

Thermolysis Kinetics of 1,1-Bis(*t*-butyldioxy)cycloalkanes and Their Utility for Styrene Polymerization

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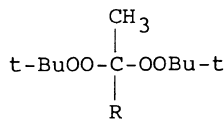
ABSTRACT: Thermolysis kinetics of 1,1-bis(*t*-butyldioxy)cycloalkanes (cycloalkane perketals) with various alkyl substituents on the cycloalkane rings were investigated in cumene. Substitution at the 2-position on the ring greatly accelerated the peroxide decomposition; the accelerating effect of substituents is in the order $H < n\text{-Pr} \approx \text{Me} < \text{iso-Pr}$. The bulk polymerization of styrene initiated by cycloalkane perketals proceeded *via* the two-step O—O decomposition and gave higher molecular weight polymers than polymerization by monofunctional initiators. It is shown that cycloalkane perketals act as unsymmetrical difunctional initiators.

KEY WORDS Styrene / Radical Polymerization / Cycloalkane Perketal / Difunctional Initiator / Kinetics /

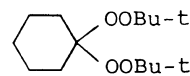
Organic peroxides are used widely as polymerization initiators in the polymer industry and numerous organic peroxides have been developed so far.¹ For polymer makers, it is important to produce polymers having the desired molecular weight at high polymerization rate to reduce production cost. Organic peroxide initiators play an important role in controlling molecular weight and polymerization rate. Although thermally active initiators which decompose at relatively low temperature can increase polymerization rate effectively, the high polymerization rate causes lowering of molecular weight of the resulting polymer. This is because polymer molecular weight is inversely proportional to polymerization rate in conventional free radical polymerization.

Recently, it was reported that difunctional peroxides which possess two O—O bonds in a molecule are more effective initiators for the

production of desired polymers at high polymerization rate than conventional monofunctional peroxides.^{2–8} Among difunctional peroxides, particular attention has been paid to decomposition and initiation chemistries of gem-diperoxides (perketals).^{9–16} We reported several studies on the thermal decomposition of acyclic (1)⁹ and cyclic perketals (2a)¹⁰ and initiation mechanism for the polymerization of vinyl monomers with perketals.^{11–13}



(1)

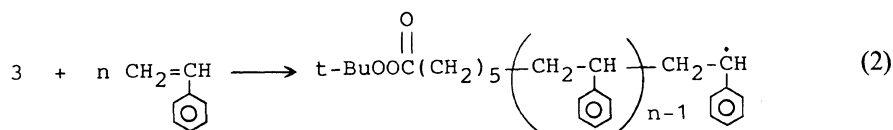
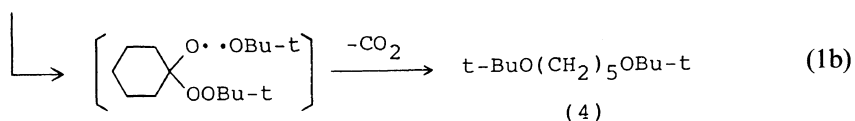
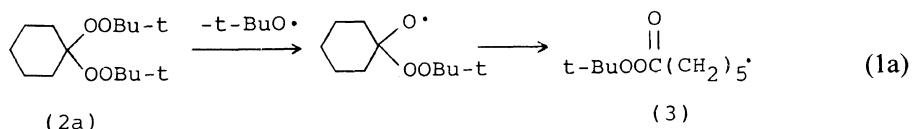


(2a)

For example, we showed that the initial decomposition of 2a occurs by mainly one O—O bond fission, the resulting cycloalkoxy radical undergoes ring opening before addition to

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styrene monomer (eq 1a), and then the ring-opened radical (3) having a perester group initiates the polymerization of styrene effectively (eq 2).¹³



Since the O–O bond of the perester group is also thermally unstable, the resulting polymer having the perester group will further initiate polymerization. Thus, it is expected that cycloalkane perketals act as unsymmetrical difunctional initiators which have two O–O bonds differing in thermal stability (*i.e.*, dialkyl and perester types). As another competitive path in 2a decomposition, more recently, Drumright *et al.*^{14,15} reported that an in-cage decomposition (eq 1b) occurs resulting in the formation of diether (4). However, since the yield of 4 is not so high (<10% for decomposition in ethylbenzene), the major decomposition path can be expressed as eq 1a and 2.

