Cycloalkane Perketal Initiators for Styrene Polymerization. 3. Decomposition Chemistry of Spiroperketals

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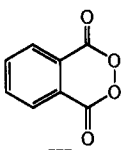
ABSTRACT: Initiators that form diradicals are of interest due to their potential for increasing polymerization rate. Spiroperketals made from 2,5-dihydroperoxy-2,5-dimethylhexane and cyclic ketones theoretically can form two diradical fragments during decomposition. However, thermolyses in ethylbenzene and styrene showed that they mainly undergo in-cage decomposition, resulting in poor performance as both hydrogen atom abstractors and polymerization initiators.

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 use of difunctional peroxides as initiators for styrene polymerization leads to the formation of high molecular weight polystyrene at faster rates than achievable using monoperoxides. This rate increase is generally viewed to arise from diradical fragments (II). However, for every diradical fragment formed, there are two *tert*-butylperoxy monoradicals also formed, which attenuates the polymerization rate actually gained by the use of typical difunctional initiators.

A class of peroxides that should theoretically form only diradicals are cyclic peroxides. However, anomalous results have been reported. For example, cyclic peroxides III–V decompose without initiating polymerization of styrene.[2]



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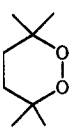

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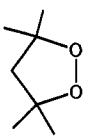
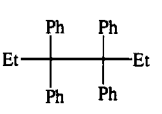


V

The earliest work[3] aimed at forming diradicals for styrene polymerization was performed in an effort to test the Flory diradical mechanism (Scheme II).[4] However, early on, there was controversy over the ability of diradical initiation to produce higher molecular weight polymers.[5,6] Later work,[7,8] however, showed successes in producing higher molecular weight vinyl polymers using biradical initiators. For example, when comparing the monoradical initiator VI and the diradical initiator VII, Borsig et al.[9] found (polymerization of methyl methacrylate at 60 °C) that significantly higher molecular weight was formed at the same monomer conversion using the diradical initiator. However, these data are complicated by the fact that at the same molar initiator concentration, the polymerization rate was slower for VII. The difference in initiating efficiency of the two initiators was explained in terms of cage reactions. The monoradicals formed from initiator VI diffuse quite efficiently from the cage and react with monomer. The diradicals, on the other hand, are in a permanent cage in that they cannot diffuse away from each other. Therefore, significantly disproportionation of the diradical (VIII) takes place to compete with initiation.



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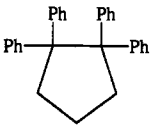

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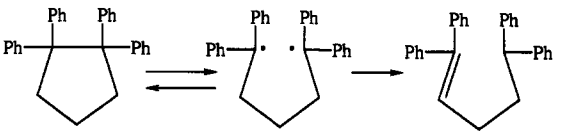
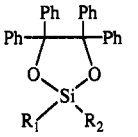
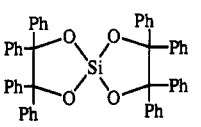


VIII

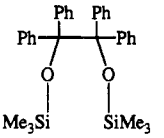
More recently, Crivello et al.[10–13] investigated diradicals produced during styrene polymerization using cyclic pinacol ethers IX and X.



IX



X



XI

Comparison of the performance of IX, X, and XI which yield di-, tetra-, and monoradicals, respectively, clearly shows a relationship between functionality and molecular weight during styrene polymerization (Figure 1). Because of the predominance of termination by chain coupling, polymerizations using the tetrafunctional initiator X gave cross-linked PS when taken to high conversion.

Recently, Hall et al.[14,15] have investigated the use of a donor–acceptor substituted cyclopropane (XII) to form carbon–carbon diradical initiators. Gel permeation chromatography (GPC) showed that the PS produced had a bimodal molecular weight distribution.[15] The low molecular weight fraction is attributed to self-termination of the growing diradical. Once a growing diradical chain becomes long enough, the diradical ends become far enough apart that they do not terminate each other. Besides the dimers and trimers of styrene normally encountered in styrene polymerization, the 1:1 adduct of styrene (XIII) was produced (Scheme III).

