

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

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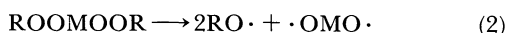
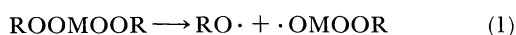
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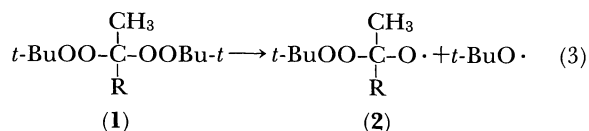
The radical polymerization mechanism of styrene initiated by 2,2-bis(*t*-butyldioxy)alkanes (**1**) has been studied in benzene. The decomposition products of **1** are acetone, alkyl methyl ketone, *t*-butyl alcohol, and *t*-butyl peracetate. Styrene monomer converts to polystyrene along with styrene oxide. The peroxides **1** cleave homolytically at one of dioxy bonds to yield intermediate alkoxy radicals with α -*t*-butyldioxy group, which undergo β -scission to afford *t*-butyldioxy or alkyl radicals. The resulting *t*-butyldioxy radical reacts with styrene to form 2-(*t*-butyldioxy)-1-phenylethyl radical, which decomposes subsequently to styrene oxide and *t*-butoxy radical via γ -scission. Alternatively, a part of *t*-butyldioxy radical adds to styrene to afford polystyrene containing dioxy bond.

gem-Bis(*t*-alkyldioxy)alkanes can be used as excellent free radical initiators for polymerization of styrene. But only a few studies have been reported on the mechanism of polymerization using them.

Yenal'ev and co-workers^{1,2)} studied the polymerization of styrene with *gem*-bis(*t*-alkyldioxy)alkanes. Interestingly, they found that parts of polystyrene molecules possessed dioxy group. It was concluded that the initial decomposition of the peroxides occurred at one of dioxy bonds (Eq. 1) rather than the synchronous two bond scission (Eq. 2), and suggested that the polystyrene molecules containing dioxy groups were produced by the addition of the alkoxy radical having dioxy group to styrene. However, the detailed polymerization mechanism has not been clear.

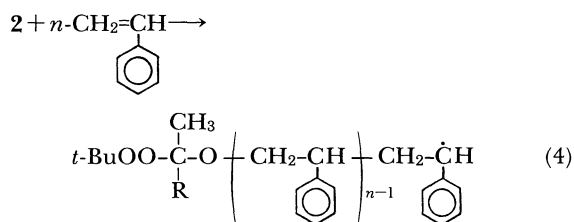


Recently we have reported on the mechanism of thermal decomposition of 2,2-bis(*t*-butyldioxy)alkanes (**1**) in diphenylmethane or cumene.^{3,4)} The results have shown that the peroxides cleave homolytically at one of dioxy bonds to yield *t*-butoxy and intermediate alkoxy radicals (**2**) with α -*t*-butyldioxy group (Eq. 3), which undergo β -scission to afford *t*-butyldioxy or alkyl radicals.



(1a): R=CH₃, (1b): R=CH₂-CH₃, (1c) R=CH(CH₃)₂

In the polymerization of styrene using **1**, if the addition reaction of **2** to styrene occurs much faster than the β -scission of **2**, the polymer radical with *t*-butyldioxy end group would be formed as suggested by Yenal'ev and co-workers (Eq. 4). The terminal dioxy group of the resulting polymer would further



cleave at O-O bond and reinitiate the polymerization of styrene, i.e., the peroxides **1** would act as bifunctional initiators. Alternatively, if the β -scission of **2** occurs much faster than the addition of **2** to styrene, radicals generated by β -scission of **2** would initiate the polymerization of styrene.

In the present paper we report the study on the polymerization of styrene using 2,2-bis(*t*-butyldioxy)alkanes **1** in order to elucidate the initiation mechanism focusing on the facile β -scission of radicals from **2**.

