

Bulk Polymerization of Styrene Catalyzed by Bi- and Trifunctional Cyclic Initiators

J. R. CERNA,¹ G. MORALES,¹ GLADYS N. EYLER,² ADRIANA I. CAÑIZO²

¹ Departamento de Química de Polímeros, Centro de Investigación en Química Aplicada, Boulevard Enrique Reyna #140, Apdo Postal 379, 25100 Saltillo, Coahuila, México

² Departamento de Ingeniería de la U.N.C.P.B.A., Avenue Del Valle 5737, 7400 Olavarría, Provincia de Buenos Aires, Argentina

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ABSTRACT: A study of the bulk free-radical polymerization of styrene in the presence of the cyclic bi- and trifunctional initiators cyclohexanone triperoxide, diethylketone triperoxide, acetone triperoxide, cyclohexanone diperoxide, and pinacolone diperoxide is reported. When these multifunctional initiators are used for styrene polymerization at high temperatures, it is possible to produce polymers with high molecular weights and narrow polydispersities at a high reaction rate. Additionally, the former initiators are used in a mixture that shows that the molecular parameters are influenced by the initiator concentration in the initiation system, in addition to the system employed. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1–11, 2002

Key words: styrene polymerization; cyclic peroxide initiators; bifunctional or trifunctional initiators

INTRODUCTION

Bulk or low solvent free-radical polymerization of styrene at high temperature with the aid of appropriate initiators is of significant industrial importance because they bring about increased polymerization rates and narrower polydispersities. It is known in a free-radical polymerization induced by common initiators that the molecular weight is inversely proportional to the polymerization rate. This is particularly true for monofunctional initiators. However, the introduction of diperoxides (DPs) as initiators is a new alterna-

tive to produce high polymerization rates without lowering the molecular weight of the final products.

The potential advantage of using those bifunctional initiators is that high polymer molecular weight and high polymerization rate can be obtained simultaneously by controlling the radical concentrations through sequential decomposition of the two labile groups of the initiator molecule through optimal reactor temperature programming. For example, Kuchanov et al.¹ studied different mono-, bi-, and trifunctional initiators of similar structures at a constant peroxide concentration and found similar polymerization rates that were independent of the initiator employed. Yoon and Choi² studied the use of 2,5-dimethyl-2,5-bis(2-ethyl hexanoyl peroxy) hexane (Lupersol 256) in styrene polymerization. They found that at high monomer conversion the weight-average molecular weight (M_w) rapidly increased; as a result, a broad molecular weight

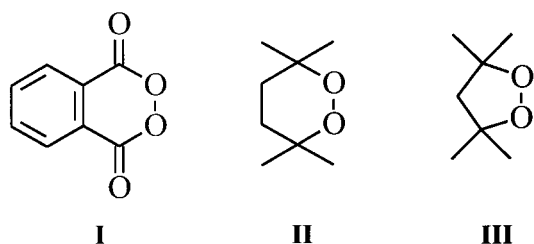
Correspondence to: G. Morales (gmorales@polimex.ciqa.mx).
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distribution was obtained.² Villalobos et al.³ reported the bulk polymerization of styrene using various commercial initiators. For polystyrene (PS) synthesis initiated with benzoyl peroxide (BPO) at a concentration of 0.01 mol/L and 90°C, Villalobos et al.³ concluded that the polymerization cycle time can be reduced by 20–75% by using bifunctional initiators at the same or lower concentrations and at adequate polymerization temperatures. In the same way, González et al.⁴ examined bulk styrene polymerization using different mixtures of mono- and bifunctional initiators in a batch reactor.

Cyclic peroxides are a class of peroxides that should theoretically form diradicals. However, anomalous results were reported for peroxides with formulas I–III, which decomposed without initiating the polymerization of styrene.⁵



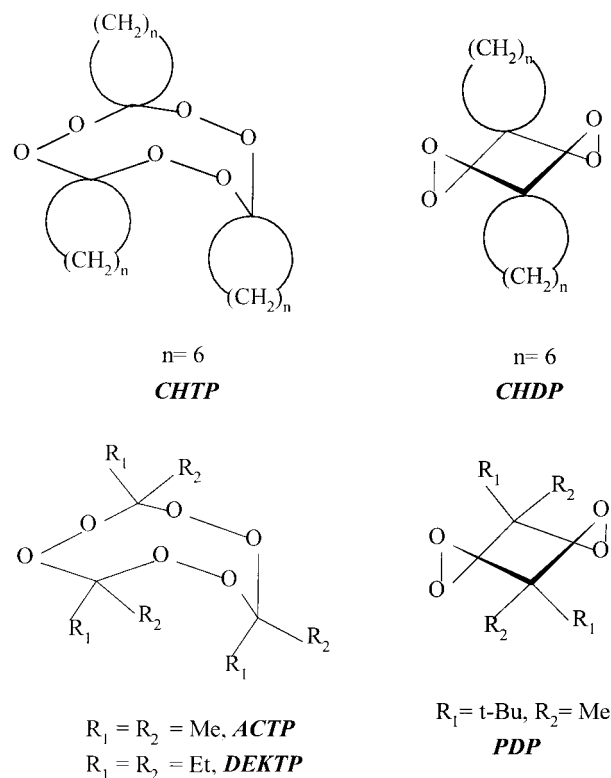
This study shows the results for bifunctionally and trifunctionally initiated systems for styrene free-radical bulk polymerization. The effects of the reaction temperature and initiator concentration on the polymerization rate and molecular weight are investigated in addition to different initiator mixtures in order to increase monomer conversion and to optimize new routes of polymer synthesis with a new class of cyclic peroxide initiators.