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. ^1H and ^{13}C NMR spectra were obtained on a General Electric QE-300 with a 5-mm probe. The NMR samples were

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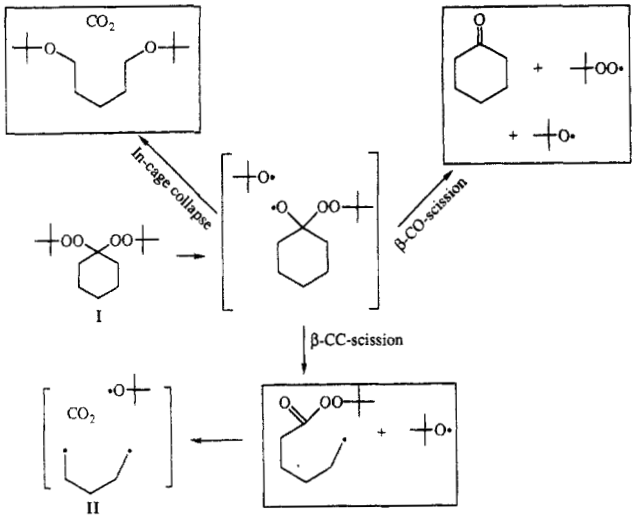
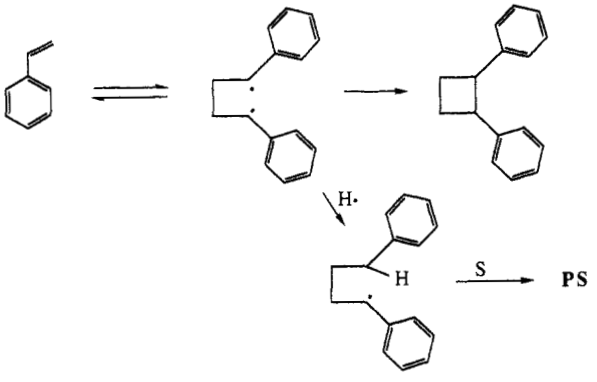
Scheme I
Pathways of Decomposition of Perketals



Scheme II
Flory Mechanism for Spontaneous Initiation of Styrene Polymerization



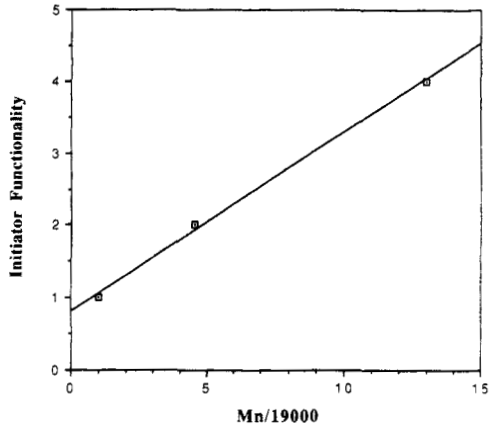
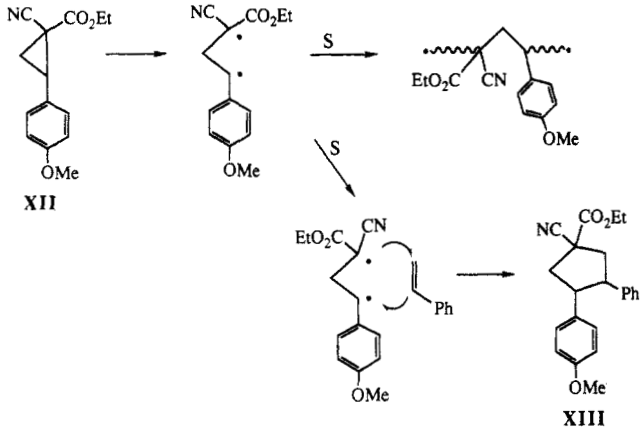


Figure 1. Variation of M_n as a function of initiator functionality during styrene polymerization.

