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Cycloalkane Perketal Initiators for Styrene Polymerization. 2. Decomposition Chemistry of *gem*-Bis(*tert*-butylperoxy)cycloalkanes

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ABSTRACT: Several ring-strained and ring-substituted *tert*-butylperoxy ketals were synthesized. Their decomposition chemistry in ethylbenzene and their performance in styrene polymerization as a function of structure were investigated. The results show that the *tert*-butylperoxy ketal structure has a significant effect upon its ability to abstract H atoms during decomposition in EB. However, no correlation was found between H-atom abstraction efficiency of the *tert*-butylperoxy ketals and their ability to make high M_w polystyrene.

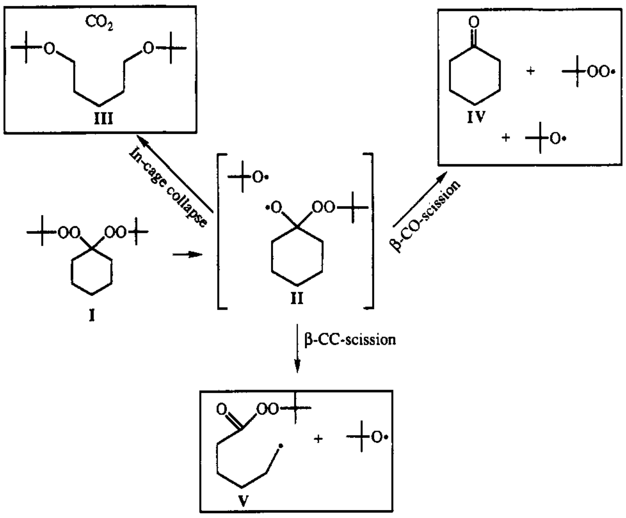
Introduction

Recently, we reported the decomposition chemistry of 1,1-bis(*tert*-butylperoxy)cyclohexane (I).[1] The decomposition chemistry of I involves three pathways (Scheme I). The pathway involving in-cage decomposition of I leads to the formation of diether III and carbon dioxide without forming any initiating radicals. The β-CO-scission pathway forms cyclohexanone (IV) and only two radicals from the two peroxide bonds in I. The pathway involving β-CC-scission is preferred since it results in the formation of four radicals and can potentially lead to a peroxide functional polystyrene (Scheme II) which is likely responsible for the excellent rate/M_w performance of I as an initiator for bulk S polymerization.

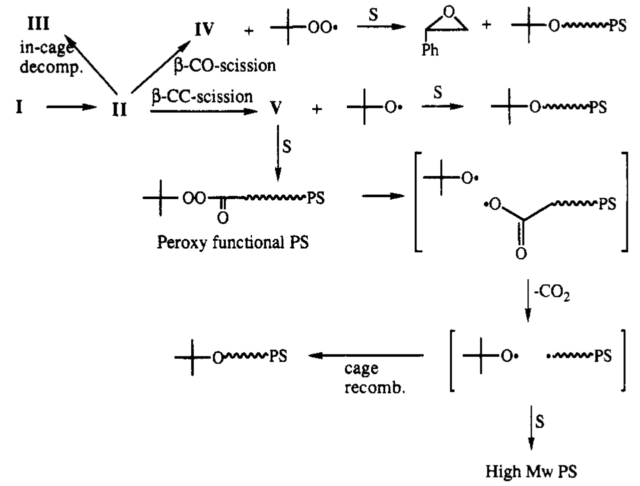
We felt that if 1,1-bis(*tert*-butylperoxy)cycloalkanes could be designed to decompose entirely by the β-CC-scission pathway, they could show improved efficiency and rate/M_w performance over I for styrene polymerization.

The β-CC-scission pathway involves the ring opening of peroxy radical II. Changes in ring size and ring substitution were examined as potential routes to promote the ring-opening pathway. Walling and Padwa[2] found that cyclopentyloxy radical VI undergoes ring opening faster than cyclohexyloxy radical VII, presumably because of the estimated 6.5 kcal/mol ring strain in the five-membered ring (Scheme III). Bailey[3] used radical stabilization by substitution to promote ring opening during the copolymerization of cyclic ketals with styrene. He found that cyclic ketene acetal VIII undergoes mainly 1,2-copolymerization with styrene. However, the phenyl-substituted derivative undergoes quantitative ring opening during copolymerization, resulting in backbone ester linkages (Scheme IV).