It is well known that peroxide decomposition is affected by certain substituents due to steric and inductive effects. Therefore, it can be expected that the decomposition temperature (*i.e.*, thermal activity) of the two O–O bonds of cycloalkane perketals can be suitably altered

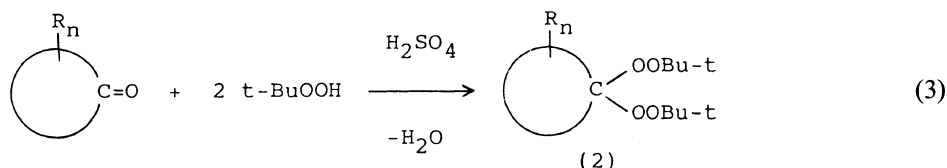
by the introduction of substituents on the cycloalkane ring.

This paper reports the thermolysis kinetics of cycloalkane perketals (2) having various alkyl substituents on the cycloalkane rings, and their utility for polymerization of styrene as initiators.

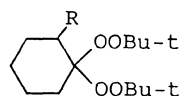
RESULTS AND DISCUSSION

Thermolysis of Cycloalkane Perketals

Seven cycloalkane perketals (2a–2g) having five or six-membered ring were prepared by the reaction of 70% *t*-butyl hydroperoxide with the corresponding cyclic ketones in the presence of 65% sulfuric acid (eq 3). Their structures were ascertained by ¹H NMR, ¹³C NMR, and other spectral measurements. Purity was determined by iodometric titration and GLC analysis and found to be over 98% for each peroxide.



Styrene Polymerization by Cycloalkane Perketals

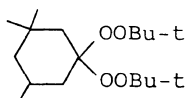


(2a): R=H

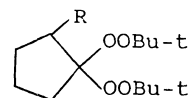
(2b): R=Me

(2c): R=n-Pr

(2d): R=i-Pr



(2e)



(2f): R=H

(2g): R=Me

Table I. Rate constants and activation parameters for the decomposition of cycloalkane perketals 2 in cumene

Perketal ^a	Temp °C	$k \times 10^5$ s ⁻¹	k_{rel} (100°C)	Activation parameters	
				ΔH^\ddagger	ΔS^\ddagger
				kJ mol ⁻¹	J K ⁻¹ mol ⁻¹
2a	80	0.347	(1.0)	139.5	44.8
	90	1.45			
	100	5.06			
	110	16.2			
2b	80	1.29	2.8	130.4	29.6
	90	4.51			
	100	14.3			
2c	80	1.20	2.7	130.6	29.4
	90	4.19			
	100	13.8			
2d	70	2.59	14.7	118.6	9.9
	80	4.86			
	90	19.8			
	100	74.6			
2e	80	0.382	1.0	140.0	47.2
	90	1.50			
	100	5.31			
	110	17.5			
2f	80	0.498	1.3	139.0	45.6
	90	1.80			
	100	6.67			
	110	21.7			
2g	80	1.55	3.7	133.3	39.3
	90	5.82			
	100	18.5			
	110	60.0			

^a Initial concentration, 0.05 mol l⁻¹.

The thermal decomposition of 2 was carried out in cumene under nitrogen. The thermolysis rates, as determined by measuring the disappearance of 2 by GLC analysis, satisfied

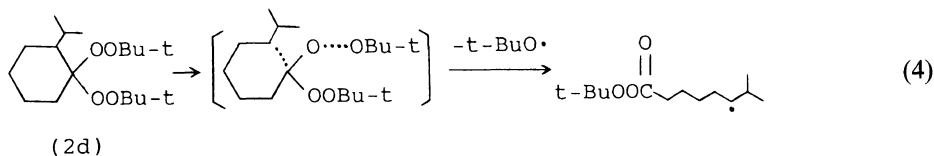
first-order kinetics over two half-lives reaction. The resulting rate constants and activation parameters are listed in Table I. In the case of 2a, the rate constants were not influenced by

change in initial concentration (0.02–0.2 M). This indicates that attack of radicals on perketals (induced decomposition) hardly occurs under the present conditions.