EXPERIMENTAL

Polymerization experiments were carried out in mass using Pyrex tubes. Styrene (Aldrich) was purified by the standard method. The bifunctional and trifunctional cyclic peroxides were synthesized at our laboratories as described in the corresponding methods: diethylketone triperoxide (DEKTP; 3,3,6,6,9,9-hexaethyl-1,2,4,5,7,8-hexaoxacyclononane),⁶ cyclohexanone TP (CHTP; tricyclohexylidene TP or 3,3,6,6,9,9-tripentamethylene-1,2,4,5,7,8-hexaoxacyclononane),⁷ acetone TP (ACTP; 3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexaoxacyclononane),⁸ cyclohexanone DP (CHDP; 7,8,15,16-dispiro [5.2.5.2]hexadecane),⁷ and pinacolone

DP (PDP; 3,6-di-*t*-butyl-1,2,4,5-tetroxacyclohexane).⁹ Trigonox 21S (T21S, *ter*-butylperoxy-2-ethylhexanoate) and Trigonox 22E-50 (T22E-50; 1,1-bis[*ter*butylperoxy]cyclohexane) were supplied by Akzo Nobel, the BPO (Aldrich) was used as received, and benzopinacolate (BPC) or 1,2-bis(trialkyl(silyloxy)tetraphenylethane) was synthesized as reported in the literature.¹⁰

The syntheses of different PSs were carried out by dissolving the appropriate amount of initiator in styrene, and equal amounts of the resulting solution were placed into glass tubes. The cooled tubes were evacuated, sealed, and kept at 130–150°C, depending on the initiator used, for 60, 120, 180, 240, and 360 min. The conversion of pure thermal polymerization of styrene was measured under the same conditions. The polymer samples were dissolved in THF and precipitated by adding excess methanol. This procedure was repeated several times to ensure that unreacted monomer was completely eliminated. The samples were dried *in vacuo*, and the monomer conversion was measured gravimetrically. The molecular weight and molecular weight distribution of PS were determined by GPC using THF as a solvent. The residual monomer was analyzed by



Scheme 1 The bi- and trifunctional initiators employed in the bulk radical polymerization of styrene.

the GC injected head space technique. The NMR spectra were recorded using a Jeol Eclipse 300-MHz spectrometer with CDCl_3 as a solvent at 20°C .

When mixtures of initiators were used, the reaction temperatures depended on the decomposition characteristics of the initiator mixture (e.g., 90°C for 3 h and 130°C for 3 h in a BPC/DEKTP mixture), but all polymerizations involved a 6-h cycle in a two-step polymerization. The cyclic initiator concentration was varied from 0.005 to 0.01M. After the predetermined period of time, the samples were treated as described above. (Note: Cyclic peroxides must be handled with care because they can be detonated by shock.)

RESULTS AND DISCUSSION

Synthesis and Thermal Decomposition of Cyclic DPs and TPs

The cyclic DPs CHDP⁷ and PDP⁹ and the cyclic TPs CHTP,⁷ DEKTP,⁶ and ACTP⁸ (Scheme 1) were synthesized in a simple and efficient one-step procedure by reacting the respective ketones with hy-

drogen peroxide. The peroxides were purified by recrystallization from a selective solvent and characterized by FTIR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, and thin layer chromatography. Figures 1 and 2 show the $^1\text{H-NMR}$ spectra of PDP and DEKTP, respectively.

The kinetic data of the thermal decomposition reaction of the synthesized and purified peroxides were measured in different solvents at different temperatures with an initial peroxide concentration of 0.020M.^{8,11-15} It was observed in all cases that they behaved in accordance with a first-order kinetic law until 50% peroxide conversion. The effect of temperature on the rate constant values was also studied, and the linearity of each equation proposed in a range of temperatures ($35-45^\circ\text{C}$) suggested that the activation parameters (ΔH and ΔS) calculated at a specific temperature for each peroxide corresponded to a simple process.^{8,11-15} It also represented the unimolecular thermal cleavage of the O—O bond of the peroxide molecule as the initial bond breaking step, which was demonstrated for other cyclic peroxides.¹⁶ The decomposition rate (k_d) and half-life duration time ($t_{1/2}$) for each cyclic peroxide were