Scheme I
Summary of the Three Main Pathways of Decomposition of I



Scheme II
Result of the Three Decomposition Pathways of I during Styrene Polymerization



Experimental Section

Materials and Methods. Solvents and inorganic materials were purchased from Fisher Scientific. Organic materials were purchased from Aldrich and used as received unless indicated otherwise. ^{1}H and ^{13}C NMR spectra were obtained on a General Electric QE-300 with a 5-mm probe. The NMR samples were dissolved in deuteriochloroform and referenced to tetramethylsilane (0 ppm). GC analyses were performed using a Hewlett-Packard 5890 gas chromatograph equipped with an autosampler, HP 3392A integrator, a DB1 megabore column (30 m, 1.5-mm film thickness), and a fid detector. HPLC was performed on a Hewlett-Packard 1090 liquid chromatograph equipped with a Keystone ODS/B column (150 × 4.6 mm, 5-mm particle size). TLC analyses were performed on Fisherbrand Silica Gel G Rediplates. The plates were eluted with heptane/ethyl acetate solvent mixtures and developed with a 2.5% solution of phosphomolybdic acid in 2-propanol. Flash column chromatography was performed on a 4-cm-diameter column packed with 230-400 mesh silica gel (Merck). The columns were eluted with heptane/ethyl acetate solvent systems. GC-MS analyses were performed using a Finnigan SSQ-700 single quadrupole GC-MS system operating in the electron impact and positive ion chemical ionization modes.

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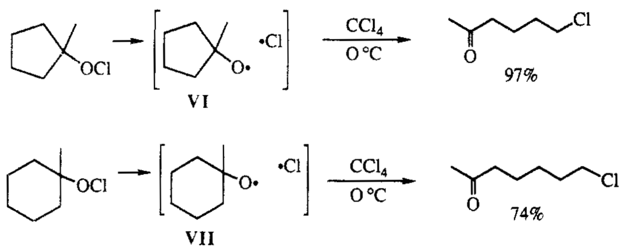
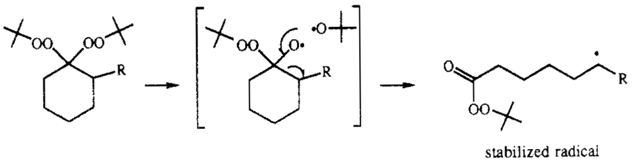
Scheme III
Promotion of Ring Opening by Ring Strain



Scheme IV
Promotion of Ring Opening Using a Radical-Stabilizing Substituent on the Ring



Ammonia was used as the reactant gas in chemical ionization analysis. Molecular weights were measured using gel permeation chromatography as described elsewhere.[4]

Syntheses. 1,1-Bis(*tert*-butylperoxy)cyclohexane (I). The synthesis of this compound is described elsewhere.[1]

1,1-Bis(*tert*-butylperoxy)cyclopentane (X). A 100-mL, three-necked flask equipped with a condenser, nitrogen inlet, and magnetic stirrer was flushed with nitrogen and then charged with 1.01 g (12 mmol) of cyclopentanone and 15 mL (45 mmol) of *tert*-butyl hydroperoxide (3.0 M in isooctane). Next, 15 mL of heptane and approximately 1 g of magnesium sulfate were added. Finally, about 50 mg of *p*-toluenesulfonic acid was added, and the reaction mixture stirred at room temperature under a nitrogen atmosphere overnight. The reaction mixture was then filtered and concentrated to yield 3.02 g of a colorless oil which was flash chromatographed with 2% ethyl acetate/98% heptane (v/v) to yield 1.04 g (35.2%) of X (R_f = 0.23). Storage in a freezer caused X to solidify. The material melted below room temperature. ^{1}H NMR ($CDCl_3$): δ 1.95 (m, 4 H), 1.68 (m, 4 H), 1.27 (s, 18 H). ^{13}C NMR ($CDCl_3$): δ 119.07, 80.23, 34.38, 27.51, 25.32. MS: *m/z* (relative intensity) 157 (0.4%), 101 (0.8%), 100 (1.5%), 85 (5.6%), 73 (23.5%), 58 (22.8%), 57 (17.7%), 43 (100%). The molecular weight was confirmed by positive ion ammonium chemical ionization: 264 $(M + NH_4)^+$, 247 $(M + H)^+$. $C_{13}H_{26}O_4$ = 246.35. One-hour half-life in ethylbenzene (EB) = 110.3 °C.

1,1-Bis(*tert*-butylperoxy)-2-methylcyclohexane (XII). The procedure described for X was used to react 1.5 g (13.4 mmol) of 2-methylcyclohexanone with 15.5 mL (46.5 mmol) of *tert*-butyl hydroperoxide (3.0 M in isooctane). The reaction mixture was filtered and concentrated to yield 3.1 g of a light yellow oil. Flash column chromatography with 1% ethyl acetate/99% heptane (v/v) yielded 2.07 g (56%) of XII as a clear colorless oil which existed as a mixture of isomers (R_f = 0.15). ^{1}H NMR ($CDCl_3$): δ 2.22 (m, 1 H), 1.60–1.90 (m, 3 H), 1.30–1.59 (m, 5 H), 1.28 (s, 9 H), 1.25 (s, 9 H), 1.01 (d, 3 H). ^{13}C NMR ($CDCl_3$): δ 109.19, 79.65, 79.57, 34.89, 32.00, 31.14, 27.82, 27.58, 27.50, 26.52, 23.42, 22.36, 15.33. MS: *m/z* (relative intensity) 185 (0.8%), 127 (0.3%), 113 (1.3%), 111 (1.7%), 83 (4.6%), 73 (100%), 57 (19.3%), 55 (21.9%), 43 (60%), 41 (37.9%). The molecular weight was confirmed by positive ion ammonium chemical ionization: 292 $(M + NH_4)^+$, 275 $(M + H)^+$. $C_{15}H_{30}O_4$ = 274.40. One-hour half-life in EB = 102 °C.