It is clear from Table I that substitution at the 2-position on the cycloalkane ring accelerates peroxide decomposition significantly, while substitution at the 3-position little affects peroxide decomposition. For example, the accelerating effect of 2-alkyl substituents increased in the order $H < n\text{-Pr} \approx \text{Me} < \text{iso-Pr}$ (1:2.7 \approx 2.8:14.7). It is notable that the accelerating effect of the iso-Pr group is about five times that of the *n*-Pr group. This clearly demonstrates that steric effects are important factors controlling the decomposition of cycloalkane perketals.

The activation parameters (ΔH^\ddagger and ΔS^\ddagger)

for iso-Pr substituted perketal (2d) are quite small. In 1958, Bartlett and Hiatt¹⁶ represented the relationship between ΔH^\ddagger and ΔS^\ddagger for a large number of *t*-butyl peresters and demonstrated that peresters undergoing concerted decomposition give relatively small ΔH^\ddagger and ΔS^\ddagger . Since perketals decompose homolytically like peresters, it is reasonable to expect that a similar relationship between ΔH^\ddagger and ΔS^\ddagger exists for perketals. That is, small ΔH^\ddagger and ΔS^\ddagger for 2d indicate that the decomposition of 2d occurs by mainly two-bond homolysis mechanism (eq 4). The mechanism is supported by the following. i) The iso-Pr-substituent can stabilize the ring-opened alkyl radical. ii) The bulky iso-Pr group increases the ring strain of the reactant perketal, but the strain can be cancelled out by decomposition.

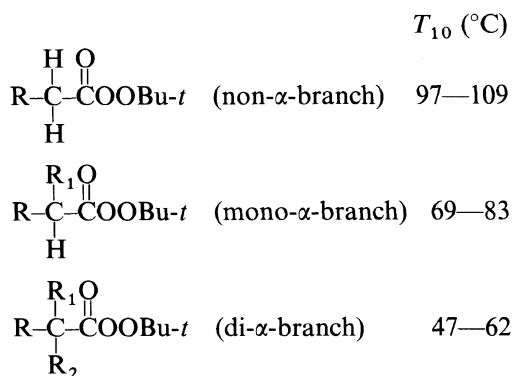


The effect of ring size, five and six-members, was not so large. For example, the cyclopentane perketals decompose only 1.3 times faster than the corresponding cyclohexane perketals. Matsuyama and Kumura¹⁷ reported a more detailed study on the effects of ring size on the decomposition of cycloalkane perketals. They showed that the rates of decomposition decrease with increasing ring size. The relative decomposition rates of cyclopentane/cyclohexane/cyclooctane/cyclododecane perketals are 1.3/1.0/0.8/0.6 at 110°C. These results indicate that ring size does not markedly influence the decomposition of cycloalkane perketals.

Thermolysis of Polymer Peroxide

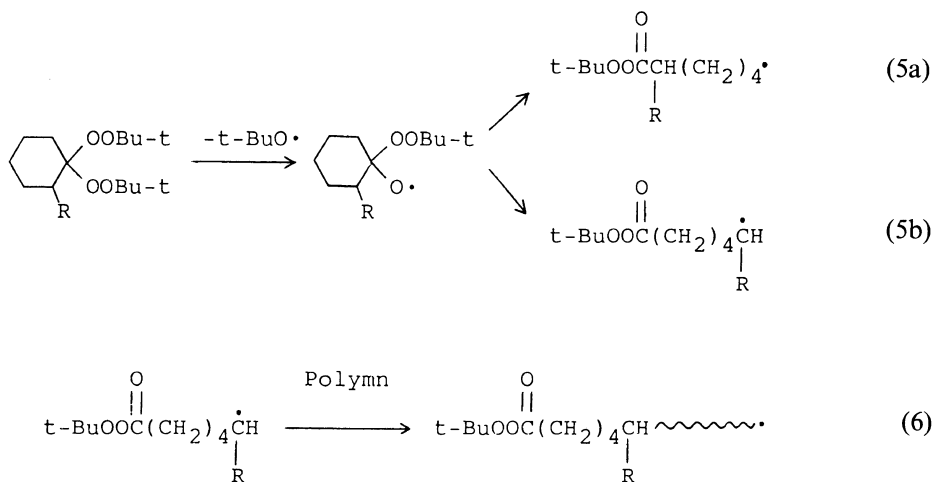
We previously showed that the polymerization of styrene with 2a mainly proceeds through the formation of polymer peroxide (PPO) with the perester group (eq 1a and 2).¹³ Though the precise decomposition rate of PPO is unclear,