Scheme III
Initiation of Styrene Polymerization with a Captodative Substituted Cyclopropane



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. Ammonia was used as the reactant gas in chemical ionization analysis. Molecular weights were measured using gel permeation chromatography as described elsewhere.[16]

Syntheses. Spiro[cyclopentane-1,3′-6′,6′,9′,9′-tetramethyl-1′,2′,4′,5′-tetraoxacyclononane] (XIV). A 100-mL, three-necked flask equipped with a Dean–Stark trap, condenser, nitrogen inlet, and magnetic stirrer was flushed with nitrogen and then charged with 4.0 g (15.71 mmol) of 2,5-dihydroperoxy-2,5-dimethylhexane (70% by weight, remainder water; Luperox 2,5-2,5 (Pennwalt)) and 50 mL of hexane. The slurry was brought to reflux and held there until no more water was collected in the trap. The slurry was then cooled and the Dean–Stark trap removed. (Note: the dihydroperoxide is soluble in heptane above 80 °C but not soluble in refluxing hexane.) Next, 1.3 g (15.5 mmol) of cyclopentanone, approximately 1 g of magnesium sulfate, and a catalytic amount (50 mg) of *p*-toluenesulfonic acid were added. The reaction mixture was brought to reflux and held there for approximately 30 min. The reaction can be visually monitored by watching the dihydroperoxide disappear. Filtration and concentration yielded 3.8 g of a clear colorless oil which was flash chromatographed with 2% ethyl acetate/98% heptane (v/v) to yield 2.5 g (66%) of XIV as a white solid (R_f = 0.28). ^{1}H NMR ($CDCl_3$): δ 2.2 (m, 4 H), 1.65 (m, 6 H), 1.33 (s, 6 H), 1.28 (m, 2 H), 1.03 (s, 6 H). ^{13}C NMR ($CDCl_3$): δ 118.85, 82.42, 34.14, 30.69, 27.66, 25.34, 23.97. MS: *m/z* (relative intensity) 244 (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: 262 $(M + NH_4)^+$, 245 $(M + H)^+$. $C_{13}H_{24}O_4$ = 244.31. One-hour half-life in ethylbenzene = 140 °C.

Spiro[cyclohexane-1,3′-6′,6′,9′,9′-tetramethyl-1′,2′,4′,5′-tetraoxacyclononane] (XV). The procedure described for XIV was used to react 1.5 g (15.3 mmol) of cyclohexanone with 4.0 g (15.7 mmol) of 2,5-dihydroperoxy-2,5-dimethylhexane (70% by weight, remainder water). The reaction mixture was filtered and concentrated to yield 3.8 g of a light yellow oil. Flash column chromatography with 2% ethyl acetate/98% heptane (v/v) yielded 2.5 g (63%) of XV as a clear colorless oil (R_f = 0.33). ^{1}H NMR ($CDCl_3$): δ 2.22 (m, 2 H), 1.75 (m, 4 H), 1.55 (m, 4 H), 1.40 (m, 2 H), 1.32 (s, 6 H), 1.25 (m, 2 H), 1.03 (s, 6 H). ^{13}C NMR ($CDCl_3$): δ 107.75, 82.11, 31.21, 30.53, 27.67, 26.40, 23.93, 23.48. MS: *m/z* (relative intensity) 258 (M^+, 0.25%), 102 (9.4%), 87 (17.4%), 85 (27.6%), 72 (100%), 69 (55.6%), 59 (17.3%), 55 (34.0%), 43 (60.0%). The molecular weight was confirmed by positive ion ammonia chemical ionization: 276 $(M + NH_4)^+$, 259 $(M + H)^+$. $C_{14}H_{26}O_4$ = 258.34. One-hour half-life in ethylbenzene = 146 °C.