1,1-Bis(*tert*-butylperoxy)cycloheptane (XI). The procedure described for X was used to react 1.35 g (12.0 mmol) of cycloheptanone with 15 mL (45 mmol) of *tert*-butyl hydroperoxide (3.0 M in isooctane). The reaction mixture was filtered and concentrated to yield 3.18 g (96%) of a clear colorless oil which did not require further purification. Storage in a freezer caused XI to solidify. The material had to be warmed slightly above room temperature to liquefy it. ^{1}H NMR ($CDCl_3$): δ 1.92 (m, 4 H), 1.55 (m, 8 H), 1.25 (s, 18 H). ^{13}C NMR ($CDCl_3$): δ 113.16, 79.92, 34.75, 31.55, 27.49, 23.92. MS: *m/z* (relative intensity) 185 (1.2%), 129 (0.3%), 127 (0.3%), 113 (1.4%), 112 (1.5%), 101 (0.1%), 100 (0.1%), 73 (86.3%), 58 (23.3%), 57 (13.4%), 56 (15.4%), 55 (18.4%), 43 (100%), 41 (29.7%). The molecular weight was confirmed by positive ion ammonium chemical ionization: 292 $(M + NH_4)^+$, 275 $(M + H)^+$. $C_{15}H_{30}O_4$ = 274.40. One-hour half-life in EB = 116 °C.

1,1-Bis(*tert*-butylperoxy)-2-phenylcyclohexane (XIII). The procedure described for X was used to react 2.1 g (12.0 mmol) of 2-phenylcyclohexanone with 15 mL (45 mmol) of *tert*-butyl hydroperoxide (3.0 M in isooctane). The reaction mixture was filtered and concentrated to yield 4.47 g of crude product. Flash column chromatography with 2% ethyl acetate/98% heptane (v/v) yielded 2.98 g (74%) of XIII as a clear colorless oil (R_f = 0.31). ^{1}H NMR ($CDCl_3$): δ 7.32 (m, 2 H), 7.18 (m, 3 H), 3.01 (m, 1 H), 2.68 (m, 1 H), 2.0 (m, 1 H), 1.5–1.9 (m, 4 H), 1.2–1.4 (m, 2 H), 1.15 (s, 9 H), 1.10 (s, 9 H). ^{13}C NMR ($CDCl_3$): δ 142.27, 130.50, 127.85, 126.66, 108.46, 80.31, 79.84, 51.72, 31.59, 31.15, 27.49, 27.33, 26.64, 23.44. MS: *m/z* (relative intensity) 247 (1.9%), 130 (7%), 117 (3.2%), 115 (2.1%), 107 (4.1%), 91 (1.9%), 73 (100%), 57 (13.2%), 43 (9.9%). The molecular weight was confirmed by positive ion ammonium chemical ionization: 354 $(M + NH_4)^+$, 337 $(M + H)^+$. $C_{20}H_{32}O_4$ = 336.47. One-hour half-life in EB = 95 °C.

8,8-Bis(*tert*-butylperoxy)tricyclo[5.2.1.0]decane (XIV). The procedure described for X was used to react 1.8 g (12 mmol) of 8-oxotricyclo[5.2.1.0]decane with 15 mL (45 mmol) of *tert*-butyl hydroperoxide (3.0 M in isooctane). The reaction mixture was filtered and concentrated to yield 4.2 g of a light yellow oil. Part of the material (2.9 g) was flash chromatographed with 2% ethyl acetate/98% heptane (v/v) to yield 1.81 g (70%) of XIV as a clear colorless oil (R_f = 0.26). ^{1}H NMR ($CDCl_3$): δ 2.45 (m, 2 H), 1.75–2.0 (m, 5 H), 1.65 (m, 12 H), 1.3–1.5 (m, 4 H), 1.28 (s, 18 H), 0.9 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ 115.93, 80.29, 79.92, 48.37, 48.14, 41.10, 40.99, 40.12, 33.23, 32.30, 32.16, 32.00, 28.24, 27.65, 27.62, 26.55. MS: *m/z* (relative intensity) 223 (1.8%), 151 (2.8%), 150 (3%), 107 (3.2%), 106 (3.1%), 91 (3.8%), 79 (11.2%), 73 (100%), 57 (14.1%), 43 (30.4%), 41 (16%). The molecular weight was confirmed by positive ion ammonium chemical ionization: 330 $(M + NH_4)^+$, 313 $(M + H)^+$. $C_{18}H_{32}O_4$ = 312.45. One-hour half-life in EB = 102 °C.

