Cycloalkane Perketal Initiators for Styrene Polymerization. 1. Decomposition Chemistry of 1,1-Bis(*tert*-butylperoxy)cyclohexane

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ABSTRACT: Perketals are extensively utilized as initiators for the commercial production of polystyrene and yet the chemistry of their decomposition is not well understood. In this paper the decomposition chemistry of 1,1-bis(*tert*-butylperoxy)cyclohexane is studied. GC–MS was utilized to determine the structure of decomposition products and this information used as evidence to determine the decomposition chemistry. The decomposition mechanism appears to involve several pathways. Special focus is given to the pathway that yields radicals which could have a beneficial impact upon polystyrene manufacture.

Introduction

Polystyrene (PS) was first manufactured commercially (1938) by The Dow Chemical Co. Styrene (S) was noncontinuously bulk polymerized, without the aid of a chemical initiator, to high conversion by heating it in metal cans. The cans were opened, and the solid PS was ground into small pieces. Over the next 35 years, much of the research focused on understanding the mechanism of self-initiated (spontaneous) S polymerization and developing continuous bulk polymerization processes. Over the past 20 years, bulk polymerization research emphasis has focused mainly upon understanding the chemistry of chemical initiators. Today, most PS is produced via continuous bulk polymerization with the aid of peroxide initiation. The use of peroxide initiators leads to both process and product advantages. The main process and product advantages are increased polymerization rate and narrower polydispersity. Peroxides are generally preferred over azo initiators for initiation of S polymerization because they are more efficient (less in-cage decomposition reactions).[1] In this paper we focus on understanding the decomposition chemistry of 1,1-bis(*tert*-butylperoxy)-cyclohexane (I), a commonly used S polymerization initiator.

Background

Since most of the bulk PS reactors were originally designed to produce spontaneously initiated polystyrene in the 100–170 °C temperature range,[2] the peroxide initiators used generally have 1-h half-lives in the range of 90–140 °C. If the peroxide decomposes too rapidly, a runaway polymerization could result and if it decomposes too slowly, peroxide exits the reactor. Since organic peroxides are significantly more expensive than sytrene monomer (10–20×), it is economically prudent to choose an initiator that is highly efficient. A further economically driven objective is to utilize initiators that increase the rate of polymerization of S to form PS having the desired molecular weight. The commercial weight-average molecular weight (M_w) range for general-purpose PS is 200 000–400 000. For spontaneous polymerization, the M_w is inversely proportional to polymerization rate (Figure 1).[3]

The main reason that the M_w decreases as the polymerization temperature increases is the increase in the initiation and termination reactions leading to a decrease in the kinetic chain length (Scheme I). At low temperature, the main termination mechanism is polystyryl radical coupling but as the temperature increases, radical disproportionation becomes increasingly important.[4] Termination by coupling results in higher M_w polystyrene than any of the other termination modes.

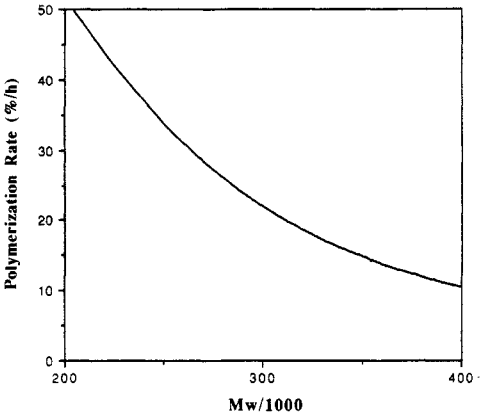
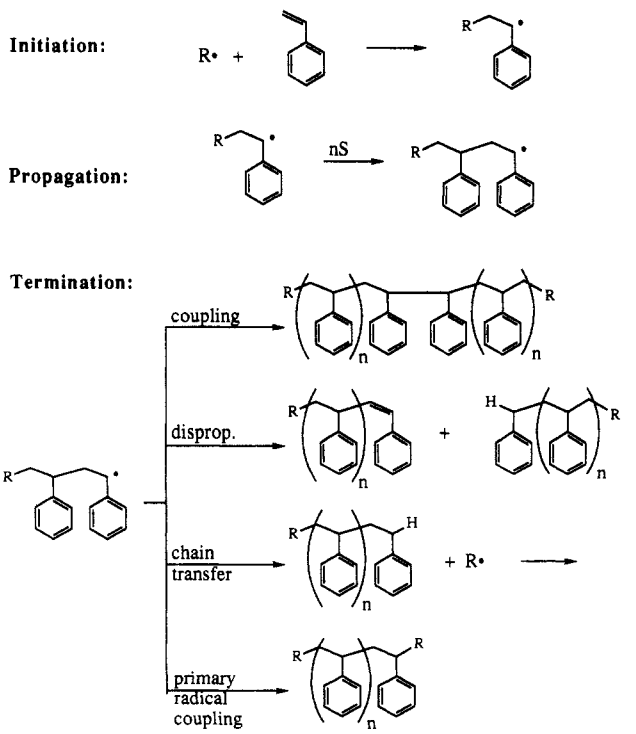


Figure 1. Rate/M_w relation for spontaneous styrene polymerization.