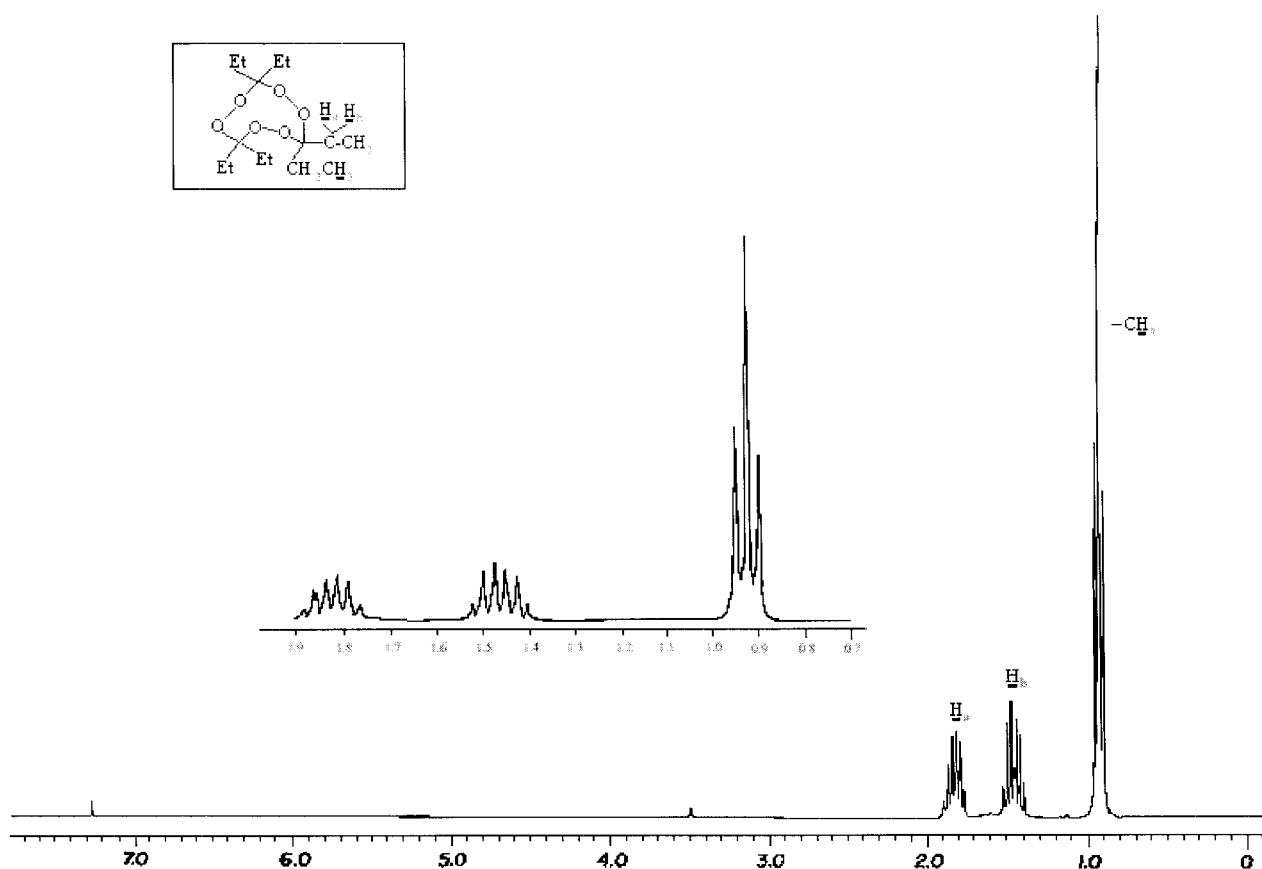


Figure 1 $^1\text{H-NMR}$ spectra (CDCl_3) for DEKTP.

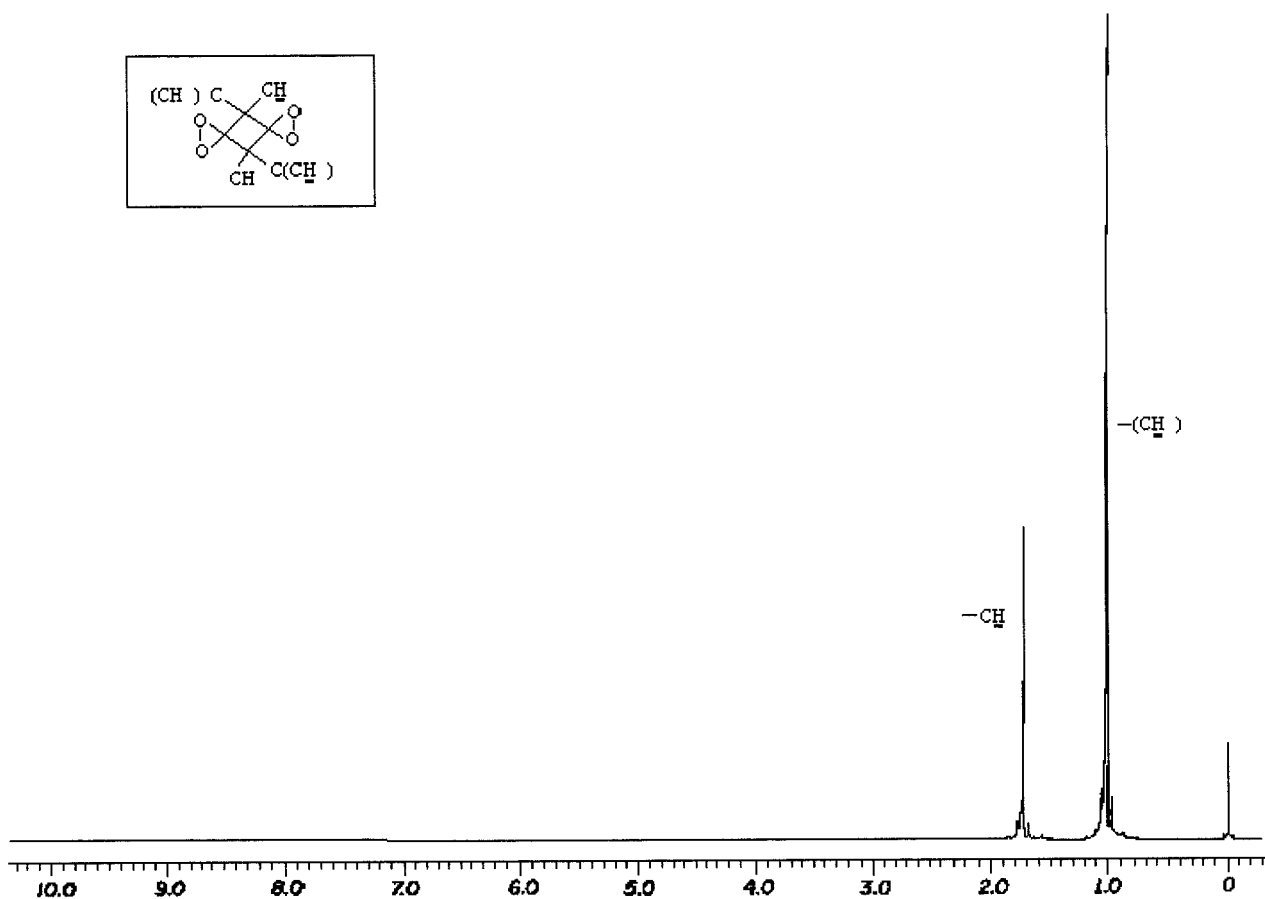


Figure 2 $^1\text{H-NMR}$ spectra (CDCl_3) for PDP.

determined using the Arrhenius equation, and the values are summarized in Table I.

Polymerization of Styrene in Presence of Cyclic DPs and TPs

The effect of temperature on the monomer conversion and polymer molecular weight were stud-

ied for each peroxide to evaluate the behavior of the cyclic peroxides as initiators of styrene mass polymerization. The temperatures at which the best results were obtained are indicated in Table II. No initiation was observed at temperatures lower than those indicated in Table II because the cyclic peroxides had high stability at the given temperatures. At higher temperatures the results

Table I Decomposition Rate (k_d) and Half-Life Time ($t_{1/2}$) of Cyclic Peroxides at Different Temperatures

| Cyclic Initiator | CHDP ^a | PDP ^b | ACTP ^a | CHTP ^a | DEKTP ^a |
|---------------------------|--|------------------------|--|------------------------|--|
| $t_{1/2}$ (h) | 1.43 ^c 3.98 ^f | 1.81 ^d | 1.0 ^e 20.9 ^c 70.16 ^f | 0.54 ^c | 14.8 ^d 108 ^g |
| k_d (s^{-1}) | 1.34×10^{-4c} 4.82×10^{-5f} | 1.06×10^{-4d} | 1.93×10^{-4e} 9.21×10^{-6c} 2.74×10^{-6f} | 3.54×10^{-4c} | 13.0×10^{-6d} 1.50×10^{-6g} |

^a In toluene.
^b In benzene.
^c At 150°C.
^d At 130°C.