***tert*-Butyl Perpentanoate (XV).** A 100-mL flask equipped with a condenser, additional funnel, nitrogen inlet, and magnetic stirrer was flushed with nitrogen and then charged with 1.91 g (15.84 mmol) of valeroyl chloride in 15 mL of isooctane. The flask was cooled in an ice bath, and then approximately 0.5 g of potassium carbonate was added. Next, 6.0 mL (18.0 mmol) of *tert*-butyl hydroperoxide (3.0 M in isooctane) was added dropwise with stirring. After addition was complete, the reaction mixture was stirred for 1 h and then the ice bath was removed and the reaction mixture stirred overnight. The reaction mixture was then filtered and concentrated to yield 1.5 g of a yellow oil. The material was flash chromatographed with 5% ethyl acetate/95% heptane (v/v), yielding 0.35 g (13%) of XV as a clear colorless oil (R_f = 0.28). ^{1}H NMR ($CDCl_3$): δ 2.32 (t, 2 H), 1.68 (m, 2 H), 1.35 (m, 11 H), 0.92 (t, 3 H). ^{13}C NMR ($CDCl_3$): δ 172.06, 83.95, 31.76, 27.76, 26.88, 22.96, 14.34. MS: *m/z* (relative intensity) 174 (M^+, 0.16%), 114 (1.3%), 85 (44.1%), 73 (2.7%), 72 (2.8%), 71 (3.7%), 58 (15.1%), 57 (62.9%), 43 (100%), 41 (41.9%). The molecular weight was confirmed by positive ion ammonia chemical ionization: 192 $(M + NH_4)^+$, 175 $(M + H)^+$. $C_9H_{18}O_3$ = 174.22. One-hour half-life in EB = 121 °C.

***tert*-Butyl Perhexanoate (XVI).** The synthesis of this compound is described elsewhere.[1]

***tert*-Butyl Perheptanoate (XVII).** The procedure described for XV was used to react 2.61 g (17.56 mmol) of heptanoyl chloride with 7.0 mL (21 mmol) of *tert*-butyl hydroperoxide (3.0 M in isooctane). The reaction mixture was filtered and concentrated to yield 2.97 g of a colorless oil. Flash column chromatography with 5% ethyl acetate/95% heptane (v/v) yielded 1.25 g (35%) of XVII as a clear colorless oil (R_f = 0.34). ^{1}H NMR ($CDCl_3$): δ 2.32 (t, 2 H), 1.68 (m, 2 H), 1.34 (m, 15 H), 0.88 (t, 3 H). ^{13}C NMR ($CDCl_3$): δ 172.0, 83.96, 32.07, 29.51, 26.90, 25.70, 23.20, 14.75. MS: *m/z* (relative intensity) 202 (M^+, 0.06%), 113 (20.6%), 85 (15.6%), 84 (10.5%), 73 (4.4%), 71 (4.3%), 59 (6.9%), 58 (9.0%), 57 (31.0%), 56 (13.5%), 55 (10.4%), 43 (100%), 41 (41.9%). The molecular weight was confirmed by positive ion ammonia chemical

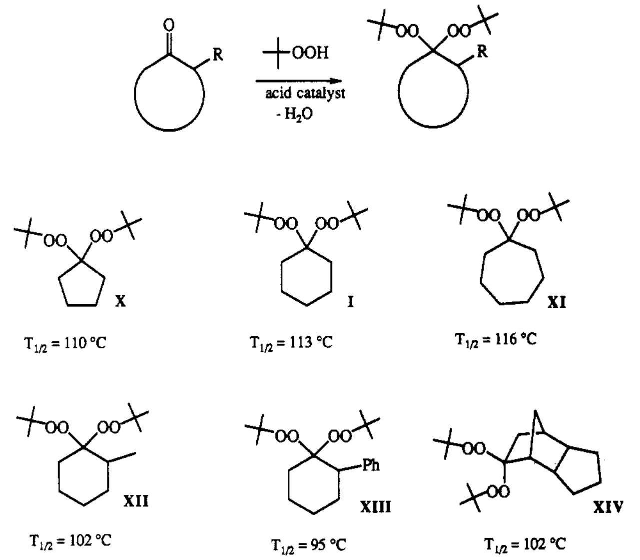


Figure 1. Perketals synthesized and studied during this work along with their respective 1-h half-life temperatures in EB.