Spiro[2-methylcyclohexane-1,3′-6′,6′,9′,9′-tetramethyl-1′,2′,4′,5′-tetraoxacyclononane] (XVI). The procedure described for XIV was used to react 1.7 g (15.2 mmol) of 2-methylcyclohexanone with 4.0 g (15.7 mmol) of 2,5-dihydroperoxy-2,5-dimethylhexane (70% by weight, remainder water). The reaction mixture was filtered and concentrated to yield 4.3 g of a yellow oil. Flash column chromatography with 2% ethyl

acetate/98% heptane (v/v) yielded 3.24 g (79%) of XVI as a clear colorless oil which existed as a mixture of isomers (R_f = 0.33). ^{1}H NMR ($CDCl_3$): δ 2.20 (m, 2 H), 1.45–1.95 (m, 5 H), 1.28–1.45 (m, 10 H), 1.25 (m, 2 H), 1.05 (m, 9 H). ^{13}C NMR ($CDCl_3$): δ 109.80, 109.91, 82.17, 81.95, 81.63, 81.76, 34.56, 33.68, 31.62, 30.70, 30.62, 30.57, 30.32, 28.42, 27.73, 27.67, 27.53, 27.51, 26.09, 24.06, 23.99, 23.97, 23.57, 23.43, 21.84, 21.43, 16.09, 15.64. MS: *m/z* (relative intensity) 272 (M^+, 0.06%), 141 (9.5%), 113 (10.4%), 111 (13.5%), 85 (13.2%), 83 (15.0%), 72 (39.4%), 69 (50.8%), 59 (67.7%), 55 (53.0%), 43 (100%), 41 (40.8%). The molecular weight was confirmed by positive ion ammonia chemical ionization: 290 ($M + NH_4$)$^+$, 273 ($M + H$)$^+$. $C_{15}H_{28}O_4$ = 272.38. One-hour half-life in ethylbenzene = 132 °C.

Spiro[cycloheptane-1,3′-6′,6′,9′,9′-tetramethyl-1′,2′,4′,5′-tetraoxacyclononane] (XVII). The procedure described for XIV was used to react 1.7 g (15.2 mmol) of cycloheptanone with 4.0 g (15.7 mmol) of 2,5-dihydroperoxy-2,5-dimethylhexane (70% by weight, remainder water). The reaction mixture was filtered and concentrated to yield 4.5 g of a light yellow oil. Flash column chromatography with 2% ethyl acetate/98% heptane (v/v) yielded 3.26 g (79%) of XVII as a white solid (R_f = 0.36). ^{1}H NMR ($CDCl_3$): δ 2.20 (m, 2 H), 2.05 (m, 2 H), 1.75 (m, 2 H), 1.55 (m, 8 H), 1.32 (s, 6 H), 1.24 (m, 2 H), 1.02 (s, 6 H). ^{13}C NMR ($CDCl_3$): δ 112.88, 82.09, 33.90, 30.83, 30.62, 27.64, 23.97, 23.69. MS: *m/z* (relative intensity) 272 (M^+, 0.08%), 213 (0.26%), 199 (0.8%), 141 (3.2%), 113 (8.9%), 111 (13.5%), 87 (18.9%), 85 (31.0%), 72 (100%), 69 (72.3%), 59 (50.6%), 55 (53.6%), 43 (75.1%), 41 (45.8%). The molecular weight was confirmed by positive ion ammonia chemical ionization: 290 ($M + NH_4$)$^+$, 273 ($M + H$)$^+$. $C_{15}H_{28}O_4$ = 272.38. One-hour half-life in ethylbenzene = 151 °C.