Scheme I
General Chemistry of Free-Radical S Polymerization Using an Initiator



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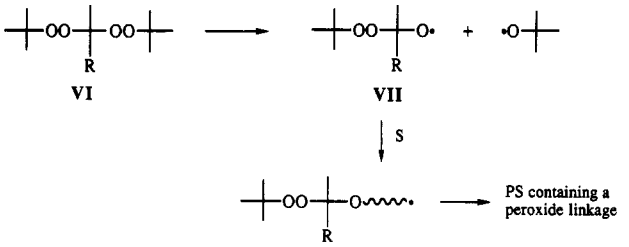
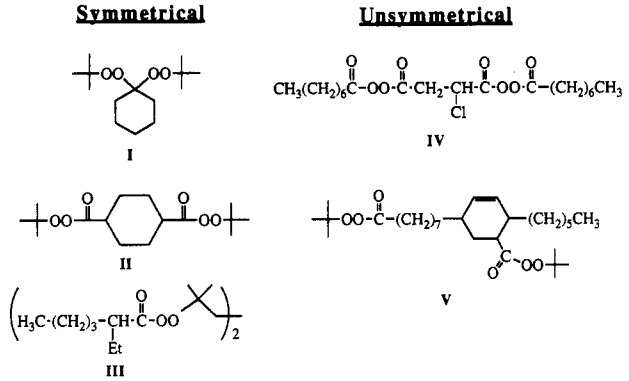
Scheme II
Proposed Nonsynchronous Mechanism for Decomposition of Perketals



In recent years there has been considerable interest in difunctional peroxide initiators. Kinetic models have been developed for bulk S polymerization using symmetrical difunctional (I,[5,6] II,[6] and III[6]) and unsymmetrical difunctional initiators (IV[7-9] and V[10,11]). One of the key

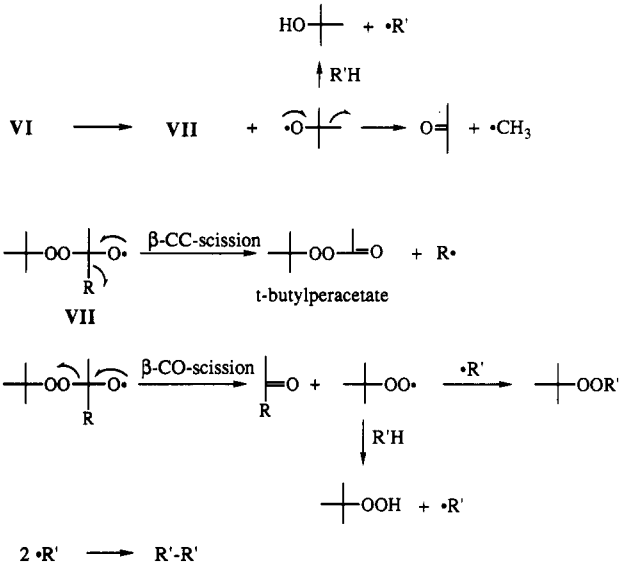


reasons for the use of difunctional initiators is their theoretical ability to form initiator fragments which can initiate polymer growth from two different sites within the same fragment, ultimately leading to "double-ended PS". If double-ended PS chains are produced, higher M_w PS can be produced at faster rates than achievable using monofunctional initiators.[12,13]

The most common class of difunctional peroxide initiators utilized for continuous bulk S polymerization and copolymerization are the *gem*-bis(*tert*-butylperoxy)alkanes (VI), also commonly referred to as perketals. There are some studies aimed at understanding the decomposition chemistry of perketals during bulk S polymerization. Yenal'ev et al.[14,15] found peroxide linkages in PS produced using these initiators. They concluded that the initial decomposition of the bisperoxide occurred at one of the peroxide bonds rather than synchronous scission of both peroxide bonds. They further suggested that the PS chains that contained peroxide linkages were produced via initiation by the intermediate peroxide containing alkoxyl radical (VII) as shown in Scheme II.

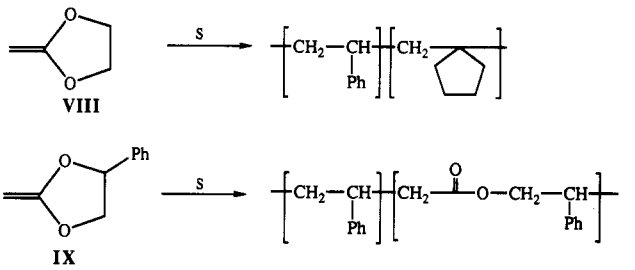
More recently, Watanabe et al.[16] also found peroxide linkages in PS produced using certain *gem*-bis(*tert*-butylperoxy)alkanes. Iodometric titration showed that about half of the polymer chains contained a peroxide linkage when using 2,2-bis(*tert*-butylperoxy)propane (VI, R = Me) as an initiator. However, when R = Et or *i*Pr, <5% of the chains contained peroxide linkages. They pursued the investigation further to elucidate the mechanism of decomposition and initiation of styrene polymerization using VI where R = Me, Et, and *i*Pr. Analysis of the liquid products left after the decomposition of VI in cumene[17,18] and S[16] showed acetone, alkyl methyl ketone, *tert*-butyl alcohol, *tert*-butyl hydroperoxide, and *tert*-butylperacetate in both solvents, as well as *tert*-butyl cumyl peroxide, and 2,3-dimethyl-2,3-diphenylbutane in cumene.