^e At 178°C.
^f At 140°C.
^g At 120°C.

Table II Temperatures for Cyclic Peroxides to Present Their Best Performance and Characteristics of Polymers Obtained after 3-h Polymerization ([Cyclic Initiator] = 0.01M)

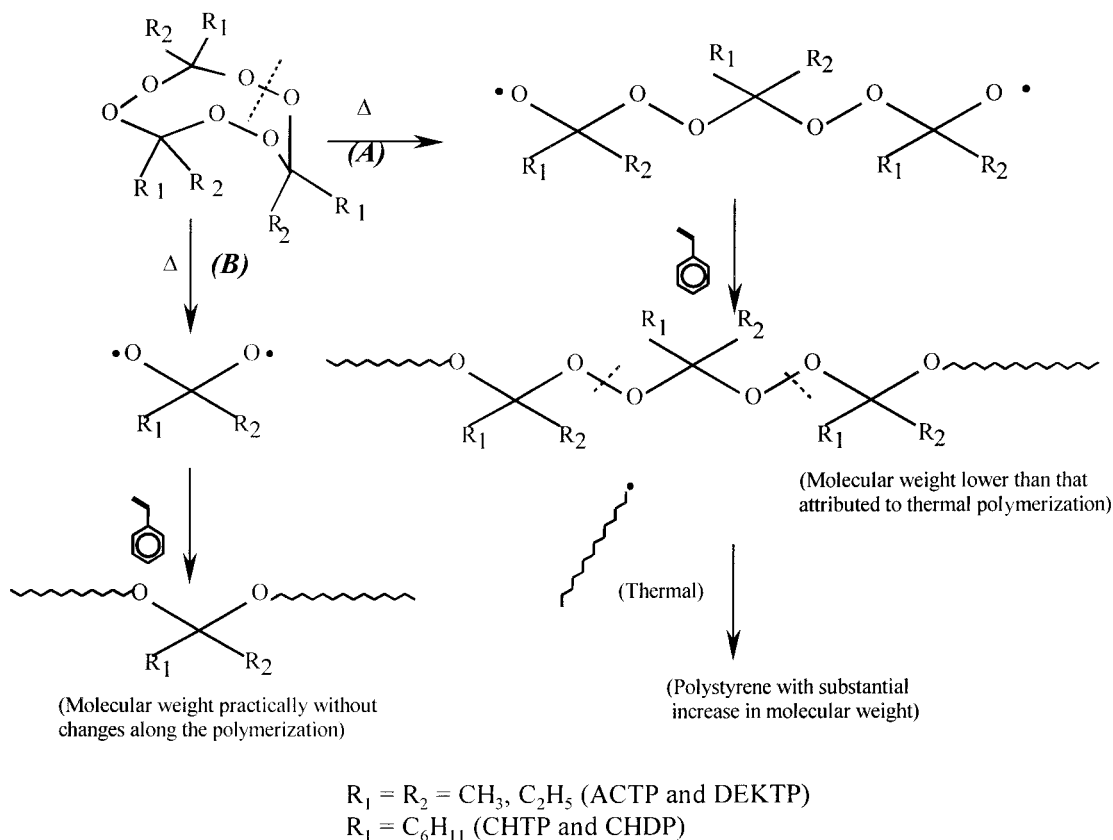
| Initiator | Temp. (°C) | Conversion (%) | M_w ($\times 10^{-5}$ g/mol) | $I = M_w/M_n$ |
|-----------|------------|----------------|---------------------------------|---------------|
| CHDP | 150 | 84.83 | 2.14 | 1.8 |
| PDP | 130 | 95.70 | 1.85 | 1.8 |
| ACTP | 150 | 95.00 | 1.00 | 2.4 |
| CHTP | 150 | 93.65 | 1.92 | 1.9 |
| DEKTP | 130 | 86.51 | 2.77 | 1.8 |

revealed a substantial increase in the conversion; however, there was a drastic decrease in the molecular weight. This last situation can be attributed to a total and no gradual decomposition of the peroxide sites in the initiators as shown in Scheme 2 (route B).

When the evolution of the conversion with time was evaluated at the temperatures indicated in Table II, the monomer conversion due to peroxide initiation was negligible for ACTP, CHTP, and CHDP if compared with pure thermal polymerization at the same temperature. On the other hand, the molecular weights of the final products

were on the order of $(1.96\text{--}2.5) \times 10^5$ g/mol, similar to those of the autoinitiated products (1.9×10^5 g/mol). These results are not clearly understood and work is in progress to elucidate them.

On the contrary, when DEKTP and PDP were used as initiators of styrene polymerization, Figure 3 shows that the rate of polymerization attributable to the cyclic initiators was substantially increased with respect to pure thermal polymerization. In both cases the conversion was on the order of 98–99%. A deflection in the conversion curve for PDP was observed that was due to a premature peroxide decomposition ($t_{1/2} = 1.81$

**Scheme 2** The possible routes of decomposition and initiation of the cyclic peroxides.

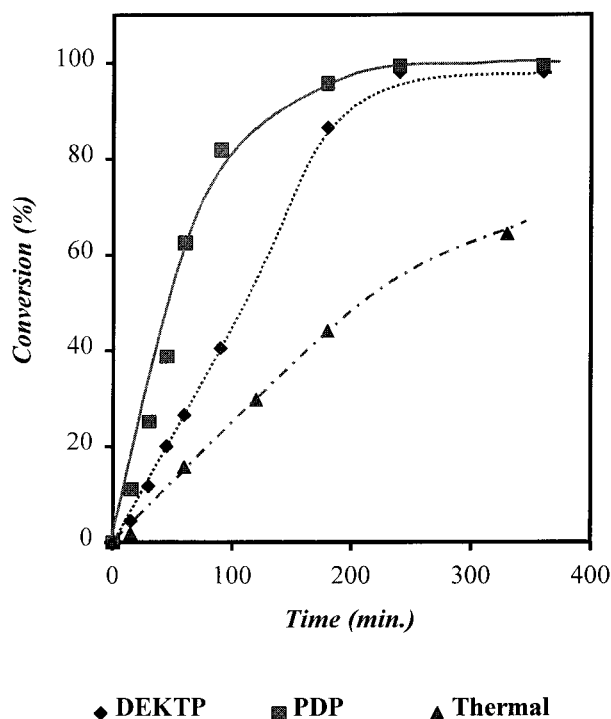


Figure 3 The effect of the polymerization temperature on the monomer conversion ([cyclic initiator] = 0.01M) at 130°C.

