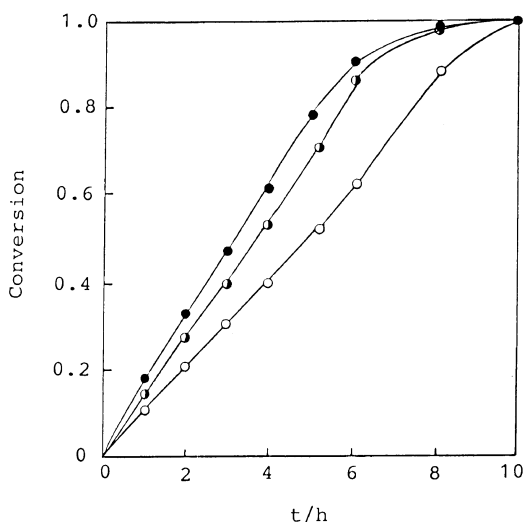


Figure 1. Bulk styrene polymerization initiated by **1** at 110°C: (○), **1a**; (●), **1b**; (●), **1c**; $[1]_0$, 2 mM.

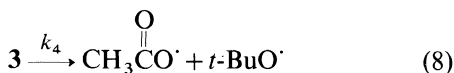
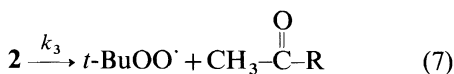
Table I. Rate constants and α values for the decomposition of **1** in cumene at 110°C^a

Initiator	$k_1 \times 10^5/\text{s}^{-1}$	α^b
1a	2.97	0.25
1b	5.87	0.82
1c	10.1	0.99

^a Initial concn, 0.1 M.

^b $\alpha = k_2/(k_2 + k_3)$. Using the reported value $k_4 = 4.92 \times 10^5 \text{ s}^{-1}$,⁷ α was calculated from eq 11. See ref 7 for calculation.

decomposition products of **1** in solvents.⁶⁻⁸



Here, eq 6 and 7 are β -scission reactions of **2**, eq 8 is the decomposition of **3** formed by eq 6, and k_1 – k_4 denote rate constants for each reaction.

From eq 5–8, the rate of generation of radicals (R_r) is expressed by

$$R_r = 2k_1[\mathbf{1}] + 2k_4[\mathbf{3}] \quad (9)$$

Where **3** is an intermediate product and the rate expression is given by

$$d[\mathbf{3}]/dt = k_1k_2[\mathbf{1}]/(k_2 + k_3) - k_4[\mathbf{3}] \quad (10)$$

Integration of eq 10 gives

$$[\mathbf{3}] = \alpha k_1[\mathbf{1}]_0 [\exp(-k_4t) - \exp(-k_1t)] / (k_1 - k_4) \quad (11)$$

where α denotes $k_2/(k_2 + k_3)$ and $[\mathbf{1}]_0$ is initial concentration of **1**.

The kinetic constants k_1 and α values in cumene at 110°C are shown in Table I. The obtained α values mean that β -scission proceeds mainly by eq 7 for **1a** ($\alpha = 0.25$), while mainly by eq 6 for **1b** ($\alpha = 0.82$) and **1c** ($\alpha = 0.99$), and

the scission rates of radicals from **2** decrease in the order $i\text{-Pr} > \text{Et} > t\text{-BuOO} > \text{Me}$.

In general, polymerization rate is given by

$$R_p = \{(fR_r k_p^2 / 2k_t)[\text{I}][\text{M}]^2 + R_{\text{th}}\}^{1/2} \quad (12)$$

where k_p is the propagation rate constant, k_t is the termination rate constant, f is the initiator efficiency, that is, the fraction of radicals actually initiating the polymerization, $[\text{M}]$ is the concentration of unreacted monomer, and R_{th} is the thermal polymerization rate. k_p is calculated from eq 13⁹

$$k_p (\text{M}^{-1} \text{s}^{-1}) = 1.051 \times 10^7 \exp(-3577/T) \quad (13)$$

At high conversion of free radical polymerization, termination reactions involving polymeric radicals become diffusion controlled and the termination rate constant decreases considerably with increase in monomer conversion (*i.e.*, gel effect). Considering the gel effect, the termination rate constant, k_t , decreases with monomer conversion. In this study, the gel effect correlation (*i.e.*, k_t vs. monomer conversion) suggested by Friis and Hamielec¹⁰ for bulk styrene polymerization was used.

$$k_t/k_{t0} = \exp[-2(Bx + Cx^2 + Dx^3)] \quad (14)$$

Where $x(0-1)$ and k_{t0} denote the monomer conversion and the termination rate constant at zero monomer conversion, respectively, and

$$k_{t0} (\text{M}^{-1} \text{s}^{-1}) = 1.255 \times 10^9 \exp(-844/T)$$

$$B(\text{K}) = 2.57 - 5.05 \times 10^{-3} T$$

$$C(\text{K}) = 9.56 - 1.76 \times 10^{-2} T$$

$$D(\text{K}) = -3.03 + 7.852 \times 10^{-3} T$$

The thermal polymerization rate R_{th} and rate constant k_{th} are given by¹¹

$$R_{\text{th}} = (k_p^2 k_{\text{th}} [\text{M}]^5 / k_t)^{1/2} \quad (15)$$

$$k_{\text{th}} (\text{M}^{-2} \text{s}^{-1}) = 2.19 \times 10^5 \exp(-13810/T) \quad (16)$$