Scheme III
Decomposition of *gem*-Bis(*tert*-alkyldioxy)alkanes in Cumene



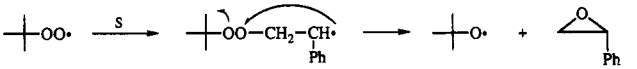
Scheme III was proposed to explain in the formation of these products.

The yield of *tert*-butylperacetate formed by decomposition of VI in cumene varied greatly with R (Me ≪ Et ≤ *i*Pr). This difference can be explained on the basis of the relative stability of the resulting alkyl radicals.[19] In a similar vein, Bailey[20] has shown that the rates of β-scission reactions of α-alkoxy radicals are dependent upon the stability of the expelled radicals. For example, copolymerization of cyclic ketal VIII with S results in simple vinyl polymerization while copolymerization of IX with S results in 100% scission to form the ring-opened copolymer.



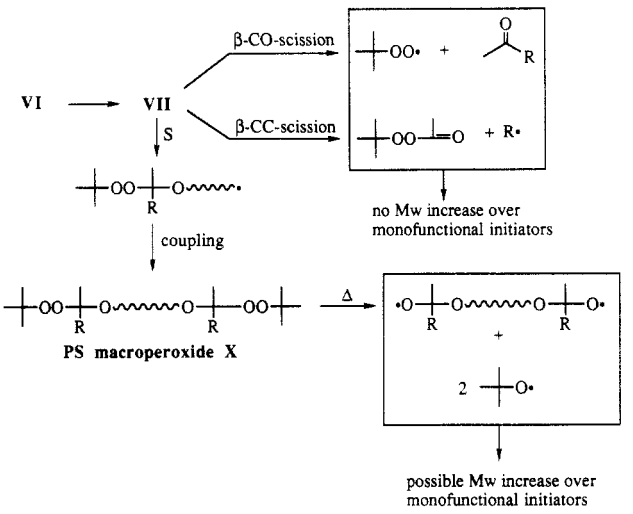
Decomposition of VI in S produced product distributions very similar to those observed in cumene. About the same amount of *tert*-butylperacetate was formed in both S and cumene, indicating that the β-scission reaction of VII (R = Et, *i*-Pr) is much faster than its rate of addition to the S double bond.

The formation of peroxy-containing PS when using VI (R = Me) as an initiator could also result from initiation of S polymerization by *tert*-butylperoxy radical. However, Watanabe et al.[16] noticed the formation of styrene oxide during the polymerization of styrene using *gem*-bis(*tert*-butylperoxy)alkanes. They suggested radical epoxidation of styrene by expelled *tert*-butylperoxy radicals as shown below.



The formation of considerable amounts of acetone and *tert*-butyl alcohol during the decomposition of 2,2-bis(*tert*-butylperoxy)butane in S indicates that the rates of

Scheme IV
Summary of Decomposition Chemistry of Acyclic Perketals in Styrene



β-scission and H abstraction are competitive with addition to the S double bond. Niki and Kamiya[21,22] are in agreement that considerable H abstraction between *tert*-butoxy radicals and PS takes place, especially at high polymerization temperatures (125 °C).

In summary, these findings indicate that perketals (VI, R ≠ Me) which yield an intermediate peroxy-containing radical (VII) will produce little or no PS macroperoxide (X). Theoretically, this macroperoxide could later fragment to reinitiate polymerization and grow in M_w. More likely, β-scission of VII takes place before its addition to S, no peroxy-containing polystyrene is formed, and the difunctional peroxide only yields monoradicals. Therefore, the structure of the perketal should have a significant effect upon the molecular weight of the PS it produces. These two initiation pathways for initiation of S polymerization using acyclic perketals are depicted in Scheme IV.

Experimental Section

Materials and Methods. Solvents and inorganic materials were purchased from Fisher Scientific and organic materials 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 (0.03% w/w). 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. 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. Ammonia was used as the reactant gas in chemical ionization analysis. Molecular weights were measured using gel permeation chromatography as described elsewhere.[3]

Synthesis. 1,1-Bis(*tert*-butylperoxy)cyclohexane (I). A 100-mL, three-necked flask equipped with a condenser, nitrogen inlet, and magnetic stirrer was flushed with nitrogen and then charged with 1.2 g (12.2 mmol) of cyclohexanone and 15.5 mL (46.5 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, *p*-toluenesulfonic acid (about 50 mg) 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 1% ethyl acetate/99% heptane (v/v), yielding 2.38 g (75%) of I (R_f = 0.20). ^{1}H NMR ($CDCl_3$): δ 1.80 (m, 4 H), 1.55 (m, 4 H), 1.40 (m, 2 H), 1.25 (s, 18 H). ^{13}C NMR ($CDCl_3$): δ 108.05, 79.71, 31.59, 27.55, 26.46, 23.47. MS: *m/z* (relative intensity) 177 (1.35%), 113 (0.23%), 99 (1.45%), 98 (0.96%), 97 (0.37%), 81 (1.67%), 80 (0.37%), 74 (4.16%), 73 (100%), 57 (13.19%), 55 (11.82%), 41 (23.09%), 39 (4.75). The molecular weight was confirmed by positive ion ammonia chemical ionization: 278 $(M + NH_4)^+$, 261 $(M + H)^+$. $C_{14}H_{28}O_4$ = 260.37. One-hour half-life in ethylbenzene (EB) = 113 °C.