Spiro[3,3,5-trimethylcyclohexane-1,3′-6′,6′,9′,9′-tetramethyl-1′,2′,4′,5′-tetraoxacyclononane] (XVIII). Akzo Chemicals graciously provided XVIII as an approximately 70% solution in 3,3,5-trimethylcyclohexanone. Flash column chromatography with 2% ethyl acetate/98% heptane (v/v) was used to yield pure XVIII as a clear colorless oil which existed as a mixture of isomers (R_f = 0.36). ^{1}H NMR ($CDCl_3$): δ 1.7–2.25 (m, 5 H), 1.2–1.4 (m, 10 H), 0.95–1.10 (m, 9 H), 0.70–0.95 (m, 8 H). ^{13}C NMR ($CDCl_3$): δ 109.26, 108.70, 82.31, 82.28, 81.82, 81.72, 49.28, 49.18, 44.87, 41.06, 39.25, 37.37, 34.64, 34.40, 32.67, 32.44, 31.89, 30.71, 30.66, 30.51, 27.71, 27.65, 27.58, 26.43, 26.31, 25.93, 23.98, 23.88, 23.48, 22.94, 14.91. MS: *m/z* (relative intensity) 300 (M^+, 0.07%), 256 (0.1%), 241 (0.04%), 141 (7.2%), 102 (20.5%), 87 (27.2%), 85 (41.6%), 83 (36.9%), 72 (100%), 69 (95.8%), 59 (19.1%), 55 (48.0%), 43 (94.5%), 41 (40.2%). The molecular weight was confirmed by positive ion ammonia chemical ionization: 318 ($M + NH_4$)$^+$, 301 ($M + H$)$^+$. $C_{17}H_{32}O_4$ = 300.42. One-hour half-life in ethylbenzene = 151 °C.

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

Results and Discussion

The spiroperketals (XIV–XVII) were prepared by acid-catalyzed condensation of 2,5-dihydroperoxy-2,5-dimethylhexane with the desired cyclic ketone (Figure 2). The half-life calculations were performed as previously described.[1]

Decomposition of Spiro[cycloalkane-1,3′-6′,6′,9′,9′-tetramethyl-1′,2′,4′,5′-tetraoxacyclononanes] (XIV–XVIII) in Ethylbenzene. Spiroperketals provide the possibility of generating only diradicals upon decomposition. Therefore, it was predicted that they would produce high molecular weight polymer at rapid rates. However, decomposition of XV in styrene gave no increased initiation over a styrene control without any added initiator. A detailed analysis of the decomposition of XV was undertaken to reconcile the disparity between the predictions and the observations.

The half-lives of the spiroperketals are about 30 °C higher than those of their di-*tert*-butyl perketal analogs.[17] This is likely due to in-cage recombination of oxy radicals formed by homolysis of the peroxide bonds.

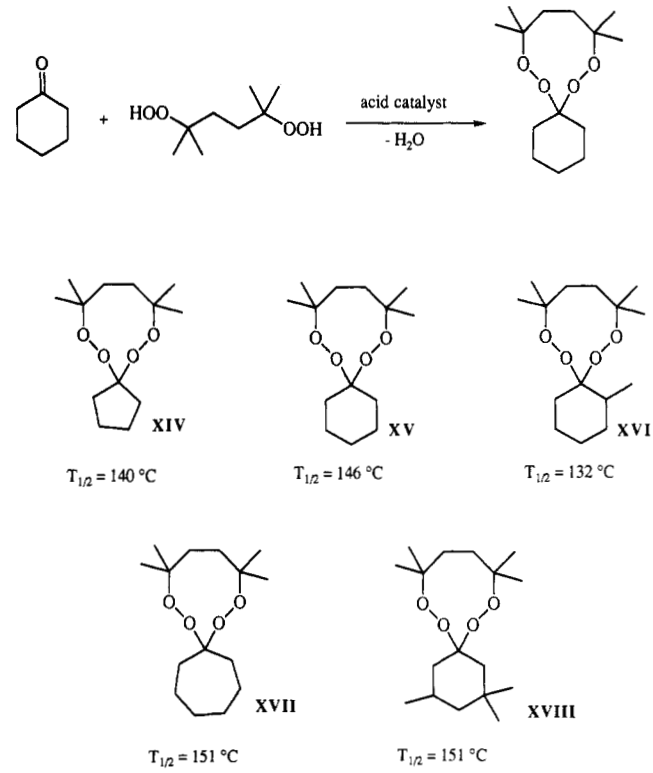


Figure 2. Spirocyclic perketals: synthesis and half-life in EB.