Polymerization rate simulation was performed

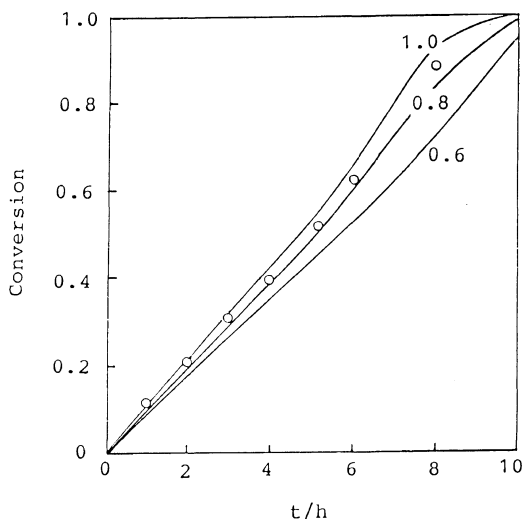


Figure 2. Model prediction of bulk styrene polymerization initiated by **1a**: (O) experimental data; (—) model prediction with $f=1.0$ (top), 0.8 (center), and 0.6 (bottom).

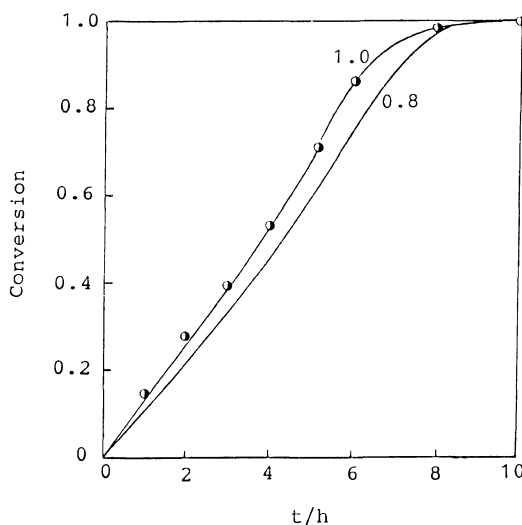


Figure 3. Model prediction of bulk styrene polymerization initiated by **1b**: (●), experimental data; (—), model prediction with $f=1.0$ (top) and 0.8 (bottom).

with above equation.

Comparison between Experimental and Predicted Results

Model simulation varying the initiator efficiency f in eq 12 is shown in Figures 2–4. It is clear that the experimental data are in fairly good agreement with simulation at high initiator efficiency (i.e., $f=0.8$ – 1.0). This indicates that the decomposition mechanism of **1** shown by eq 5–8 is reasonable and all radicals formed from **1** effectively initiate the polymerization.

gem-Bis(*t*-alkyldioxy)alkanes belong to a kind of dialkyl peroxide. Pryor *et al.*^{12,13} studied the kinetics of dialkyl peroxides in styrene polymerization using the general polymerization rate equation (eq 17).

$$R_p = \{k_d f [I][M]^2 k_p^2 / k_t\}^{1/2} \quad (17)$$

where k_d is decomposition rate constant for dialkyl peroxides. They obtained values of $k_d f$ for various dialkyl peroxides from the slope of the plot of R_p vs. $[M][I]^{1/2}$. For example, $k_d f$ for di-*t*-butyl peroxide in styrene polymerization in benzene solvent is $1.5 \times 10^{-9} \text{ s}^{-1}$ at

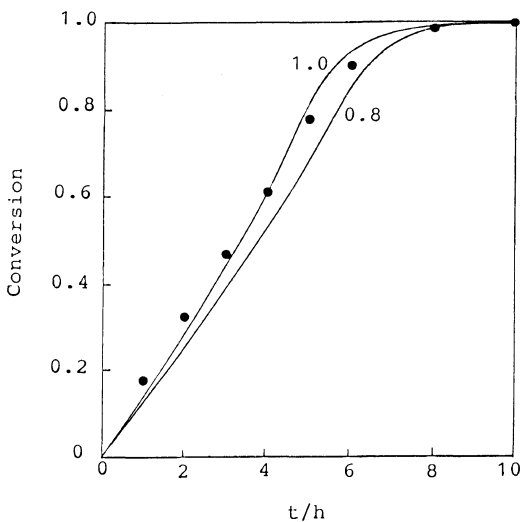
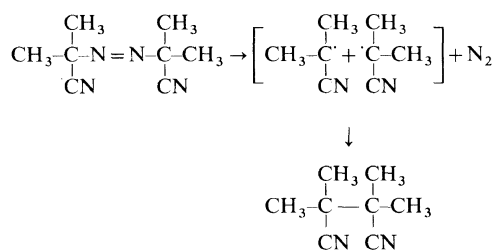


Figure 4. Model prediction of bulk styrene polymerization initiated by **1c**: (●), experimental data; (—), model prediction with $f=1.0$ (top) and 0.8 (bottom).