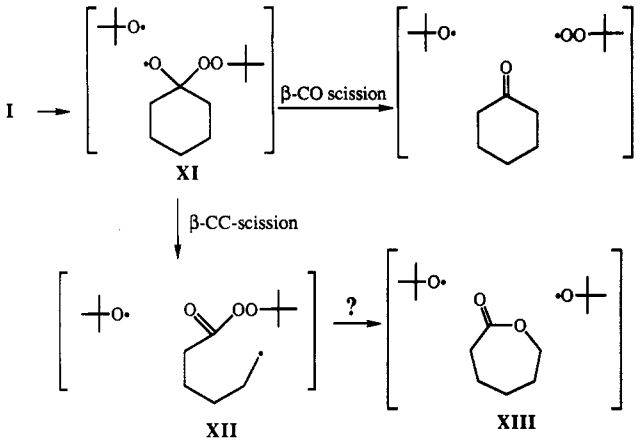
***tert*-Butyl Perhexanoate (XIV).** A 100-mL flask equipped with a condenser, addition funnel, nitrogen inlet, and magnetic stirrer was flushed with nitrogen and then charged with 2.5 g (18.57 mmol) of hexanoyl chloride in 15 mL of isooctane. The flask was cooled in an ice bath and then approximately 0.5 g of potassium carbonate was added. Next, 6.5 mL (19.5 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 2.9 g of a colorless oil. The material was flash chromatographed with 5% ethyl acetate/95% heptane (v/v), yielding 1.14 g (33%) of XIV as a clear colorless oil (R_f = 0.32). ^{1}H NMR ($CDCl_3$): δ 2.31 (t, 2 H), 1.68 (m, 2 H), 1.34 (m, 13 H), 0.92 (t, 3 H). ^{13}C NMR ($CDCl_3$): δ 172.30, 83.97, 32.03, 31.98, 26.89, 25.42, 22.96, 14.62. MS: *m/z* (relative intensity) 188 (M^+, 0.06%), 129 (0.7%), 99 (28.3%), 85 (2.3%), 73 (3.2%), 72 (1.6%), 51 (18.0%), 59 (5.8%), 58 (10.7%), 57 (37.2%), 43 (100%), 41 (35.4%). The molecular weight was confirmed by positive ion ammonia chemical ionization: 206 $(M + NH_4)^+$, 189 $(M + H)^+$. $C_{10}H_{20}O_3$ = 188.27. One-hour half-life in EB = 121 °C.

1,5-Di-*tert*-Butoxypentane (XXI). A 250-mL flask equipped with a dry ice condenser, addition funnel, nitrogen inlet, and magnetic stirrer was flushed with nitrogen and then charged with 5 g (48 mmol) of 1,5-pentanediol and 75 mL of hexane. Amberlyst 15 ion exchange resin (3.3 g) (H form) was added. Next, 13 g (232 mmol) of 2-methylpropene was condensed in the flask, and the mixture stirred for 24 h. After the addition was complete, the reaction mixture was stirred for 1 h. Then the ice bath was removed and the reaction mixture stirred overnight. GC analysis of the reaction mixture showed that all of the 1,5-pentanediol had been consumed, but the main product was the monoether. Thus an additional 12.2 g of 2-methylpentene was condensed in the flask and stirring was continued for another 24 h. GC analysis then showed about 90% conversion to the desired diether. At this point another 1 g of Amberlyst 15 ion exchange resin and 20 g of 2-methylpropene were added followed by 24 h of stirring. GC analysis now showed >97% conversion to the diether. The reaction mixture was then filtered and concentrated to yield 9.82 g of XXI as a colorless oil (94%). ^{1}H NMR ($CDCl_3$): δ 3.33 (t, 4 H, J = 6.72 Hz), 1.54 (m, 4 H), 1.38 (m, 2 H), 1.18 (s, 18 H). ^{13}C NMR ($CDCl_3$): δ 72.39, 61.51, 30.53, 27.54, 22.84.

2,3-Diphenylbutane (XV). A 100-mL flask equipped with a condenser, magnetic stirrer, and nitrogen inlet was charged with 2.0 g (13.7 mmol) of di-*tert*-butyl peroxide (ATOCHEM) and 70 mL of EB. The reaction mixture was refluxed for 5 h and then evaporated, yielding 1.4 g (48%) of XV as a white solid which existed as a mixture of isomers.