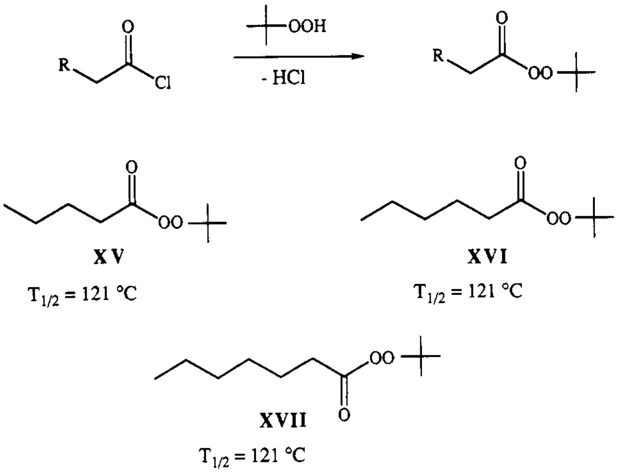


Figure 2. Peresters synthesized and studied during this work along with their respective 1-h half-life temperatures in EB.

ionization: 220 $(M + NH_4)^+$, 203 $(M + H)^+$. $C_{11}H_{22}O_3 = 202.29$. One-hour half-life in EB = 121 °C.

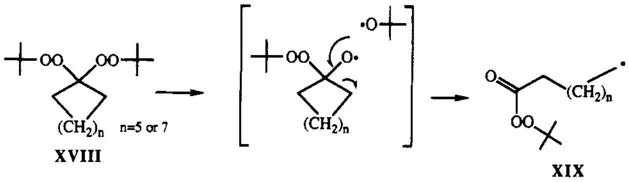
2,3-Diphenylbutane (XX), decomposition of peroxides in ethylbenzene (EB) and styrene (S), and half-life determination in EB are described elsewhere.[1]

Results and Discussion

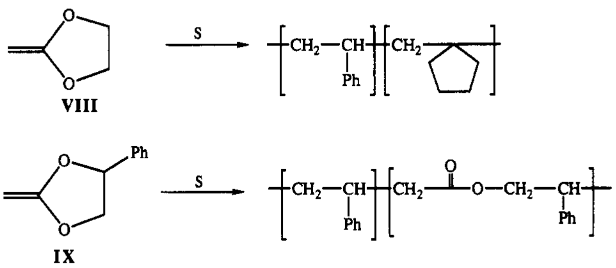
The perketals (I, X–XIV) studied in this report were prepared by condensation of hydroperoxides with cyclic ketones (Figure 1). The *tert*-butyl peresters (XV–XVII) were synthesized by reaction of *tert*-butyl hydroperoxide with acid chlorides (Figure 2). The 1-h half-life decomposition temperature ($T_{1/2}$) of each peroxide was determined in ethylbenzene (EB) as described elsewhere.[1]

The ring-strained perketals (X, XI, XIV) (Scheme V) and ring-substituted perketals (XII, XIII) (Scheme VI) were decomposed in both EB (H-atom source) and styrene (S) as previously described for I.[1] Samples decomposed in EB were subjected to both chromatographic and mass spectral analyses. GC–MS was used to identify decomposition products, and gas chromatography was used to quantitate some of the decomposition products with *o*-terphenyl as an internal standard. The identities of the products are analogous to those described for the decomposition of I.[1]

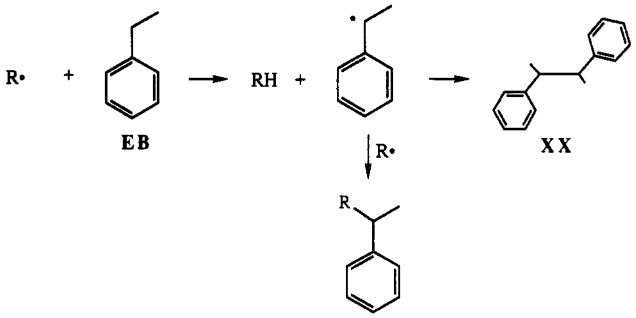
Scheme V
Use of Ring Strain to Promote the Decomposition of *gem*-Bis(*tert*-butylperoxy)cycloalkanes by the Ring-Opening Pathway



Scheme VI
Use of Radical Stability To Promote the Decomposition of *gem*-Bis(*tert*-butylperoxy)cycloalkanes by the Ring-Opening Pathway



Scheme VII
Radical Dimerization of EB



Ring-strained perketals X and XI, ring-substituted perketal XII, and I were compared in EB for both overall radical efficiency and difunctional efficiency. The amount of ring-opened perester XIX formed during the decompositions was taken to be a measure of difunctionality. Overall radical efficiency was measured by normalizing the amount of 2,3-diphenylbutane (XX) (EB dimer) formed (Scheme VII). The amount of XX formed provides an indirect measure of how many radicals were produced by the initiator. Overall efficiency is defined as indicated in eq 1. It should be pointed out, however, that the

$$\text{efficiency} = \frac{\text{mmol of XX formed}}{2(\text{initial mmol of perketal})(\%\ \text{perketal consumed})} \quad (1)$$

phenethyl radical coupling reaction to form XX shown in Scheme VII does not proceed in 100% yield due to coupling of phenethyl radicals with R•. However, it does serve as a good comparative measurement of the efficiencies of similarly functionalized initiators.