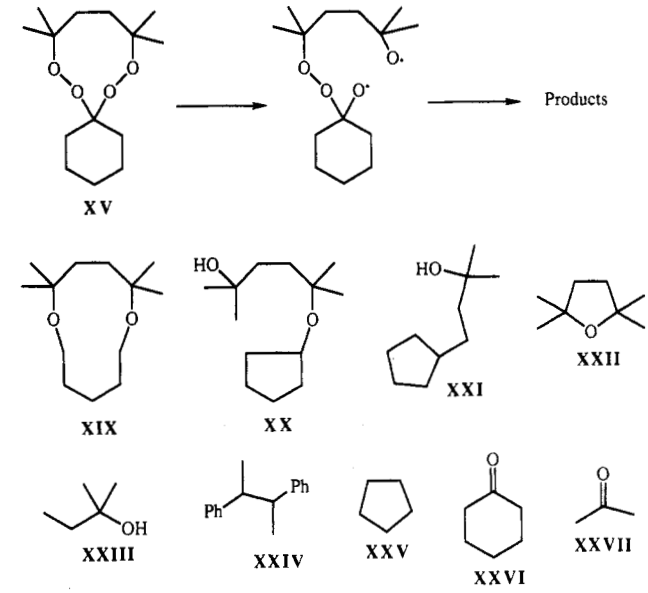


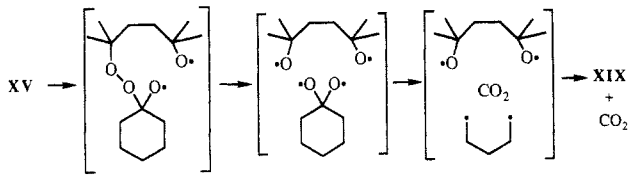
Figure 3. Decomposition products of sprio[cyclohexane-1,3′-6′,6′,9′,9′-tetramethyl-1′,2′,4′,5′-tetraoxacyclononane] (XV).

The products of the decomposition of XV in EB are shown in Figure 3. The products were identified by GC–MS. Product yields were measured relative to *o*-terphenyl. The amount of each product observed depended upon the decomposition temperature and the length of time that the sample was heated. The products in approximate order of abundance were XIX > XX > XXI, XXIV > XXII, XXIII, XXV, XXVI, XXVII.

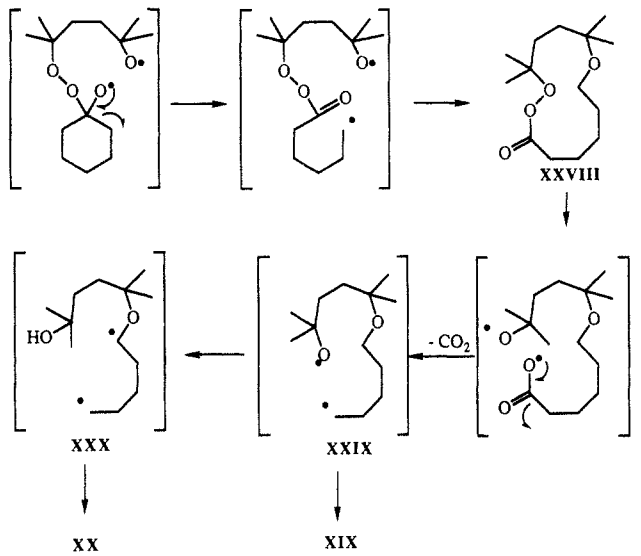
A mechanism rationalizing the formation of the main product, the macrocyclic diether XIX, is depicted in Scheme IV. This mechanism of decomposition is reminiscent of the proposed in-cage decomposition pathway for I (Scheme I). However, for XV, this is the major mode of decomposition versus a minor mode for I.