Decomposition of Peroxides in Ethylbenzene (EB). Stock solutions of individual peroxides were prepared in anhydrous EB (Aldrich, Sureseal). The target concentration for the peroxides was 0.1 M. A clean, oven-dried 10-mL volumetric flask was charged with approximately 1 mmol of the peroxide and a known amount of *o*-terphenyl as an internal standard. The flask was then diluted to the mark with ethylbenzene, sealed with a septum, and stored in a freezer until used. Aliquots of the stock solution were transferred to Pyrex tubes (20 cm × 9 mm o.d., 5 mm i.d.). The tubes were cooled in dry ice and sealed under vacuum. The ampules were then placed in an oil bath at the desired temperature for the desired length of time. Upon removal from the oil bath, the tubes were rapidly cooled and broken open, and their contents analyzed by GC and GC–MS.

Scheme V
Predicted Decomposition Chemistry of I Based on the Decomposition Chemistry of Acyclic Perketals



Decomposition of Peroxides in Styrene (S). The S used was obtained from The Dow Chemical Co. It was stored under refrigeration and contained 12 ppm of *tert*-butylcatechol. Aliquots of the S + initiator solutions were transferred to Pyrex tubes (20 cm × 9 mm o.d., 5 mm i.d.), frozen in dry ice, and sealed under vacuum. The ampules of S + initiator were polymerized by immersion in a silicone oil bath heated at 124 °C. Tubes were removed from the bath after 60 min, cooled rapidly, and broken open, and the contents were analyzed for percent PS and molecular weight. The percent PS data were obtained by devolatilizing the PS + S syrup under vacuum (20 mmHg) at 250 °C for at least 30 min in a vacuum oven. To prepare samples for GPC analysis, the PS + S syrup was dissolved in methylene chloride, precipitated with methanol, air dried, and then redissolved in tetrahydrofuran (0.25% by weight).

Results and Discussion

One of the most commonly used initiators for the commercial production of PS and its copolymers is 1,1-bis(*tert*-butylperoxy)cyclohexane (I)[12,13,23-29] and yet its decomposition chemistry has only recently been reported.[30] If I decomposes similarly to the acyclic perketals described in the background section (Scheme III), it may have a greater potential for improving the polymerization rate of PS since the β-CC-scission pathway of intermediate radical XI would yield a radical (XII) containing a perester group. However, XII may undergo cyclization to form ε-caprolactone (XIII) before it can escape its cage and react with S (Scheme V).

Decomposition of I in Ethylbenzene (EB). The 1-h half-life temperature of I was determined by heating a dilute EB solution in glass ampules. The percent of I decomposed was determined by GC analyses. A plot of the percent I decomposed versus temperature at constant time (t = h) was curve fitted to obtain a binomial equation. The resulting binomial was solved for the temperature at which 50% of the peroxide had been decomposed to give a calculated 1-h half-life of 113 °C (Figure 2).

The products of the decomposition of I in EB (Figure 3) were identified by GC–MS. The structures of XIV, XV, and XXI were confirmed by independent synthesis. No caprolactone was observed.

The starting peroxide (I), *tert*-butyl perhexanoate (XIV), and EB dimer (XV) were measured quantitatively relative to *o*-terphenyl. The remaining products were not quantitatively measured due to either peak coelution or lack of an authentic sample to obtain a GC response factor. The amount of each product obtained depended upon both the temperature at which the decomposition was performed and the length of time that the sample was heated. For samples of I decomposed near its 1-h half-life

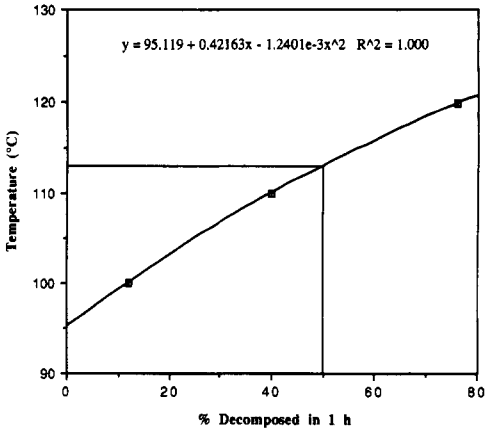


Figure 2. Binomial fit of the decomposition data obtained by heating I in EB.

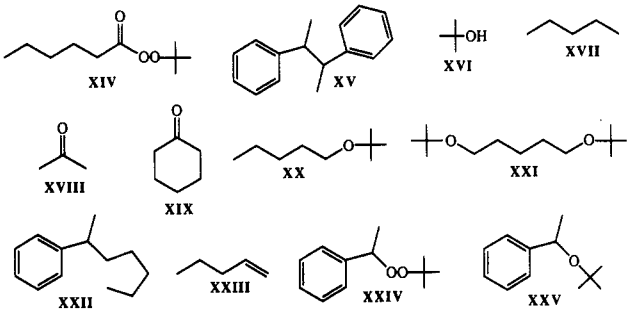
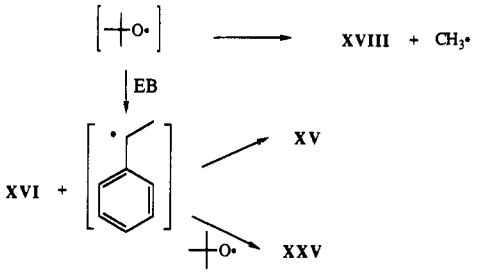


Figure 3. Decomposition products of I in EB.

