

Thermal decomposition of diethyl ketone triperoxide in methyl methacrylate: Theoretical and experimental study of the initial solvation state and its influence on the polymerization process

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ABSTRACT: The decomposition rate constant (k_d) of diethyl ketone triperoxide (DEKTP, 3,3,6,6,9,9-hexaethyl-1,2,4,5,7,8-hexaoxacyclononane) in methyl methacrylate (MMA) was determined by the kinetic study of its thermal decomposition at temperatures from 110 to 140°C. The calculated k_d for DEKTP in MMA was 2.4 times lower (at 130°C) compared with that previously determined and reported in styrene (St). Density functional theory (DFT) calculations demonstrated that the decomposition of DEKTP molecule in MMA required higher interaction energy than in St, thus explaining its lower k_d value. Bulk polymerization kinetics of MMA using DEKTP as the initiator revealed the presence of an induction period, in contrast with St polymerization, providing clear evidence of the solvation state influence at early polymerization stages. This work provides mechanistic insights into the interactions among the multi-functional cyclic peroxide DEKTP and vinyl monomers; St and MMA, and their influence on the polymerization kinetics.

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INTRODUCTION

Organic peroxides are extensively used as initiators in industrial polymerization processes. However, in recent years, multi-functional cyclic peroxides have gained interest to be used in such applications, as they offer the possibility to obtain both; higher polymerization rates and polymeric chains with higher molecular weights in comparison with those obtained using typical noncyclic mono-functional peroxides.^{1–5} The multi-functional cyclic peroxides can be obtained through the reaction of hydrogen peroxide with ketone compounds at low temperatures (–10, –15°C), using an inorganic acid, such as sulfuric acid, as a catalyst. Regarding the thermal decomposition kinetics of some cyclic organic peroxides, it has been extensively

reported.^{6–13} For instance, the thermolysis of pinacolone diperoxide [PDP, 3,6-ditertbutyl-3,6-dimethyl-1,2,4,5-tetraoxacyclohexane, [Figure 1(a)], acetone cyclic triperoxide [ACTP, 3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexaoxacyclononane, [Figure 1(b); R = –CH₃]] and diethyl ketone triperoxide [DEKTP, 3,3,6,6,9,9-hexaethyl-1,2,4,5,7,8-hexaoxacyclononane [Figure 1(b); R = –CH₂–CH₃]] has been reported in different organic solvents (or mixtures of them), including acetone, toluene, ethylbenzene, chlorobenzene, acetonitrile, ethanol, among others. Regarding the cyclic triperoxides previously mentioned, the DEKTP has been the most studied as a consequence of its higher stability in the solid state in comparison with ACTP, which is considered as a highly explosive compound that can easily detonate by friction, heat or shock.^{14,15}

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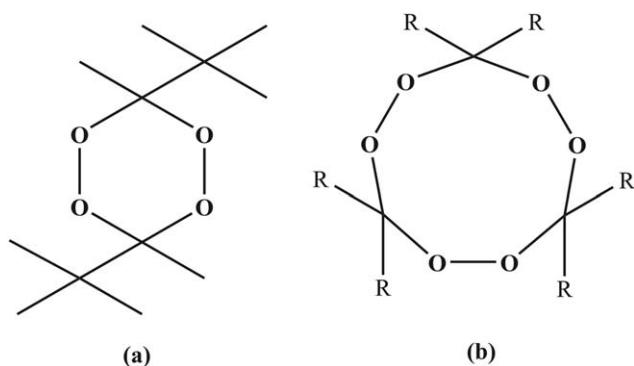


Figure 1. Multi-functional cyclic peroxides; (a) PDP, (b) ACTP when $R = -CH_3$ and DEKTP when $R = -CH_2-CH_3$.

All the early works have mainly focused on the decomposition behavior of these initiators in organic solvents with different physico-chemical characteristics (protic or aprotic; polar or non-polar), and it has been demonstrated that the decomposition reaction is strongly solvent-dependent, due to variations in the molecular interactions that modify their solvation capabilities.^{6–13} Therefore, the decomposition rate constant (k_d) of DEKTP at 150°C in toluene ($1.6 \times 10^{-4} \text{ s}^{-1}$) is approximately three times lower than that in acetonitrile ($4.79 \times 10^{-4} \text{ s}^{-1}$) at the same temperature.¹⁶ On the other hand, for this type of cyclic peroxides, there is a limited number of reports in the scientific literature, related to their thermal decompositions entirely carried out in vinyl monomers, such as styrenic, methacrylic or acrylic monomers. In this regard, Cañizo *et al.* reported the thermal decomposition of DEKTP at 130°C in styrene (St), toluene-St and chlorobenzene-St (both mixtures at a volume ratio of 50:50), and the k_d values reported were 1.53×10^{-3} , 5.65×10^{-4} and $4.68 \times 10^{-4} \text{ s}^{-1}$, respectively.¹⁰ Meanwhile, Barreto *et al.* reported the thermal decomposition of DEKTP at 130°C in 0.1 mol L⁻¹ and 1 mol L⁻¹ solutions of methyl methacrylate (MMA) in ethylbenzene.¹³