h in comparison to DEKTP $t_{1/2} = 14.8$ h) resulting in much less than 100% monomer conversion. A slight increase in the monomer conversion after the depletion of the peroxide was attributed to thermal polymerization.

On the other hand, for DEKTP the deflection in the curve could not be attributed to a rapid decomposition of the initiator; it occurred only as a consequence of species with peroxide groups that had not yet been decomposed. The evolution of the molecular weight with the polymerization time for PDP and DEKTP initiators is shown in Figure 4.

Once again, the evolution of the M_w in DEKTP strengthened the situation described above, and no bimodality in the molecular weight distribution curves was observed. Our experimental data showed that the polydispersity values (M_w/M_n) were in the 1.8–2.2 range and they increased as the monomer conversion increased. This last situation can be explained by considering the three factors of the gel effect, primary radical termination, and the multiple reactions (e.g., initiation, propagation, and combination termination) that some polymers with undecomposed peroxides may undergo (Scheme 2, route A).

The differences between PDP and DEKTP arose from the fact that the radical generated

from PDP was more unstable and indeed more reactive than that generated from DEKTP, which was demonstrated by the kinetic data cited before previously.^{8,11–15} For this reason the conversion reached in polymerizations initiated with PDP were higher; consequently, the rate of polymerization was also larger (by a factor of 2) when compared with DEKTP and the lower molecular weight of the polymers obtained.

Several studies were carried out on DEKTP to demonstrate that the initiator gradually decomposed and that the polymers with undecomposed peroxides in their chain were responsible for the increase in the M_w .

In this context the sequential decomposition of DEKTP was studied by DSC using a 0.01M solution of the initiator in chlorobenzene at a heating rate of 2°/min; three peaks were observed at 143, 164, and 172°C, corresponding to the three peroxide units. In addition, styrene polymerization was carried out using the DSC technique with 0.2M initiator at the same heating rate and three distinct peaks at 121, 134, and 172°C were shown.

On the other hand, a PS obtained using 0.01M DEKTP at 130°C ($M_w = 303,000$ g/mol) was

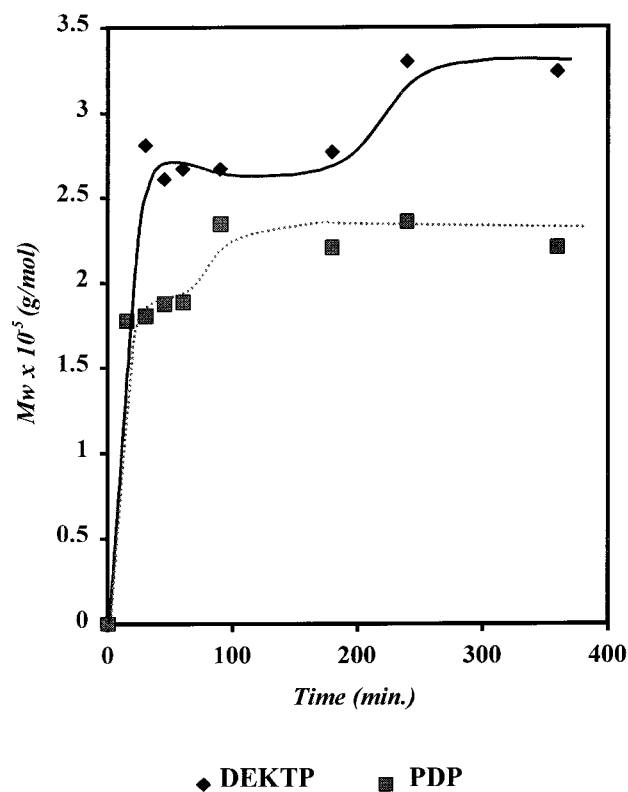


Figure 4 The effect of the polymerization time on the weight-average molecular weight (M_w), [cyclic initiator] = 0.01M) at 130°C.

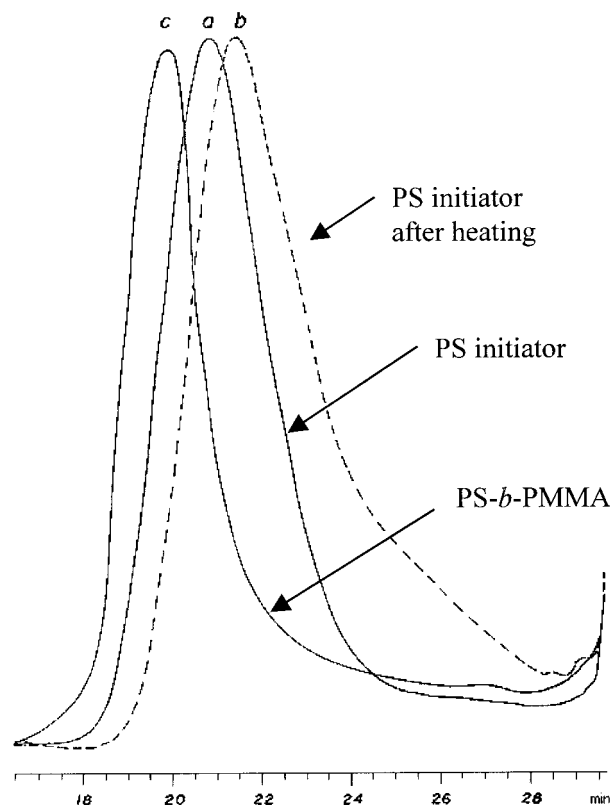


Figure 5 A chromatogram corresponding to a DEKTP initiated polystyrene before (curve a) and after (curve b) heating in chlorobenzene at 130°C for 3 h and (c) the corresponding PS-*g*-PMMA block copolymer obtained from before heating.

heated in chlorobenzene for 3 h and the analyzed product presented a M_w of 293,000 g/mol. This can be explained by the decomposition of peroxide groups still present in the former polymer. The corresponding chromatogram is presented in Figure 5. Moreover, when the same PS was heated in the presence of methylmethacrylate (MMA), it acted as a macroinitiator, conducting the formation of a block copolymer [PS-*b*-poly(MMA) (PMMA), $M_w = 365,000$ g/mol, PS : PMMA = 60 : 40; Fig. 5]. All of these results corroborated the fact that DEKTP decomposed and polymerized through route A presented in Scheme 2. It must be supposed that the same behavior was presented by PDP according to the results obtained.