Scheme VI
Chemistry of the *tert*-Butoxy Radical in EB



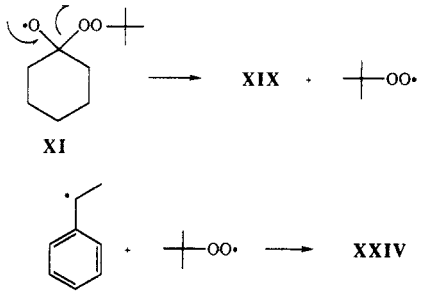
temperature, the following general product distributions held. Products XXII, XXIII, XXIV, and XXV are minor (<1% w/w of total). Moderate amounts (1–10% w/w of total) of XVIII, XIX, XX, and XXI are obtained. The major (>10% w/w of total) products are XIV, XV, XVI, and XVII.

Cleavage of the first peroxide bond of I yields a *tert*-butoxy radical and oxy radical XI. Products XV, XVI, XVIII, and XXV can be explained by the subsequent chemistry of the *tert*-butoxy radical in EB (Scheme VI).

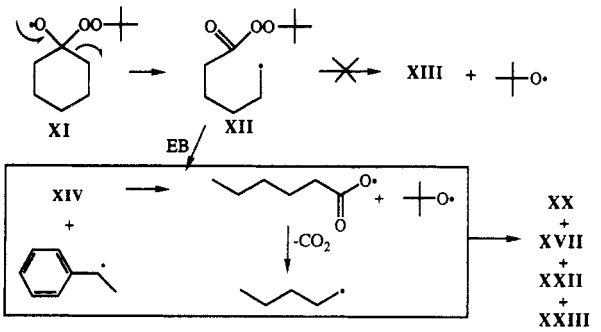
Cyclohexanone (XIX) probably arises from β-CO-scission of intermediate XI (Scheme VII). This decomposition route also provides an explanation for the observation of small amounts of phenethyl *tert*-butyl peroxide (XXIV). The *tert*-butylhydroperoxy radical can combine with an α-phenethyl radical to yield XXIV. Decomposition of the initiator through this pathway destroys 50% of the potential radical-generating capacity of I.

The products derived from β-CC scission of XI are XIV, XVII, XX, XXII, and XXIII. A likely mechanism of formation of these products is depicted in Scheme VIII. β-CC-Scission of XI produces radical perester XII, which can subsequently abstract a H atom from EB and decompose further (Scheme VII). Hydrogen abstraction

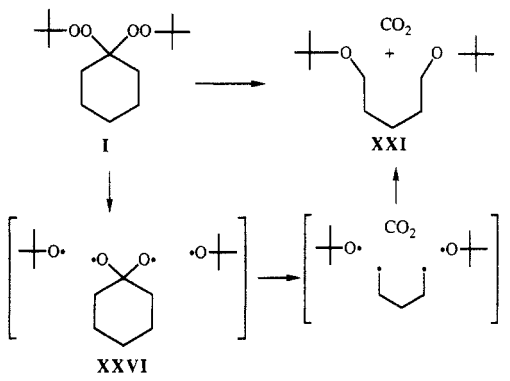
Scheme VII
Decomposition of I by β-CO-Scission



Scheme VIII
Decomposition of I by β-CC-Scission



Scheme IX
In-Cage Decomposition of I



yields XIV. Subsequent decomposition of XIV leads to the formation of XVII, XX, XXII, and XXIII. Cyclization of XI to give XIII is not observed in EB. Decomposition of I by this pathway maximizes its potential for increasing the rate/M_w performance in styrene polymerization.

A final mode of decomposition of I can be rationalized as an "in-cage" collapse of the initiator to yield XXI as shown in Scheme IX. The oxygen-centered radical of XI can assist cleavage of the other peroxide linkage, yielding the unstable dioxy radical XXVI. The chances of this intermediate escaping the solvent cage in which it is formed are remote. Most likely, XXVI would undergo a cascade of stepwise or concerted in-cage reactions culminating in extrusion of carbon dioxide and then radical recombination. Decomposition of I by this pathway destroys all the efficiency of the initiator since all radicals produced are self-consumed.

The proposed decomposition chemistry of I in EB is summarized in Scheme X. The preferred pathway to maximize radical efficiency and the rate/M_w for polystyrene is the β-CC-scission pathway.