Further polymerization studies concluded that DEKTP could be also used to initiate St polymerization and act as a multi-functional initiator yielding polymers with large molecular weights at higher polymerization rates than those obtained when a typical mono-functional initiator is employed.^{5,17}

Given the significant dependence of multi-functional cyclic initiators with the reaction medium (solvent and/or monomer) during the decomposition stage, this work deals with the thermal decomposition kinetic of DEKTP in pure MMA and the results are compared with those previously calculated in St.¹⁸ Furthermore, the corresponding results for MMA bulk polymerization using DEKTP as the initiator are also discussed.

EXPERIMENTAL SECTION

Materials

Sulfuric acid (H₂SO₄, 98%) and hydrogen peroxide (H₂O₂, 50%) purchased from J. T. Baker were used as received. Ammonium chloride (NH₄Cl, ≥99.5%), 3-pentanone (≥99%), anhydrous sodium sulfate (Na₂SO₄, ≥99%), petroleum ether (ACS reagent), methanol (99.8%), and tetrahydrofuran (THF, ≥99%), supplied by Sigma-Aldrich, were used without further purifica-

tion. MMA (99%) and styrene (St, 99%), provided by Sigma-Aldrich, were purified before use by vacuum distillation over calcium hydride and sodium, respectively.

DEKTP Synthesis

DEKTP was obtained according to a method reported in the literature.¹⁹ 3-Pentanone (50 mmol) was slowly dropped into a stirring mixture of H₂O₂ (56 mmol) and H₂SO₄ (195 mmol) at -15 to -20°C. After 3 hours of reaction, the mixture was extracted with petroleum ether (three times with 25 mL). The organic layer was freed of H₂O₂ with successive washes using a saturated aqueous solution of ammonium chloride (three times with 10 mL) and water (three times with 10 mL). The organic layer was dried over Na₂SO₄ during 24 hours. The solution was filtered and the product was isolated by solvent evaporation. The white solid obtained was re-crystallized twice from methanol and its purity was confirmed by proton and carbon nuclear magnetic resonance (¹H and ¹³C NMR, spectra can be consulted in the Supporting Information Figures S1 and S2) at room temperature on a Jeol 300 MHz NMR spectrometer, deuterated chloroform (CDCl₃) was used as the solvent.

Thermal Decomposition of DEKTP in MMA

A stock solution 0.01 mol L⁻¹ of DEKTP in MMA was prepared with naphthalene (0.01 wt %) as an internal standard. The solution was placed in pyrex glass ampoules to be thoroughly degassed by freeze-pump-thaw cycles before being sealed with a flame torch. The ampoules were immersed in a thermostatic silicone oil bath stabilized at the selected temperature and they were withdrawn after predetermined periods of time. The reaction was stopped by cooling the ampoules at 0°C, subsequently, the polymeric products were dissolved in THF and precipitated adding drop-wise over methanol (volume ratio 1 : 10). The polymer was decanted and the supernatant was analyzed by gas chromatography-mass spectrometry (GC-MS) using the internal standard method.

Analytical Techniques

The DEKTP quantification in the solutions was carried out by GC-MS analysis in a BPX70 capillary column (70% cyanopropyl polysilphenylene-siloxane, 30 m, 0.25 mm I.D., 0.25 μm film thickness), installed in a Thermo Quest Trace 2000 GC model gas chromatograph with helium as carrier gas (1 mL min⁻¹), and the injection port at 150°C in split mode. The detection was performed with a Finnigan Polaris Ion trap MS equipment with its transfer line at 210°C and the ion source at 200°C. Chromatographic analyses were performed as follow: 5 minutes at 80°C, heating rate 10°C min⁻¹ to a final temperature of 200°C. Under these conditions the elution time of DEKTP was about 16 minutes.

Monomer conversion was determined by gravimetric procedures and the molecular weights of polymer samples were determined by size exclusion chromatography (SEC) at 40°C using a Hewlett-Packard instrument (HPLC series 1100) equipped with a refractive index detector. A series of three PLGel columns with porosities of 10³, 10⁵, and 10⁶ Å was used. Calibration was carried out with poly(methyl methacrylate) standards and THF (HPLC grade) was used as the eluent at a flow rate of 1 mL min⁻¹.