Figures 3–6 show the results of decomposing I, X, XI, and XII in EB for 1 h at the indicated temperatures. Of these four perketals, X has superior difunctional character. For example, compare the results of decomposition of X (Figure 3) with the results of decomposition of I (Figure 4) at 120 °C. After 1 h at 120 °C, about 80% of I has decomposed and about 25% of the maximum theoretical amount of perester XV is present. Since the 1-h half-life of the perester is near 120 °C, the actual amount of perester formed was 50% of the maximum. Therefore, for approximately every two molecules of I that decompose, one

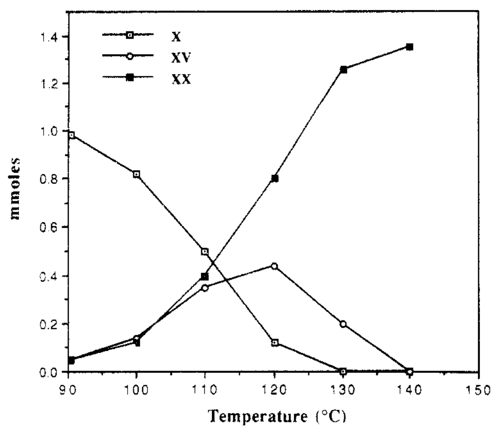


Figure 3. Decomposition of X in EB.

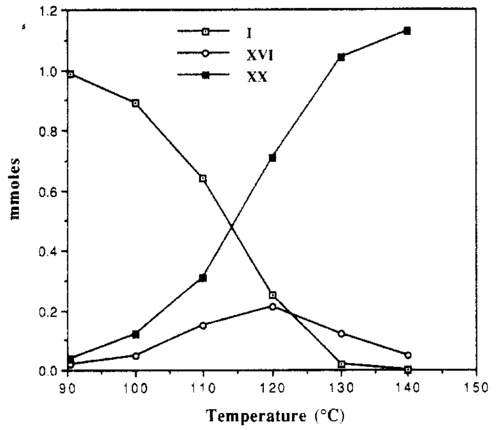


Figure 4. Decomposition of I in EB.

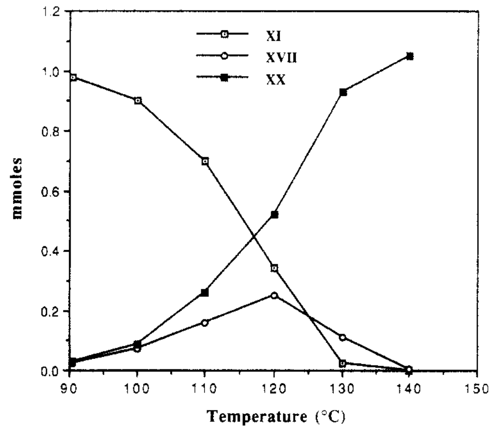


Figure 5. Decomposition of XI in EB.

molecule of perester arises; or, stated differently, the difunctionality of I is 50% of the theoretical amount. After 1 h at 120 °C, about 90% of X has been consumed and about 50% of the maximum theoretical amount of perester is present—again, double the amount of perester observed because of its 1-h half-life of 120 °C. Therefore, almost every molecule of X decomposes through the perester, or the difunctionality of X is almost 100% of the theoretical amount. Applying the same argument to the decomposition of XI and XII reveals that their difunctional behavior is inferior to that of X.

Figure 6 shows the results of decomposition of XII in EB. Substitution of a methyl group on the cyclohexane ring lowered the 1-h half-life of the initiator but did not have a positive effect upon its efficiency or difunctionality. Unfortunately, XIII and XIV could not be examined in an analogous fashion. Because of their relatively high molecular weights and low 1-h half-lives, GC and GC–MS analyses were unsuccessful. However, chromatographic analyses of XIII and XIV by HPLC allowed estimation of their 1-h half-lives and overall efficiencies. It should be mentioned, however, that the precision of the HPLC technique was inferior to that of the GC method. The precision of the half-life analysis by HPLC for XIV was especially poor due to its extremely low UV absorptivity. Therefore, the reported 1-h half-life for XIV (102 °C) could be several degrees in error. The radical efficiency of XIV was similar to that of I, but the efficiency of XIII was extremely poor (i.e., very little XX was formed).