we can roughly estimate it from the known structure-activity relationship of peresters. It is well known that the decomposition rates of peresters mainly depend on the structures of carboxylic acid moieties of peresters.^{16,18} With peresters derived from aliphatic carboxylic acids, their decomposition rates significantly depend on the degree of α -branch of the carboxylic acid moiety as shown below¹⁸:



Where T_{10} means the temperature at which the peroxide is 50% decomposed in 10 hours. Since PPO formed by 2a contains the perester group derived from non- α -branched carboxylic acid, the decomposition rate is assumed to be equal to those of lower linear peresters, *e.g.*, *t*-butyl peroxy laurate (TBPL).

The O—O homolysis of 2b—2d will also give intermediate cycloalkoxy radicals with 2-alkyl substituents on the cyclohexane ring. The alkoxyl radicals may undergo two possible ring openings to afford primary alkyl radicals (eq 5a) or secondary alkyl radicals (eq 5b).



It is well known that the β -scission of alkoxy radicals takes place predominantly to produce more stable radicals.^{19–21} For example, the rate of elimination of secondary alkyl radicals is approximately 50 times faster than the elimination of primary alkyl radicals.²¹ Therefore, it is reasonable to assume that eq 5b occurs mainly and the more stable secondary alkyl radicals initiate the polymerization of styrene. Thus, it is predictable that the polymerization of styrene initiated by 2b—2d also proceeds through the formation of PPO with the perester group derived from the non- α -branched carboxylic acid.

Polymerization of Styrene

First, we carried out the two-stage bulk polymerization of styrene using iso-Pr-substituted perketal 2d as the initiator. The polymerization temperature was increased stepwise from 80 to 110°C. For comparison, the same polymerizations were carried out

using mono functional peroxides as initiators. Here, we used *t*-butyl peroxy-2-ethylhexanoate (TBPE) and TBPL as monofunctional initiators, since T_{10} of TBPE and TBPL are expected to be comparable to the lower and higher T_{10} of 2d, respectively (Table II). As seen from the time-conversion curves (Figure 1), in the first stage polymerization at 80°C, the slope for 2d was similar to that for TBPE (higher active monofunctional initiator). In the second stage polymerization at 110°C, the slope for 2d was similar to that for TBPL (lower active monofunctional initiator). This clearly demonstrates that the thermal stability of the peroxide groups of 2d is not the same and suggests that the polymerization activity of 2d is nearly equal to that of the mixture of TBPE and TBPL.

Next, we carried out non-isothermal bulk polymerizations of styrene with 2d and the mixture of TBPE and TBPL. The polymerization temperature was continuously increased

Table II. Two-stage bulk styrene polymerization^a

Initiator ^b	$T_{10}/^{\circ}\text{C}$	Conversion/%	
		1st ^c	2nd ^d
(A) Polymerization with perketal			
2d	69.6 ^e	39.6	97.6
	100.1 ^f		
(B) Polymerization with monofunctional peroxide			
TBPE	75.5	31.7	74.2
TBPL	100.1	7.6	90.6

^a Polymerization temperature was increased stepwise from 80 to 110°C.

^b Initial concentration, 5 mM. TBPE, *t*-butyl peroxy-2-ethyl hexanoate; TBPL, *t*-butyl peroxy-laurate.

^c After the first stage polymerization at 80°C for 5 h.

^d After the second stage polymerization at 110°C for 5 h.

^e T_{10} for the first decomposing O–O bond.

^f T_{10} for the second decomposing O–O bond.