Experimental

GLC analysis was performed with a Shimadzu GC-9A gas chromatograph with a flame ionization detector by 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. Mass spectra were obtained on a JEOL JMS-DX300 mass spectrometer at 70 eV under electron impact condition. GPC analysis was accomplished on a Shimadzu CTO-6A equipped with 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 the methods previously described.⁴⁾ 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.

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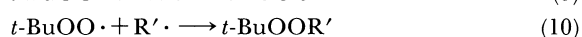
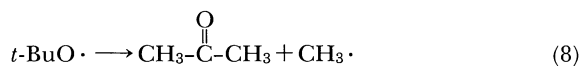
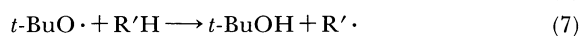
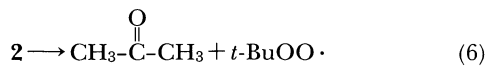
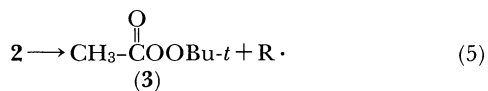
tions of styrene with peroxides were carried out in a sealed-glass ampoule in benzene at 110°C. After polymerization for a given time, the molecular weight of polystyrene was determined by GPC analysis and reaction products were analyzed by GLC and/or GC-MS in comparison with authentic samples.

Thermolyses of **1** were carried out in cumene under the same conditions as those of polymerization, and reaction products were analyzed by GLC and/or GC-MS.

Determination of Active Oxygen. After polymerization, the content of the ampoule was poured into large amount of methyl alcohol to isolate the polymer. The resulting polymer was purified by two reprecipitations with methyl alcohol and dried in vacuum at room temperature to constant weight. A weighed amount of the purified polystyrene was added to isopropyl alcohol containing acetic acid, sodium carbonate, and potassium iodide. After boiled for 5 min, 36% hydrochloric acid was added to the mixture and boiled further for 3 min. Then the liberated iodine was titrated with aqueous sodium thiosulfate solution.

Results and Discussion

The thermal decomposition of **1** was carried out in cumene under nitrogen. The products obtained by the decomposition were acetone, alkyl methyl ketone, *t*-butyl alcohol, *t*-butyl hydroperoxide, *t*-butyl peracetate (**3**), *t*-butyl 1-methyl-1-phenylethyl peroxide, and 2,3-dimethyl-2,3-diphenylbutane (Table 1A). A likely scheme leading to the products in cumene is shown by following equations. Here, R'H denotes cumene



and R'-R' is 2,3-dimethyl-2,3-diphenylbutane. As shown in Eq. 3, the O-O homolysis of **1** produces *t*-butoxyl radical and 1-*t*-butyldioxy-1-methylalkoxyl radical (**2**). The resulting alkoxyl radical **2** undergoes β -scission to afford *t*-butyl peracetate (**3**) and alkyl methyl ketone (Eqs. 5 and 6). *t*-Butyl alcohol and acetone are formed by a hydrogen abstraction of *t*-BuO $\cdot$ from solvent cumene (Eq. 7) and scission of methyl radical from *t*-BuO $\cdot$ (Eq. 8). *t*-BuOO $\cdot$ generated by Eq. 6 undergoes a hydrogen abstraction to afford *t*-BuOOH (Eq. 9) or a coupling reaction with R' $\cdot$ to afford *t*-BuOOR' (Eq. 10). Another coupling reaction of R' $\cdot$ affords R'-R' (Eq. 11).

It is noted that the yield of **3** in cumene changes dramatically with the structure of **1** (i.e., **1a** $\ll$ **1b** $\leq$ **1c**). As shown by the previous report,⁴⁾ this result can be explained by the difference in elimination rates of alkyl radicals from **2** (i.e., Me < Et < *i*-Pr).