MMA Bulk Polymerization Initiated with DEKTP

Polymerization experiments were also carried out in glass ampoules following the same degasification and experimental procedures previously detailed. The polymeric products were dissolved in THF, drop-wise added over methanol; and the precipitated polymers were filtered and dried under vacuum at room temperature until constant weight.

Kinetic Methods

The decomposition rate constant (k_d) values were calculated according to a pseudo-first order kinetic law [eq. (1)]:

$$\ln[I]_t = \ln[I]_0 - k_d t \quad (1)$$

where $[I]_0$ and $[I]_t$ are the initial peroxide concentration and its concentration at different reaction times, respectively.

The temperature effect on k_d values was evaluated using the Arrhenius equation [eq. (2)]:

$$\ln k_d = \ln A - \frac{E_a}{RT} \quad (2)$$

where T is the experimental temperature (expressed in K), A is the pre-exponential factor, E_a is the Arrhenius activation energy (expressed in cal mol^{-1}) and R is the universal gas constant ($1.9872 \text{ cal mol}^{-1} \text{ K}^{-1}$).

The corresponding activation parameters (ΔH^\ddagger , ΔS^\ddagger , and ΔG^\ddagger), were deduced from the Eyring equation [eq. (3)], where the error limits indicated are standard deviations from a least mean squares data treatment:

$$\ln\left(\frac{k_d}{T}\right) = -\frac{\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R} + \ln\left(\frac{R}{N_A h}\right) \quad (3)$$

where ΔH^\ddagger is the activation enthalpy, ΔS^\ddagger is the activation entropy, N_A is the Avogadro's number ($6.023 \times 10^{23} \text{ mol}^{-1}$) and h is the Planck's constant ($1.5835 \times 10^{-34} \text{ cal s}^{-1}$).

The free activation energy (ΔG^\ddagger) was calculated at the average experimental temperature using the [eq. (4)], deduced from the activated complex theory:

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (4)$$

The polymerization rate (R_p) values at different temperatures were calculated from [eq. (5)] by plotting $\ln([M]_0/[M]_t)$ as a function of reaction time (t) attending to the initial monomer (M) concentration.

$$\ln\left(\frac{[M]_0}{[M]_t}\right) = k_{ap} t \quad (5)$$

where k_{ap} is the apparent polymerization rate constant.

The R_p determinations were carried out at low MMA conversions (*ca.* 15%) to avoid side reactions and the Trommsdorff effect, characteristic of this particular system.

Computational Details

Quantum chemical calculations were performed to study the interaction systems DEKTP-MMA and DEKTP-St in the initial molecular state, with *Gaussian 98* program package.²⁰ The geometry optimization was performed with PBE0 functional^{21–23} using the 6-31+G(d,p)²⁴ basis set, Grimme's D3 model^{25,26} for dispersion. Figure 2 shows the optimized geometries of

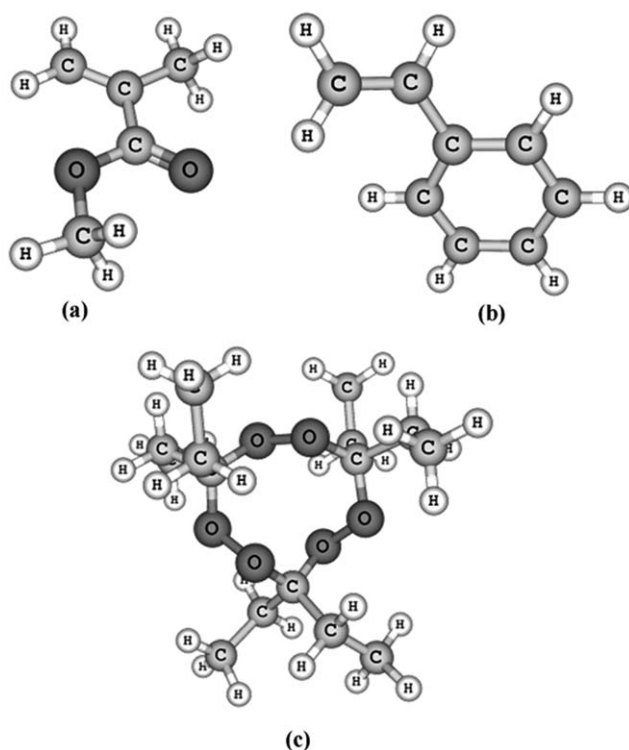


Figure 2. Optimized geometries of: (a) MMA, (b) St and (c) DEKTP molecular structures.

tries of (a) MMA, (b) St and (c) DEKTP structures, which were visualized with the Chemcraft graphical program.