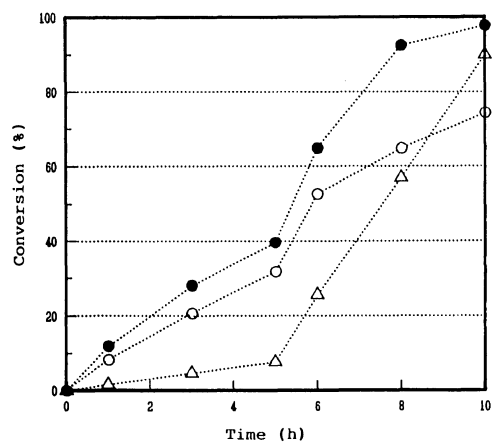


Figure 1. Time-conversion relationships for two-stage bulk styrene polymerization at 80°C (0–5 h) and 110°C (5–10 h): [initiator], 5 mM; (●) 2d; (○) TBPE; (△) TBPL.

from 80 to 140°C. The resulting time-conversion curves are shown in Figure 2. As expected, the curves for 2d were in good agreement with those for the mixed initiator when the same initiator concentration was used. GPC curves for 2d were unimodal but somewhat broader than those for the mixed initiator. The effect of 2d on the polymer molecular weight properties is shown in Table III and Figure 3.

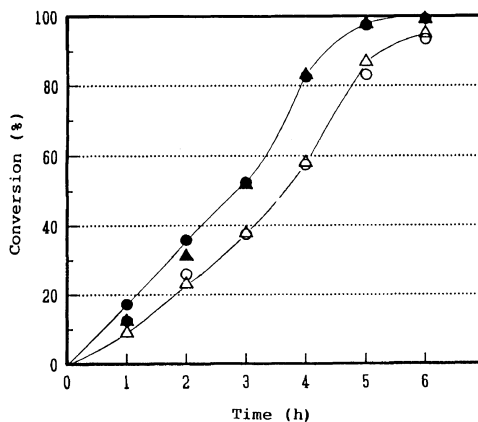


Figure 2. Time-conversion relationships for bulk styrene polymerization at continuously increasing temperature from 80 to 140°C (10°C h⁻¹): (○) 2d (2.5 mM); (●) 2d (5 mM); (△) TBPE (2.5 mM) + TBPL (2.5 mM); (▲) TBPE (5 mM) + TBPL (5 mM).

Table III. Comparison of perketal initiator 2d and mixed mono-functional initiators in bulk styrene polymerization^a

Initiator	Concn	Conversion ^b		
	mM	%	$10^{-4}\bar{M}_w^b$	\bar{M}_w/\bar{M}_n^b
2d	2.5	93.5	41.8	1.97
	5.0	99.3	35.0	2.25
Mix ^c	2.5 ^d	95.1	33.2	1.84
	5.0 ^d	99.0	27.8	2.02

^a Polymerization temperature was increased continuously (10°C h⁻¹) from 80 to 140°C.

^b After polymerization for 6 h.

^c Mixture of TBPE and TBPL.

^d Concentration of each monofunctional initiator.

Compared with the use of mixed monofunctional initiators, it is clear that when 2d is used, the polymer molecular weight considerably increases with increase in monomer conversion, and higher molecular weight polymers with slightly larger polydispersity (\bar{M}_w/\bar{M}_n) can be obtained finally. These results are easily understood due to the formation of intermediate polymer peroxide having the ability to further initiate polymerization. Thus, it was confirmed that 2d acts as a typical unsymmetrical difunctional initiator.

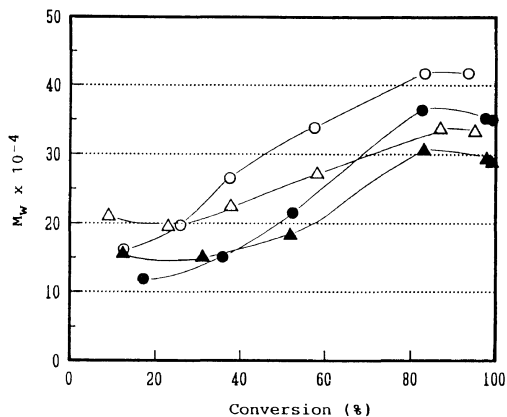


Figure 3. Effect of perketal initiator 2d on polymer molecular weights in bulk styrene polymerization at continuously increasing temperature from 80 to 140°C ($10^{\circ}\text{C h}^{-1}$): (○) 2d (2.5 mM); (●) 2d (5 mM); (△) TBPE (2.5 mM) + TBPL (2.5 mM); (▲) TBPE (5 mM) + TBPL (5 mM).