The polymerization of styrene using **1** was carried out in benzene. The liquid products in the reaction were acetone, alkyl methyl ketone, *t*-butyl alcohol, **3**, and styrene oxide (Table 1B). It is worth to note that the yields of **3** obtained in the polymerization of styrene are very close to those obtained in cumene. The result indicates that the addition reaction of **2** to styrene (Eq. 4) is negligibly slow in comparison with the scission reaction of **2**. If Eq. 4 occurs faster than Eq. 5 or 6, the yields of **3** formed in the styrene polymerization should be reduced appreciably compared to those of **3** formed in cumene.

The difficulty in addition reaction of **2** to styrene is quite interesting since the analogous alkoxyl radical, *t*-BuO $\cdot$, is well known to react with styrene easily. For example, Solomon and co-workers⁵⁾ showed that the relative rate of β -scission of *t*-BuO $\cdot$ vs. addition reaction to styrene in benzene at 60°C was 0.11, revealing the facile addition reaction. The difference in reactivity between *t*-BuO $\cdot$ and **2** is explained mainly

Table 1. Products on Decomposition of **1**^{a)}

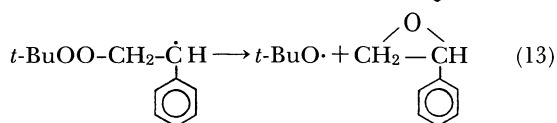
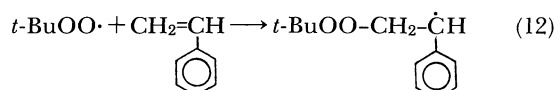
Peroxide	Product yield ^{b)} /%							
	Me ₂ CO	RCOMe	<i>t</i> -BuOH	<i>t</i> -BuOOH	MeCO ₃ Bu- <i>t</i>	<i>t</i> -BuOOR'	R'-R'	Epoxide ^{c)}
A) Decomposition in cumene								
1a	44	d)	51	19	16	46	44	
1b	30	7	56	<1	61	9	82	
1c	35	3	71	<1	70	2	73	
B) Decomposition in styrene/benzene ^{e)}								
1a	67	d)	18	<1	17			21
1b	25	8	17	<1	66			2
1c	29	1	28	<1	69			2

a) Decomposition was carried out at 110°C. Initial concentration: [**1**]₀=0.1 mol dm⁻³. Reaction time: **1a**, 4 h; **1b**, 2 h; **1c**, 1 h. b) Yields of products: [(moles of products)/(moles of **1** consumed)] $\times$ 100. The conversion of **1** was 30–40%. R: **1a**=CH₃, **1b**=CH₂-CH₃, **1c**=CH(CH₃)₂. Me=CH₃, R'=C₆H₅C(CH₃)₂. c) Styrene oxide. d) RCOMe=Me₂CO. e) Styrene/benzene=50 v/v%.

on the basis of the difference in scission rates of radicals from alkoxy radical. We have recently shown that relative rates of β -scission of radicals from **2** in cumene at 100 °C are isopropyl : ethyl : *t*-butyldioxy : methyl = 133 : 33 : 7 : 1.⁴⁾ This result indicates that the β -scission reaction of **2** occurs much faster than that of *t*-BuO• having only methyl groups.

Considerable amounts of acetone and *t*-butyl alcohol were obtained even in styrene/benzene, e.g., for the case of **1b**, the yields were 25% and 17%, respectively. The result indicates that β -scission and hydrogen abstraction reactions of *t*-BuO• occur comparably to the addition reaction of *t*-BuO• to styrene under the present conditions (i.e., at 110 °C). Here, polystyrene produced in the polymerization may be considered as a hydrogen donor. Niki and Kamiya⁶⁾ reported the reactivity of polystyrene toward *t*-BuO• and showed that an appreciable amount of *t*-butyl alcohol was obtained by the hydrogen abstraction from polystyrene at relatively high temperature (125 °C). Peroxides **1** are also considered as hydrogen donors. But we have previously showed that the induced decomposition of **1** is negligible in diphenylmethane³⁾ or cumene.⁴⁾ It suggests that the hydrogen abstraction from **1** by *t*-BuO• is a minor reaction, if any, under these conditions.