To assess the radical efficiency of I, we determined the amount of XV formed during decomposition of I in EB. Also, formation and loss of intermediate perester XIV was monitored. To accomplish the determination, authentic

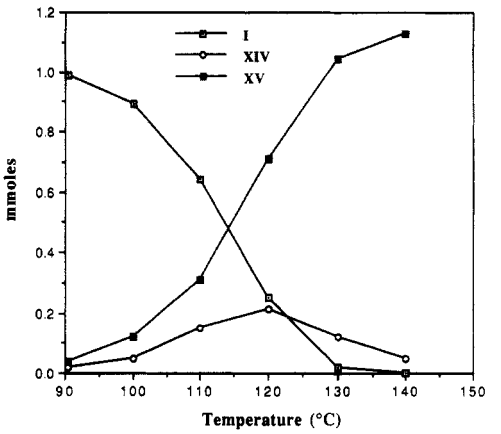
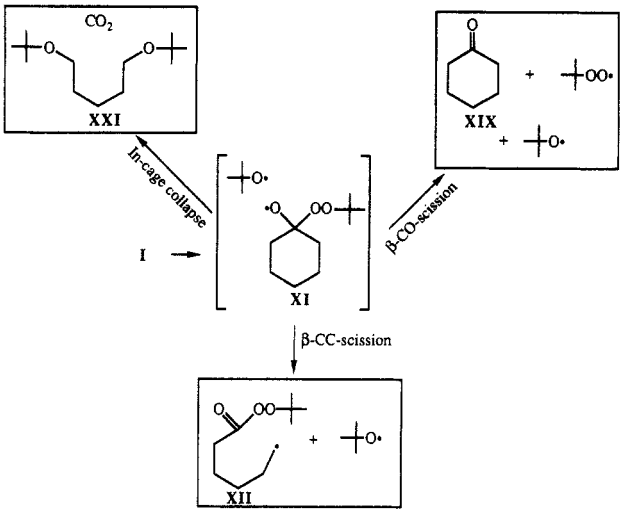


Figure 4. Comparison of the loss of I and the formation of XIV and XV during the decomposition of I in EB for 1 h at various temperatures.

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



samples of XIV and XV were synthesized and used to generate response factors for GC analysis. The data obtained from the decomposition of a dilute solution of I in EB for 1 h at various temperatures are shown in Figure 4. These data were used to calculate the radical efficiency. At 100% efficiency (I can yield a maximum of four radicals), the decomposition of 1 mmol of I should form almost 2 mmol of XV (products XXII, XXIV, and XXV also consume phenethyl radicals but their amounts are small relative to XV). At each temperature, the yield of XV was calculated based on the amount of I decomposed. The results (Figure 5) show that a change in efficiency with temperature takes place. If the ratio of the rates of the three decomposition pathways remain constant with temperature, a steady increase in efficiency with increase in temperature is expected. The intermediate perester XIV is more thermally stable than I and is formed with the production of only two radicals. Its subsequent decomposition yields two more radicals to continue formation of XV. The initial decrease followed by an increase in efficiency with temperature indicates a change in the ratio of rates of the three decomposition pathways with temperature. At 110 °C, "in-cage" reactions predominate.

The decomposition products we observed for the decomposition of I are somewhat different from those reported by Sugihara et al.[30] They did not observe the diether XXI but instead reported the formation of

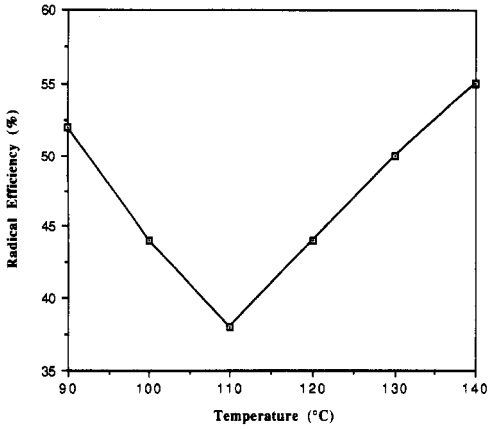


Figure 5. Radical efficiency of I vs decomposition temperature in EB.

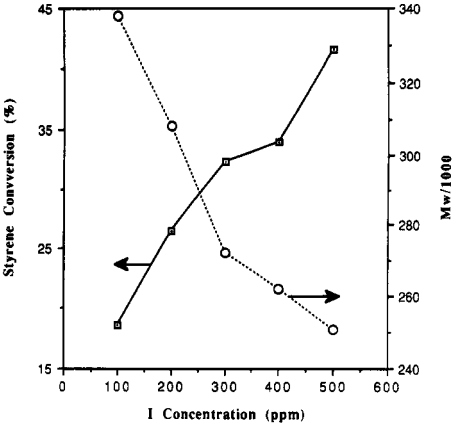
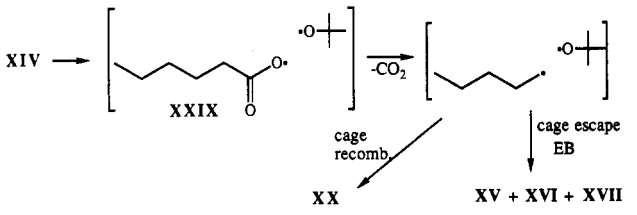
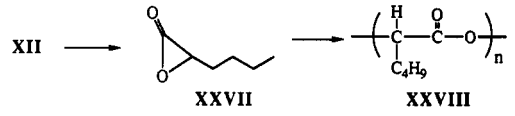


Figure 6. Initiation of S polymerization using I for 1 h at 124 °C.