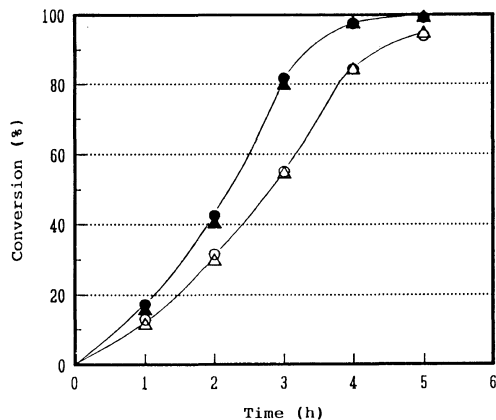


Figure 4. Time-conversion relationships for bulk styrene polymerization at continuously increasing temperature from 90 to 140°C ($10^{\circ}\text{C h}^{-1}$): (○) 2b (2.5 mM); (●) 2b (5 mM); (△); THMC (2.5 mM) + TBPL (2.5 mM); (▲) THMC (5 mM) + TBPL (5 mM).

Similarly, bulk styrene polymerization initiated by Me-substituted perketal 2b was carried out under the non-isothermal conditions. For comparison, the same polymerization was carried out using a binary mixture of monofunctional initiators consisting of 1-*t*-hexyldioxy-1-methoxy cyclohexane (THMC) and TBPL. As seen in Figure 4, the time-

Table IV. Comparison of perketal initiator 2b and mixed mono-functional initiators in bulk styrene polymerization^a

Initiator ^b	$T_{10}/^{\circ}\text{C}$	Conversion ^c		
		%	$10^4 \bar{M}_w^c$	\bar{M}_w/\bar{M}_n^c
2b	85.2 ^d	99.2	32.4	2.06
	100.1 ^e			
THMC ^f	86.2	99.1	26.4	1.89
+ TBPL	100.1			

^a Polymerization temperature was increased continuously ($10^{\circ}\text{C h}^{-1}$) from 90 to 140°C.

^b Initial concentration: 2b, 5 mM; THMC, 5 mM; TBPL, 5 mM.

^c After polymerization for 5 h.

^d T_{10} for the first decomposing O–O bond.

^e T_{10} for the second decomposing O–O bond.

^f 1-*t*-Hexyldioxy-1-methoxycyclohexane.

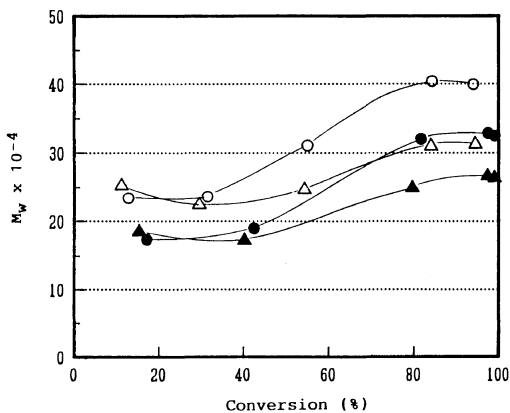


Figure 5. Effects of perketal initiator 2b on polymer molecular weights in bulk styrene polymerization at continuously increasing temperature from 90 to 140°C ($10^{\circ}\text{C h}^{-1}$): (○) 2b (2.5 mM); (●) 2b (5 mM); (△) THMC (2.5 mM) + TBPL (2.5 mM); (▲) THMC (5 mM) + TBPL (5 mM).

conversion curves for 2b are in good agreement with those for the mixed initiator. This indicates that 2b also has two thermally different O–O bonds and our estimation of the thermal stability of each O–O bond was accurate. As seen from Table IV and Figure 5, perketal initiator 2b showed the same effect as 2d on the polymer molecular weight properties.