Interestingly, appreciable amount of styrene oxide (21%) was obtained in the polymerization of styrene with **1a**. The formation mechanism of styrene oxide can be explained by radical epoxidation of styrene by dioxy radical:⁷⁾ *t*-BuO• adds to styrene to produce 2-(*t*-butyldioxy)-1-phenylethyl radical (Eq. 12), which decomposes subsequently to styrene oxide and *t*-BuO• by γ -scission process (Eq. 13). The mechanism is



supported by the dependence of the yield of styrene oxide on the amount of *t*-BuOO• generated from the decomposition of **1**. *t*-BuOO• is a precursor for *t*-BuOOH and *t*-BuOOR' as shown by Eqs. 9 and 10; therefore the total yield of *t*-BuOOH and *t*-BuOOR' on the decomposition in cumene roughly coincides with that of *t*-BuOO• generated from the decomposition of **1** (i.e., 65% for **1a** and <10% for **1b** and **1c**). The significant *t*-BuOO• scission process for **1a** can contribute to the styrene oxide formation.

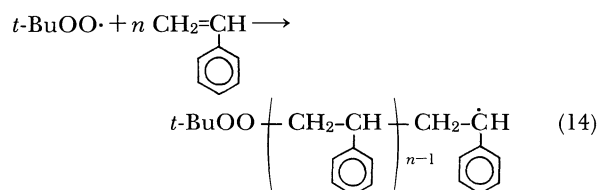
There is a difference between the total amount of *t*-BuOO• generated from β -scission of **2a** (65%) and the amount of *t*-BuOO• consumed by styrene oxide formation (21%). It can be assumed that the residual *t*-BuOO• (44%) would mainly initiate the polymerization of styrene, resulting in the production of polysty-

Table 2. Characteristics of Polystyrenes^{a)}

Peroxide	Yield of polystyrene/%	$\bar{M}_n \times 10^4$	Active oxygen ^{b)} /%	Active polymer ^{c)} /%
1a	94	1.4	0.052	46
1b	91	1.2	<0.005	<4
1c	82	1.1	<0.005	<3

a) Polystyrenes were obtained by the same condition as footnote a in Table 1. b) $[16 \times (\text{number of O-O in a polystyrene molecule}) / (\text{molecular weight of polystyrene})] \times 100$. See experimental section for the detection. c) Proportion of polystyrene molecules having a dioxy bond: Active oxygen(%) $\times \bar{M}_n / 16$.

rene containing *t*-butyldioxy group at the polymer end (Eq. 14).



The characteristics of polystyrenes obtained by the polymerization with **1** are given in Table 2. The molecular weight ($\bar{M}_n$) of each polystyrene was about 10000. Interestingly, active oxygen (0.052%) was found to be contained in polystyrene obtained with **1a** by iodometric titration; however we could not detect it in polystyrenes obtained with **1b** and **1c** (<0.005%). The detection of active oxygen is an important evidence indicating the existence of dioxy bond. From the values of active oxygen and molecular weight, we can estimate the proportion of polystyrene molecules containing a dioxy bond. For the case of **1a**, it was found that about half of polystyrene molecules had a dioxy bond (Table 2). In analogy with the styrene oxide formation, the amount of active oxygen in polystyrene is consistent with that of *t*-BuOO• generated from **1**. The considerable generation of *t*-BuOO• for **1a** is responsible for the production of the polystyrene containing dioxy bond as shown in Eq. 14.

Yenal'ev and co-workers¹⁾ reported that the polystyrene obtained by the polymerization with gem-bis(*t*-pentyldioxy)alkanes contained dioxy group. From the results, they suggested that the polystyrene was given by the reaction of alkoxy radical having α -dioxy group with styrene. However, our detailed investigation on polymerization mechanism with **1** rules out the possibility of Eq. 4 and leads to the conclusion that *t*-BuOO• eliminated from **2** contributes to the production of active polystyrene. It is attractive that the polymer containing dioxy group can be obtained easily by the use of **1a** because such active polymer gives the possibility to be applied to the syntheses of block polymers.

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