In the unsymmetrical bifunctional initiators there were two different slopes that were observed at low and intermediate conversion, which were due to the different thermal stabilities of the two peroxide groups.^{17–19} However, this behavior was not observed for the bi- and trifunctional cyclic initiators used in this study, which indicated that there was no substantial difference in

the reactivities of the two or three peroxide groups contained by initiator molecules under isothermal conditions. Another important feature was that there was no physical evidence of the gel effect in the temperature range of 90–200°C and conversion range of 95–99%, in spite of it being demonstrated that termination reactions involving polymeric radicals became diffusion controlled and the termination rate constant decreased considerably with an increase in the monomer conversion.^{2,20,21}

Because of the complexity of the polymerization kinetics and the large number of species involved during polymerization, it was not quite feasible to determine the exact value of the initiator efficiency. Theoretically, the two or three peroxide groups in the initiators may have different initiating efficiencies; however, to determine an apparent (or overall) initiator efficiency, we assumed that the efficiencies of the peroxide groups were identical. Using the experimental conversion data obtained at 120–130°C with an initiator concentration of 0.01M, we obtained an efficiency factor of 0.18 for DEKTP and 0.27 for PDP. Moreover, the initiator efficiency decreased with an

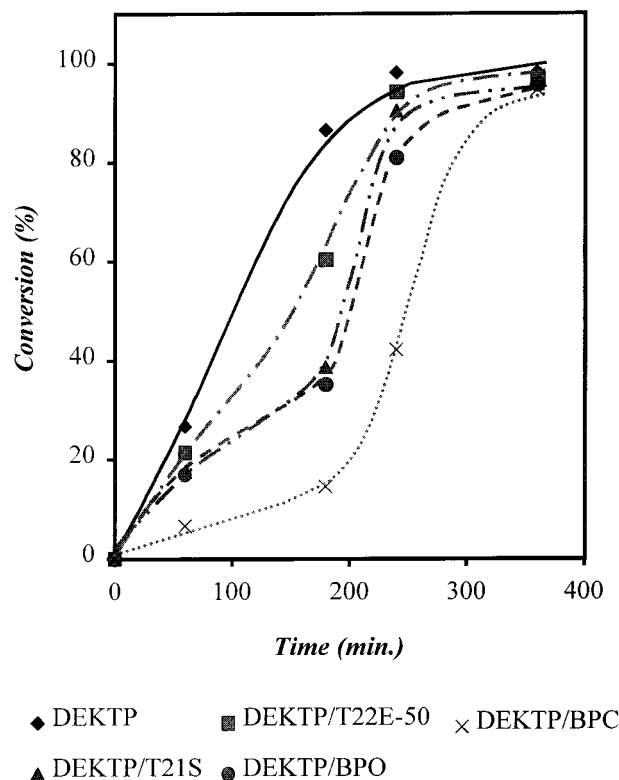


Figure 6 The evolution of conversion for different mixtures of DEKTP initiator with low temperature initiators ($[DEKTP] = 0.01M$).

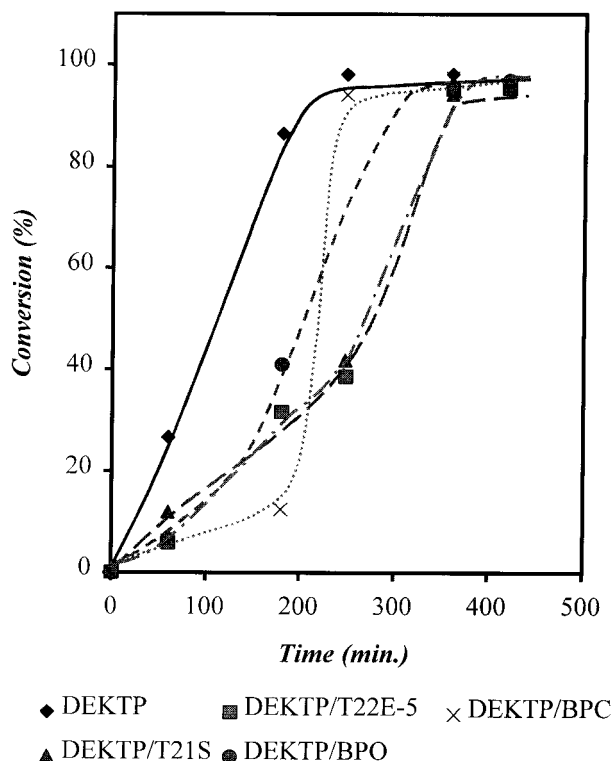


Figure 7 The evolution of conversion for different mixtures of DEKTP initiator with low temperature initiators ($[\text{DEKTP}] = 0.005M$).

increase in the number of labile functional groups in the initiator molecule and with the initiator concentration. This last behavior suggested that the initiating efficiencies of the two or three peroxide groups may not have been identical, probably because of primary radical termination and induced decomposition.