In conclusion, the polymerization of styrene initiated by cycloalkane perketals proceeds *via* the formation of polymer peroxide with the perester group which can further initiate styrene polymerization. That is, cycloalkane perketals act as typical unsymmetrical difunctional initiators with two thermally different O–O bonds. The introduction of a bulky group (*e.g.*, iso-Pr group) at the 2-position on the cycloalkyl ring greatly accelerates the O–O decomposition due to mainly steric effect. Such perketals with the large difference in decomposition temperature between the two O–O bonds should be useful as initiators for block polymer syntheses.

EXPERIMENTAL

Measurements

IR and NMR spectra were recorded on a JASCO A-3 and a JEOL JNM-GSX 270 spectrometers, respectively. GLC analyses were performed with a Shimadzu GC-14A 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-R4A integrator was used for quantitative analyses. Mass spectra were obtained on a JEOL JMS-DX300 mass spectrometer at 70 eV under electron impact conditions. GPC analysis was conducted on a Shimadzu LC-6A equipped with a Shimadzu RID-6A using THF as the eluent. Two columns, a Shodex KF-80M (60 cm) and Shimadzu HSG-10S (60 cm), were connected in series. The calibration curve was made using standard samples of polystyrene.

Materials

1,1-Bis(*t*-butyldioxy)cyclohexane (2a) was prepared by methods previously described.¹⁰ Other cycloalkane perketals were prepared using the corresponding cyclic ketones.

Monofunctional peroxides, *t*-butyl peroxy-laurate (TBPL) and *t*-butyl peroxy-2-ethylhexanoate (TBPE), were commercially available.

1-*t*-Hexyldioxy-1-methoxycyclohexane (THMC) was prepared by the following procedure: To dimethyl sulfoxide (16.0 g) containing *p*-toluenesulfonic acid (1.3 g) was added dropwise a mixture of 1,1-dimethoxycyclohexane (28.8 g) and *t*-hexyl hydroperoxide (23.8 g) at 20°C. After being stirred for 3 h at 20°C, the reaction mixture was diluted by the addition of petroleum ether 20 ml, washed with 5% aqueous NaOH and water, dried over anhydrous sodium sulfate, and then evaporated to dryness. Vacuum distillation of the crude product yielded THMC as a colorless oil with bp 47–50°C/0.1 mmHg. ¹H NMR (CDCl₃) σ = 0.87 (t, 3H, *J* = 7.0 Hz), 1.16 (s, 6H), 1.32–1.80 (14H), and 3.22 ppm (s, 3H); ¹³C NMR (CDCl₃) σ = 14.5 (CH₃), 17.0 (CH₂), 22.5 (CH₂), 24.5 (CH₃), 25.3 (CH₂), 31.5 (CH₂), 41.5 (CH₂), 47.3 (CH₃), 85.3 (C), and 103.0 ppm (C); IR (neat) 2920, 2850, 1450, 1380, 1360, 1340, 1280, 1260, 1240, 1180, 1160, 1100, 1040, 930, 880, and 820 cm⁻¹; *Anal.* Cald for C₁₃H₂₆O₃: C, 67.8; H, 11.4. Found: C, 67.6; H, 11.3.

Cumene was purified by distillation after washing with concentrated sulfuric acid. Styrene was washed with 2% aqueous NaOH and water, and distilled under reduced pressure before use.

Typical Procedure for the Thermolysis

A 2 ml solution of 2 in cumene was charged into a glass ampoule. The ampoule was purged with nitrogen, sealed, and immersed in a constant temperature bath. After thermolysis for a given time, the remaining perketal was determined by GLC analysis.

Polymerization of Styrene

All polymerizations were carried out in the presence of peroxide initiator in bulk in a sealed glass ampoule purged with nitrogen. Polymerization temperature was increased stepwise or continuously. Conversion of the monomer was determined by GLC and/or GPC. Number and weight average molecular weights (\bar{M}_n and \bar{M}_w , respectively) were determined by GPC.

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