Scheme XI
Proposed Decomposition Mechanism of XIV in EB



polyester XXVIII. They postulate an intramolecular hydrogen abstraction of XII resulting in the formation of 2-hexanolide XXVII which subsequently polymerizes to form XXVIII. However, they performed their thermolyses at 50–100 times higher concentrations and in cumene or benzene instead of EB. Since the concentration range studied by Sugihara et al. is several orders of magnitude higher than used for initiation of styrene polymerization, we feel the decomposition chemistry they observed is unique to their experimental conditions and is not appropriate for the purpose of understanding the decomposition chemistry of I as it relates to styrene polymerization.



Decomposition of XIV in EB. Since XIV is an intermediate in the decomposition of I, its decomposition chemistry was also explored. The 1-h half-life (121 °C) and products of decomposition of XIV in EB were determined using the same methods described for I. The products of decomposition are in approximate order of abundance XV, XVI, XVII > XX > XVIII, XXII.

A proposed decomposition mechanism for XIV is shown in Scheme XI. Cleavage of the peroxide bond yields a caged acyloxy radical (XXIX) and *tert*-butoxy radical. Rapid decarboxylation of XXIX yields a solvent cage containing an *n*-pentyl radical, *tert*-butoxy radical, and carbon dioxide. Cage recombination of the paramagnetic species yields *tert*-butyl pentyl ether (XX) while diffusion from the cage yields XVII and *tert*-butoxy radicals which can undergo subsequent reactions to yield the observed products.

Decomposition of I in Styrene (S). Polymerizations of S initiated using I were conducted in glass ampules at 124 °C. The concentration of I in S was varied from 100 to 500 ppm (w/w). All of the ampules were placed in a hot oil bath for 60 min. The S conversion and PS M_w were determined for the PS produced in each ampule (Figure 6). The results show the clear rate/M_w advantage of I over spontaneous polymerization of S (Figure 7).

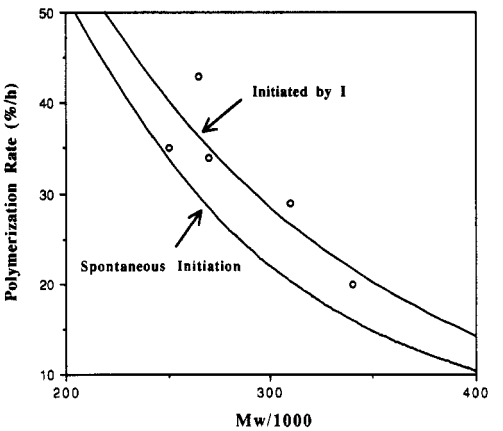


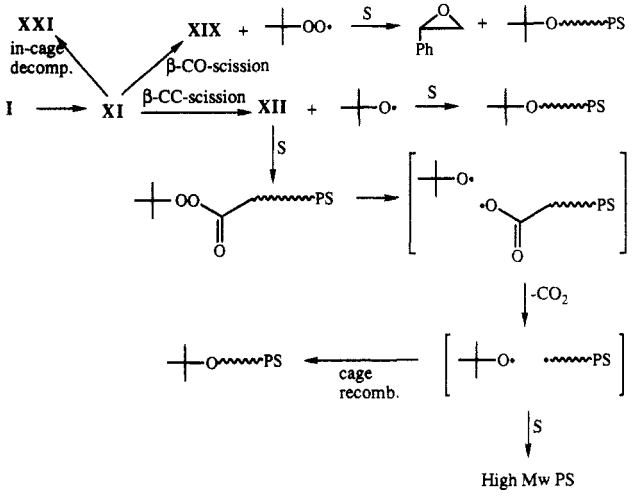
Figure 7. Rate/M_w comparison of PS spontaneously initiated and initiated by I.

The decomposition mechanism proposed in EB is likely to be the same as or very similar to that which occurs in styrene. Based on our observations in EB and the previously reported work on acyclic *tert*-butyl perketals,[16] it is unlikely that oxy radical intermediate XI would add to S before undergoing further decomposition by one of the three pathways (Scheme IX). Evidence for extension of the proposed mechanism of decomposition in EB to decomposition in styrene was obtained by the finding of XIX and XXI by GC analysis of volatile fragments remaining after S polymerization initiated using I. In S, only volatile products arising from the pathways forming nonradical products were observed. Volatile products of I arising from β-CC-scission were not seen because the radicals were rapidly scavenged by S, initiating polymerization yielding polymer-bound fragments. A likely explanation of the improved rate/M_w balance for initiation of S polymerization using I is delineated in Scheme XII. Since the decomposition pathway involving β-CC-scission results in the highest yield of radicals and forms radicals that are peroxy functional, steps to direct the decomposition of I toward the β-CC-scission pathway should lead to increased efficiency and further rate/M_w increases.

Conclusions

The products of decomposition of I and XIV in EB were determined. This information was used to propose three pathways of decomposition of I and helped to rationalize the superior performance of I as an initiator for bulk S

Scheme XII
Proposed Mechanism of Decomposition of I in Styrene



polymerization. Of the three decomposition pathways of I, the pathway involving β-CC-scission is best for achieving maximum efficiency and rate/M_w during S polymerization. Future papers will describe the results of our efforts to synthesize cyclic perketal analogs of I which decompose entirely by the preferred β-CC-Scission pathway.

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