Another potential decomposition mechanism which could explain formation of XIX and also provides a potential route to XX is shown in Scheme V. The

Scheme IV
Proposed Mechanism of Decomposition of XV Resulting in Formation of the Macrocyclic Diether XIX



Scheme V
Proposed Decomposition Mechanism for XV Initiated by β-Scission of a Carbon–Carbon Bond and Followed by Subsequent Rearrangements



macrocyclic perester XXVIII is not observed in the reaction mixture; this is not surprising since it is likely to have a shorter half-life than the starting spirocyclic perketal XV. Subsequent in-cage rearrangements lead to the pivotal intermediate XXIX, which can collapse on itself to yield XIX or undergo an intramolecular hydrogen abstraction to yield XXX. The second most abundant product, XX, could then be formed by collapse of this caged intermediate.

Formation of the minor products can be explained by invoking similar mechanistic themes (Scheme VI). Leakage of any of the proposed intermediates from the cages in which they are formed can be used to explain other products.

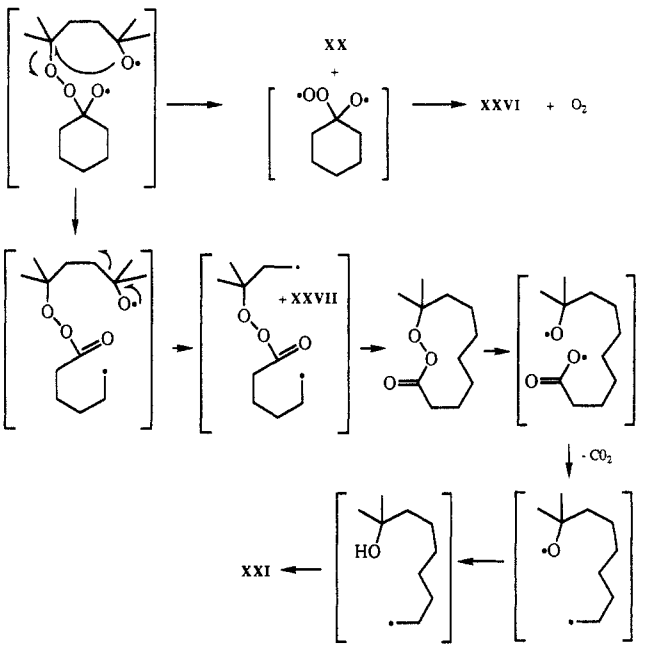
Comparative radical efficiency of the spiroperketals was measured by normalizing the amount of 2,3-diphenylbutane (XXIV) (EB dimer) formed (Scheme VII). The amount of XXIV formed provides an indirect measure of how many radicals escape the cage when the peroxide decomposes. Overall efficiency is defined as indicated in eq 1. It should be pointed out, however, that the phenethyl

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

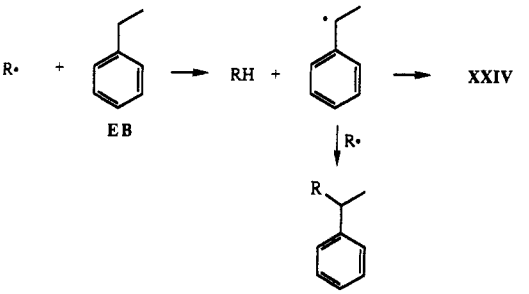
radical coupling reaction to form XXIV shown in Scheme VII does not proceed in 100% yield due to coupling of phenethyl radicals with R•. However, it does serve as a good comparative measurement of the efficiencies of similarly functionalized initiators.

It is important to note that all major products from the decomposition of XV result from rearrangements and in-cage recombinations; very little interaction (i.e., hydrogen abstraction) with EB is observed. Decomposition of other

Scheme VI
Potential Mechanistic Pathways Which Explain Formation of Some Minor Products of the Decomposition of XV