Polymerization of Styrene in Presence of Mixtures of Mono- and Bifunctional Initiators and DEKTP

The DEKTP was used in a mixture with other commercial initiators such as T21S and BPO (both monofunctional initiators) or T22E-50 (bifunctional initiator) and the noncommercial initiator BPC (monofunctional, carbon centered initiator). The plots of conversion versus time for a global initiator concentration of 0.01 or 0.015M and a cyclic peroxide concentration of 0.005 or 0.01M are presented in Figures 6 and 7, respectively, where the concentration of the low temperature initiator was maintained constant 0.005M. In these figures the initial temperature (T_1) was 90°C for T21S, BPO, and BPC and 110°C for T22E-50. At these initial temperatures the initiators had a half-life of 1 h. The T_1 was applied for

3 h in all cases to ensure the total consumption of the low temperature initiator. The second temperature (T_2) was 130°C for all systems for 3 h. In DEKTP alone the temperature was 130°C during the course of polymerization.

A comparison of Figures 6 and 7 shows that in all cases the values of conversion in the interval of time studied were larger (95–97%) regardless of the mixture used when DEKTP was used in high proportion (0.01M). If compared with the polymerization initiated with DEKTP alone at 130°C, no mixture overtook the final conversion value of 98.2% that was reached in this last case.

In the case of the different mixtures it must be pointed out that before 3 h of polymerization the slope of the conversion curve was fewer for BPC than in the other cases for both DEKTP concentrations used. It must be taken into account that it was demonstrated for BPC²² that the polymerization initiated with these kinds of initiators presents a certain control over the polymerization mechanism that is due to the formation of a reversible bond between the last polymerizable monomer unit and the hemi-BPC (HBPC) radical generated upon the decomposition of BPC. That

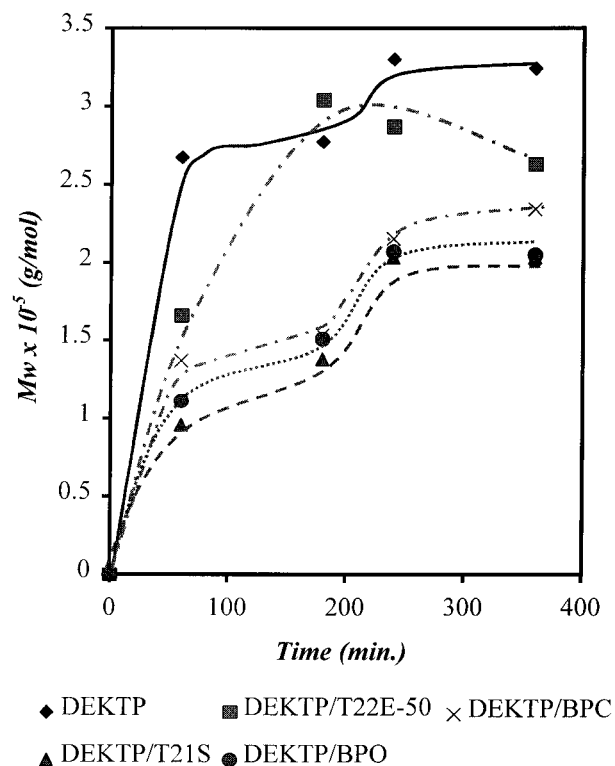


Figure 8 The evolution of the weight-average molecular weight (M_w) for different mixtures of DEKTP initiator with low temperature initiators ($[\text{global initiator concentration}] = 0.015M$, $[\text{DEKTP}] = 0.01M$).

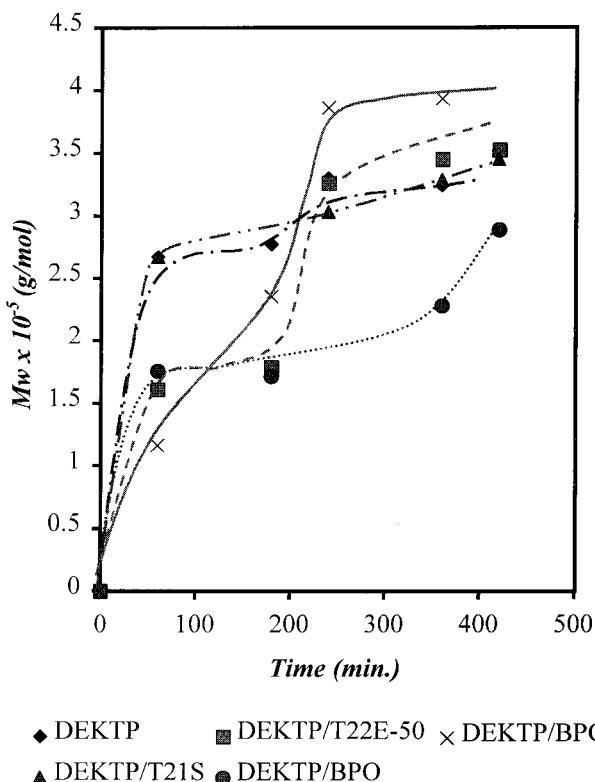


Figure 9 The evolution of the weight-average molecular weight (M_w) for different mixtures of DEKTP initiator with low temperature initiators ([global initiator concentration] = 0.01M, [DEKTP] = 0.005M).

explains the linear increase of conversion with time, as well as the low values of conversion, reached at 90°C. After 3 h of reaction and with 0.01M DEKTP, there was a higher reaction rate in the DEKTP/T22E-50 mixture (1 order of magnitude greater than DEKTP alone) and there was only a difference of 3% in the final value of conversion. In this particular mixture the behavior could be attributed to the combined effects of reinitiation and autoacceleration due to the presence of the peroxide groups contained in the cyclic initiator and to the biradical formed as a consequence of the decomposition of T22E-50.

By contrast, the molecular weights decreased as the global initiator concentration changed from 0.01 to 0.015M as expected, which was a consequence of the increased rate of termination at a higher free-radical concentration. Comparisons of the molecular weights at 0.01 and 0.005M DEKTP are presented in Figures 8 and 9, respectively.

If DEKTP/T22E-50 is compared to DEKTP/T21S, the M_w values produced with T22E-50 were slightly higher than those produced with the sec-

ond initiator as a consequence of the multifunctionalities of the initiators involved. Moreover, the higher polydispersity achieved with the first mixture DEKTP/T22E-50 (tri- and bifunctional initiators) was in accord with the results presented by Villalobos et al.³ and corroborated the fact that the reinitiation reaction occurred to a more significant extent when compared with the DEKTP/T21S (tri- and monofunctional initiators).