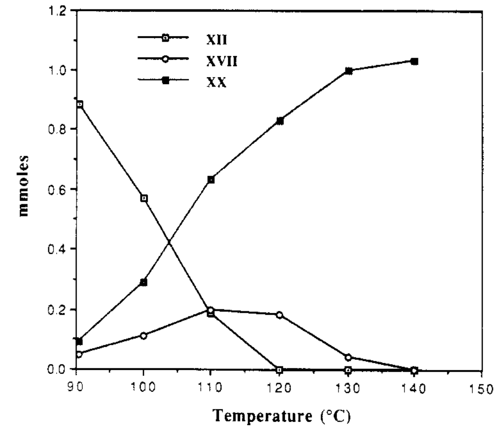


Figure 6. Decomposition of 1,1-bis(*tert*-butylperoxy)-2-methylcyclohexane (XII).

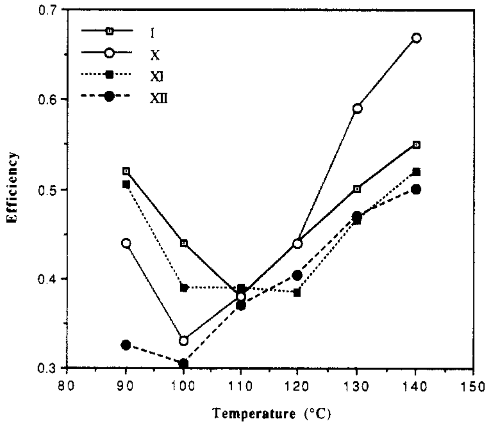


Figure 7. Effect of ring size and substitution on the radical efficiencies of 1,1-bis(*tert*-butylperoxy)cycloalkanes.

The effect of ring size and substitution on radical efficiency is shown in Figure 7. All perketals studied showed an initial decrease followed by an increase in efficiency as a function of increasing temperature. Above 120 °C, X was clearly the most efficient (H-atom abstraction from EB) of all perketals studied.

Comparison of Perketals in Styrene Polymerization. Clearly, from comparison of the performance (decomposition in EB) of the ring-strained and ring-substituted perketals evaluated during this study, it is predicted that X should be the most efficient and have the highest amount of difunctionality during styrene polymerization.

Since the half-lives of the peroxides synthesized during this study are all different, their performance in styrene polymerization could not be meaningfully compared at the same polymerization temperature. Thus a temperature-programmed oil bath was used to heat ampules of styrene containing the same molar amounts of the peroxides. The temperature program consisted of a linear ramp from 80 to 170 °C at a heating rate of 10 °C/h. Three

Table I
Evaluation of Perketals and Peresters in Styrene Polymerization Using a Temperature-Programmed Oil Bath

initiator (ppm)	temp (°C)	% conv.	MW/1000
I (260)	130	58.2	410
I (260)	150	87	391
I (260)	170	94.5	366
X (246)	130	59.1	407
X (246)	150	85.7	394
X (246)	170	93	365
XI (274)	130	57.7	406
XI (274)	150	87.4	386
XI (274)	170	95.1	378
XII (274)	130	56.2	419
XII (274)	150	85.7	398
XII (274)	170	94.4	358
XIII (331)	130	54.6	407
XIII (331)	150	84	388
XIII (331)	170	94	359
XIV (314)	130	56.2	429
XIV (314)	150	84	401
XIV (314)	170	95.6	373
XV (349)	130	55.2	338
XV (349)	150	84.8	333
XV (349)	170	91	319
XVI (376)	130	61.4	343
XVI (376)	150	83.8	335
XVI (376)	170	91.6	317
XVII (406)	130	58.3	366
XVII (406)	150	83.2	337
XVII (406)	170	91.1	316

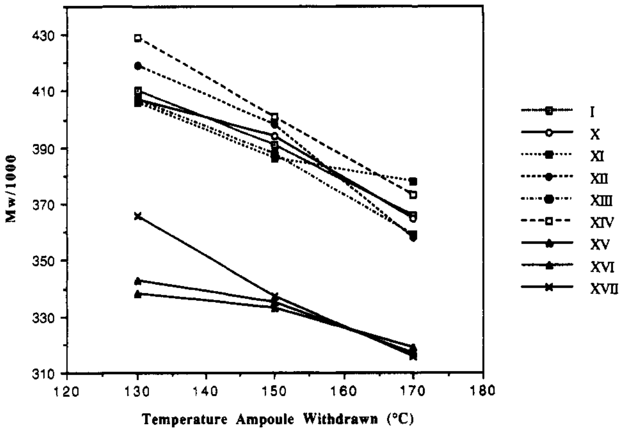
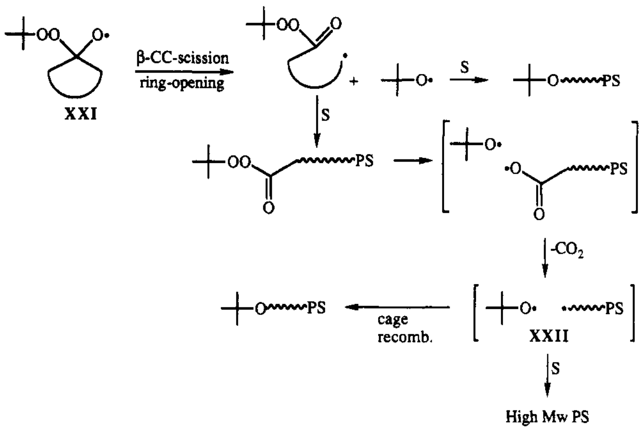