Scheme VII
Radical Dimerization of EB



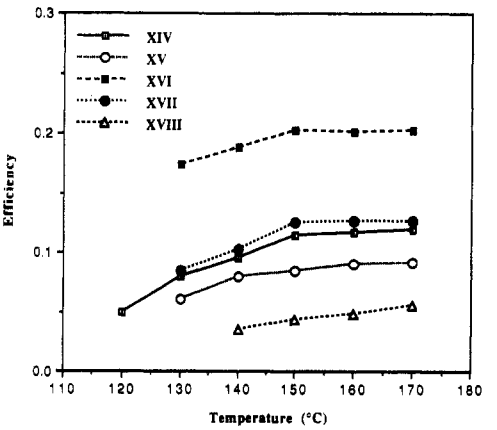


Figure 4. Radical production efficiency of spiroperketals in EB.

spirocyclic perketals (XIV, XVI, XVII, and XVIII) gave analogous products with similar distributions. The efficiencies of these species are shown in Figure 4. All were poor.

Comparison of Perketals in Styrene Polymerization. Clearly, from comparison of the performance (decomposition in EB) of the spiroperketals with bis(*tert*-butylperketals),[17] it is predicted that spiroperketals would be poor initiators for styrene polymerization. However, of the spiroperketals, XVI should be the most efficient and have the highest amount of difunctionality during styrene polymerization.

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

initiator (ppm)	temp (°C)	% conv	M_w/1000
none	130	27.4	444
none	150	70.8	355
none	170	91.1	318
XV	130	25.7	432
XV	150	71.7	349
XV	170	91.6	303
XIV	130	28.1	430
XIV	150	73.6	347
XIV	170	91.9	310
XVII	130	27.2	441
XVII	150	74.2	356
XVII	170	92.9	306
XVI	130	31.4	399
XVI	150	73.1	350
XVI	170	91.2	310
XVIII	130	26.6	434
XVIII	150	70.8	356
XVIII	170	92.1	310

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 ampules of styrene containing no initiator and each of the spiroperketals 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 26–31, 71–74, and 91–93%, respectively. The M_w of the polystyrene produced and percent styrene conversion are about the same using the spiroperketals or no initiator at all (Figures 5 and 6). Initiation of styrene polymerization using the common bis(*tert*-butylperketal) I is shown for comparison.

Conclusions

Spiroperketals appear to decompose mainly by in-cage processes. As a result, spiroperketals display low efficiency toward H abstraction when decomposed in EB. The low efficiency of spiroperketals in styrene polymerization is prediced based upon decomposition in EB. However, the efficiency is lower than expected. Although one of the spiroperketals (XVI) stands out as superior to the rest for dimerization of EB, it showed no advantage in styrene polymerization.

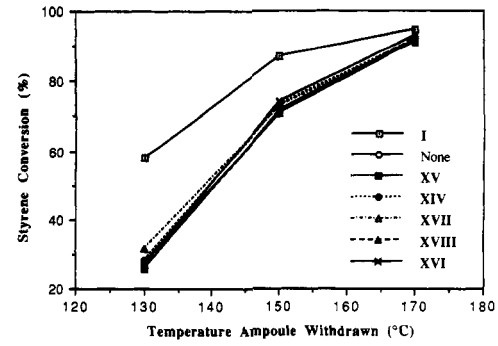


Figure 5. Comparison of styrene conversion without initiator in the presence of I and in the presence of spiroperketals.

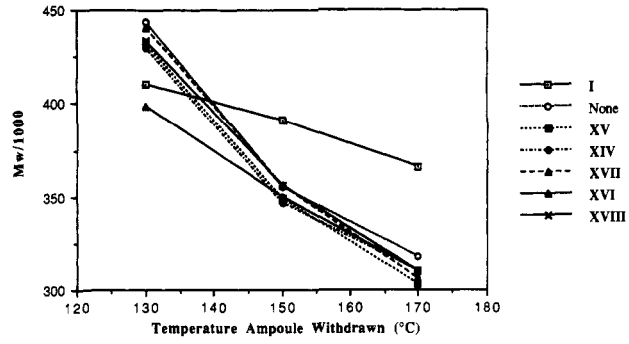


Figure 6. Comparison of polystyrene M_w without initiator in the presence of I and in the presence of spiroperketals.

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