60°C .¹³ If k_d is taken as $1.7 \times 10^{-9} \text{ s}^{-1}$ at 60°C , as calculated from Arrhenius parameters ($A=9.99 \times 10^{-15} \text{ s}^{-1}$, $E_a=37.75 \text{ kcal mol}^{-1}$) in benzene,¹⁴ we can estimate the f value of di-*t*-butyl peroxide as 0.88 . The high initiator efficiency of both dialkyl peroxides and present

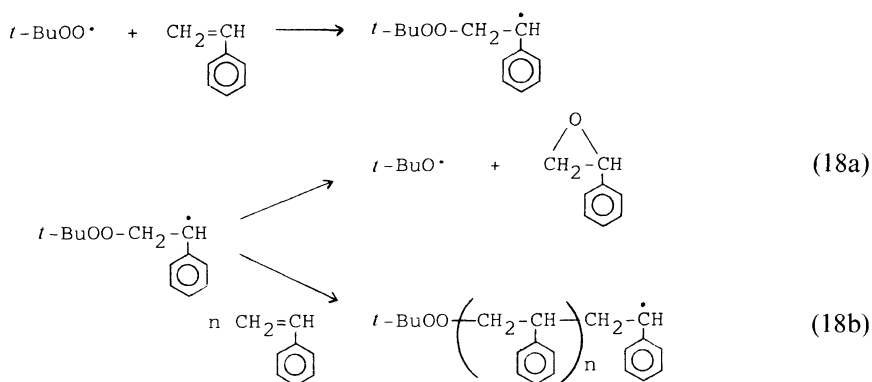
2,2-bis(*t*-butyldioxy)alkanes means that cage reactions leading to formation of inert products are less important for dialkyl type peroxides.

DeSchrijver and Smets¹⁵ reported that the initiator efficiency of azobisisobutyronitrile (AIBN) was affected appreciably by the viscosity of the reaction medium. This is because the following cage reaction that lowers the initiator efficiency is preferable in high viscous medium. However, the initiator



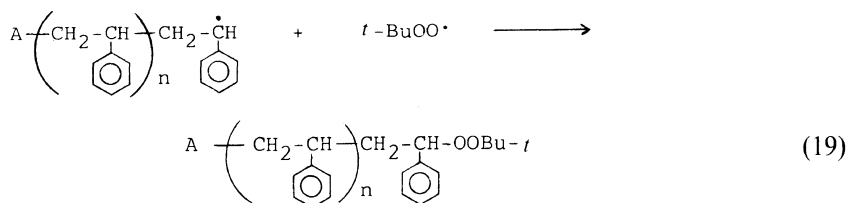
efficiency of **1** was almost constant up to high monomer conversion as shown by Figures 2–4. This suggests that cage reactions of **1** are minor even in high viscous media and **1** acts as an effective initiator all through the polymerization of styrene.

Previously, we⁸ carried out the thermal decomposition of **1** in styrene/benzene (50 v/v%). Interestingly, on the decomposition of **1a**, it was found that about 20 mol% of styrene oxide (based on **1a** decomposed) was produced and about half of polystyrene molecules contained one O–O bond. On the basis of the considerable generation of *t*-BuOO[•] for **1a** (0.75 mol of *t*-BuOO[•] per mol of **1a** decomposed), it was inferred that *t*-BuOO[•] added to styrene to afford styrene oxide (**18a**) or polystyrene containing a O–O bond (**18b**). But *t*-BuOO[•] is a relatively stable radical, so that



possibly polystyrene containing a O–O bond is produced by the coupling reaction of *t*-BuOO[•]

with polystyryl radical (*i.e.*, primary radical termination as shown by eq. 19).



Here, A represents a radical initiating the polymerization. If *t*-BuOO[•] contributes to the

termination reaction, the polymerization rate initiated by **1a** will be reduced considerably.

For example, when all *t*-BuOO \cdot generated from the decomposition of **1a** acts as the termination reaction, the maximum initiator efficiency is estimated to be 0.6 from the equation of $(1 + \alpha)/2$. This equation was simplified by excluding the contribution of radicals generated from the decomposition of **3**, since **3** is a minor decomposition product from **1a**. The simulation curve using $f=0.6$ for **1a** appreciably deviates from the experimental data (Figure 2). Judging from the polymerization efficiency, *t*-BuOO \cdot mainly contributes to the initiation of polymerization to afford the polystyrene containing a dioxy bond.

It is interesting to note that the radical species initiating the polymerization significantly change with the structure of **1**. The species and distribution of initiating radicals depend on the β -scission ratio between eq 6 and 7. We can roughly estimate the initiating radicals for **1a** (R = Me) to be *t*-BuO \cdot (or Me \cdot from the β -scission of *t*-BuO \cdot) and *t*-BuOO \cdot , while for **1b** (R = Et) and **1c** (R = iso-Pr) to be *t*-BuO \cdot , R \cdot , and radicals from the decomposition of **3**.

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