If DEKTP/T21S is compared to DEKTP/BPC (the former a monofunctional oxygen centered radical, and the latter a monofunctional carbon centered radical), it can be observed that with BPC and a DEKTP concentration of 0.005M the values of conversion were higher during the course of polymerization, the molecular weights were higher, and the polydispersity increased with time. This increase in the polydispersity was evidence that with carbon centered radicals there were less in-cage reactions of DEKTP radicals. This meant that, in this case, the effective concentration of DEKTP was greater conducting to a greater extent in the multiple reactions (reinitiation, propagation, and termination), which con-

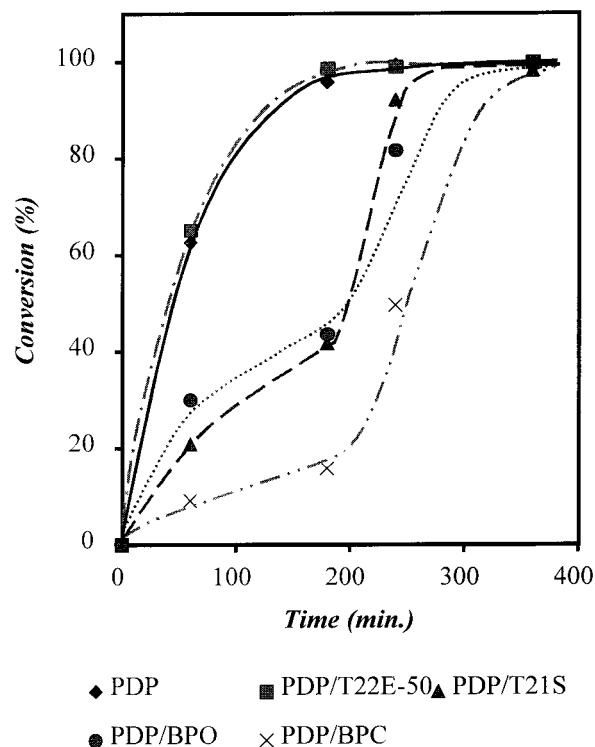


Figure 10 The evolution of conversion for different mixtures of PDP initiator with low temperature initiators ([global initiator concentration] = 0.015M, [PDP] = 0.01M).

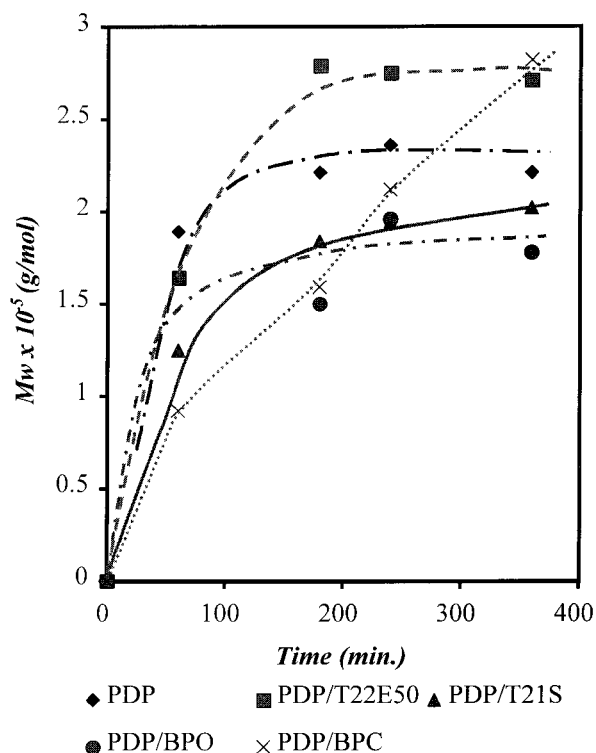


Figure 11 The evolution of the weight-average molecular weight (M_w) for different mixtures of PDP initiator with low temperature initiators ([global initiator concentration] = 0.015M, [PDP] = 0.01M).

firmed the theory stated previously about the polymerization mechanism.

Polymerization of Styrene in Presence of Mixtures of Mono- and Bifunctional Initiators and PDP

The PDP was used under the same experimental conditions as those described for DEKTP: in binary systems with commercial mono- and bifunctional initiators (BPO, T21S, and T22E-50) and a carbon centered initiator (BPC). The evolution of the conversion and molecular weight with time are reported in Figures 10 and 11, respectively.

From Figure 10 it can be observed that, independent of the nature of the initiating system employed, the values of conversion were greater than for DEKTP, reaching 99–99.8% of conversion when PDP was used in a concentration of 0.01M. This can be explained by taking into account that the half-life of PDP at 130°C was much lower than that for DEKTP under similar conditions and the radicals formed were more reactive than the DEKTP ones. Once again, if the PDP concentration was lowered to 0.005M, the values

of conversion decreased and the M_w increased as in the case of DEKTP.

Nevertheless, for the PDP/T22E-50 system the best results were obtained not only when the conversion values were analyzed but also when the molecular weights were higher than the ones obtained with pure PDP. The content of residual styrene in this particular mixture was 450 ppm. The synergistic effect of the two initiators was evident in this case. The behaviors of the other mixtures were similar to those observed with DEKTP. When BPC was used a yellowish product was obtained when the polymer was exposed to sunlight for 1 month. This can be explained as being a consequence of degradation of some residual HBPC radicals to benzophenone, which in turn can cause the degradation of the polymeric chain. This fact must be considered in great detail and needs more investigation.

CONCLUSION

Herein is reported the styrene bulk polymerization through cyclic bi- and trifunctional peroxide initiators. The experimental data reveals that DEKTP and PDP, tri- and bifunctional initiators, respectively, present typical multifunctional initiator behavior, simultaneously yielding PS at a high reaction rate with high molecular weights. The use of these initiator mixtures that include mono- and bifunctional commercial initiators, as well as carbon centered initiators, seems to be of no benefit to increase the rate of polymerization and molecular weights with respect to the multifunctional initiators alone. Only one of them, mixture PDP/T22E-50, as an initiating system presents the highest value of conversion and molecular weight with respect to PDP alone. Although this result seems to be promising, better general results are obtained in the presence of DEKTP as an initiator.

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