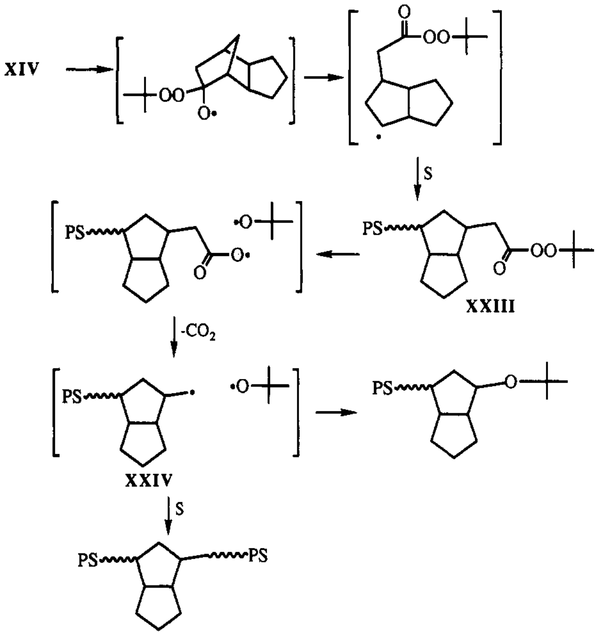
Figure 8. Comparison of the styrene polymerization performance of the perketals and peresters evaluated during this study.

ampules of styrene containing each of the peroxides were placed in the oil bath. An ampule was withdrawn from the bath when the oil bath temperature reached 130, 150, and 170 °C or after 5, 7, and 9 h, respectively. The styrene conversion and polystyrene M_w in each ampule were measured (Table I). The styrene conversion of all of the ampules withdrawn at 130, 150, and 170 °C fell in the ranges of 55–61, 83–87, and 91–96%, respectively. The M_w of the polystyrene produced using the perketals is significantly higher than using the peresters (Figure 8). However, the performance of the perketals in styrene polymerization does not correlate with their performance in EB dimerization. Perketal XIV showed very poor efficiency during EB dimerization, yet overall gave the best M_w performance during styrene polymerization.

Scheme VIII
Proposed Mechanism of Formation of High M_w Polystyrene via Ring Opening



Scheme IX
Proposed Chemistry of Initiation of Styrene Polymerization Using XIV



The difference in performance of the perketals in styrene polymerization versus EB dimerization is not surprising since the reaction pathways for H abstraction and initiation of styrene polymerization are quite different. However, we expected some correlation between the M_w of the polystyrene formed with the amount of ring opening of the intermediate radical XXI (Scheme VIII). Assuming that the amount of ring opening is the same in EB and styrene, X should have produced the highest M_w polystyrene. Another factor that could be controlling the M_w is the ratio of in-cage recombination of XXII versus initiation of styrene polymerization. Since the radicals formed in EB are small, they likely can diffuse more readily from the cage than macroradicals (XXII) formed in styrene.

Another factor that can have an effect upon M_w is the temperature range that the initiator is decomposing during the polymerization program. As the polymerization temperature increases, the ratio of termination by radical disproportionation versus radical coupling also increases. Thus the perketals with lower half-lives may give a slightly higher M_w due to the lower temperature at which the bulk of the polymerization had taken place. This may explain why XIV performed so well; i.e., it was one of the lower half-life temperature perketals.

Another possible explaination for the observed behavior of XIV is that β-CC-scission of the intermediate oxy radical provides both relief of ring strain and a stable secondary carbon centered radical. Also, a feature of XIV that is unique is that the proposed perester functional polystyrene intermediate XXIII yields a sterically hindered radical

(XXIV) after decarboxylation. This added steric bulk may contribute favorably to the ratio of in-cage recombination to cage escape and subsequent styrene initiation (Scheme IX).

Conclusions

Ring strain does increase the ring-opening decomposition pathway of *tert*-butylperoxy ketals. The performance of one of the ring-strained *tert*-butylperoxy ketals (X) shows significantly improved efficiency toward hydrogen abstraction during decomposition in EB as evidenced by increased formation of EB dimer. However, no correlation was found between H-atom abstraction efficiency of the perketals and their ability to make high M_w polystyrene. All of the perketals produce higher M_w polystyrene than equivalent levels of their corresponding *tert*-butyl perester intermediates, but there does not appear to be a significant difference in performance between the different perketals.

References and Notes

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