The interaction energy (E_i) was calculated in order to determine the most favorable energy and to define the total energy (E_{tot}) [eq. (6)].

$$E_i = E_{\text{tot}}(\text{DEKTP}+M) - E_{\text{tot}}(\text{DEKTP}) - E_{\text{tot}}(M) \quad (6)$$

RESULTS AND DISCUSSION

Thermal Decomposition of DEKTP in MMA

The thermal decomposition kinetic study of DEKTP in pure MMA was carried out in the temperature interval of 110–140°C. The thermal decomposition reaction of DEKTP at the different evaluated temperatures followed a pseudo first-order kinetic law until at least 52% of the cyclic triperoxide conversion. The obtained k_d values were in reasonable agreement within the typical experimental error of this kind of studies (3%).²⁷ As it was expected k_d values increased with temperature (Table I). The temperature effect on the k_d values evaluated by the Arrhenius equation is represented in [eq. (7)], where the exhibited errors corresponded to the standard deviations obtained in the kinetic data treatment with the least mean squares method.

$$\ln k_d = (25.13 \pm 3.6) - \frac{(26741 \pm 1414.6)}{RT} \quad (7)$$

The Arrhenius equation plot for k_d was linear ($r = 0.9987$) (see Figure S3 in Supporting Information) in a relatively wide temperature range (*ca.* 30°C), which suggested that the calculated activation parameters for the DEKTP reaction corresponded to a single process, that would be certainly the thermolysis to

Table I. Pseudo First-Order Rate Constants for DEKTP Decomposition in MMA Solution (0.01 mol L^{-1})

T [°C]	$k_d \times 10^5$ [s^{-1}]	$t_{1/2}$ [min] ^a	r^b
110	4.50	256.6	0.9980
120	9.87	117.0	0.9940
130	33.48	34.5	0.9924
140	50.64	22.7	0.9713

^aHalf-life time.^bLinear correlation coefficient [eq. (1)].

generate the bi-radical species [initial and transition states in Figure 3, route (a)].

The kinetic parameters obtained from the Eyring equation were compared with those published for other solvents in related works, (Table II)^{10,13,18} where it can be observed that DEKTP reactivity increased when monomers (MMA and St) were employed as the reaction medium instead of organic solvents (ethylbenzene and chlorobenzene).

It is widely recognized, that solvation is a complex process that depends on the structure of the reactants, the reaction mechanism, and the solvent properties; in this regard, important solvent effects were found for the thermal decomposition reaction of DEKTP in solution. The molecules of vinyl monomers used as solvents can trap the bi-radical species generated by the initiator decomposition (Figure 3, both routes) promoting the equilibrium to shift towards the formation of products; contrary to conventional organic solvents that generally do not act as radical trapping agents.

In the special case of ethylbenzene as the solvent, the radical species generated from the initiator decomposition abstracted hydrogen atoms from the solvent, thus generating new radicals of the type $\text{C}_6\text{H}_5\text{CH}\cdot\text{CH}_3$, where 2,3-diphenylbutane was the principal product as a consequence of the combination of these carbon-centered radicals. However, this product was neither identified by GC-MS when the decomposition was carried out in mixtures of ethylbenzene/MMA²⁸ nor in MMA. These results clearly indicated that in the case of using vinyl monomers as the reaction medium, the peroxy radicals quickly reacted with the monomer to initiate the polymerization process instead of abstracting hydrogen atoms from the solvent. Moreover, there was no evidence of branched polymers when DEKTP was used as initiator, so it could not be assumed C—C ruptures derived from the peroxide structure during the polymerization, as it was described for decomposition studies in pure organic solvents.²⁹

Furthermore, when thermal decomposition reaction was studied in pure organic solvents, an increase in the polarity of the medium increased the k_d .²⁹ One such behavior was not observed when monomers were used as solvents. In this regard, the kinetic parameters obtained in MMA were compared with those calculated in St by Cerna¹⁸ under the same reaction conditions, and the k_d of DEKTP in MMA was around 2.4 times lower than in St; although activation parameters presented higher values. In this case, the polarity effect became negligible and other factors like monomer reactivity, molecular structures, and initiator-monomer interactions, have to be taken into account to elucidate this behavior.

On the other hand, data analysis of the activation parameters in organic solvents and monomers showed that a change in the ΔH^\ddagger value was accompanied by a change in the corresponding

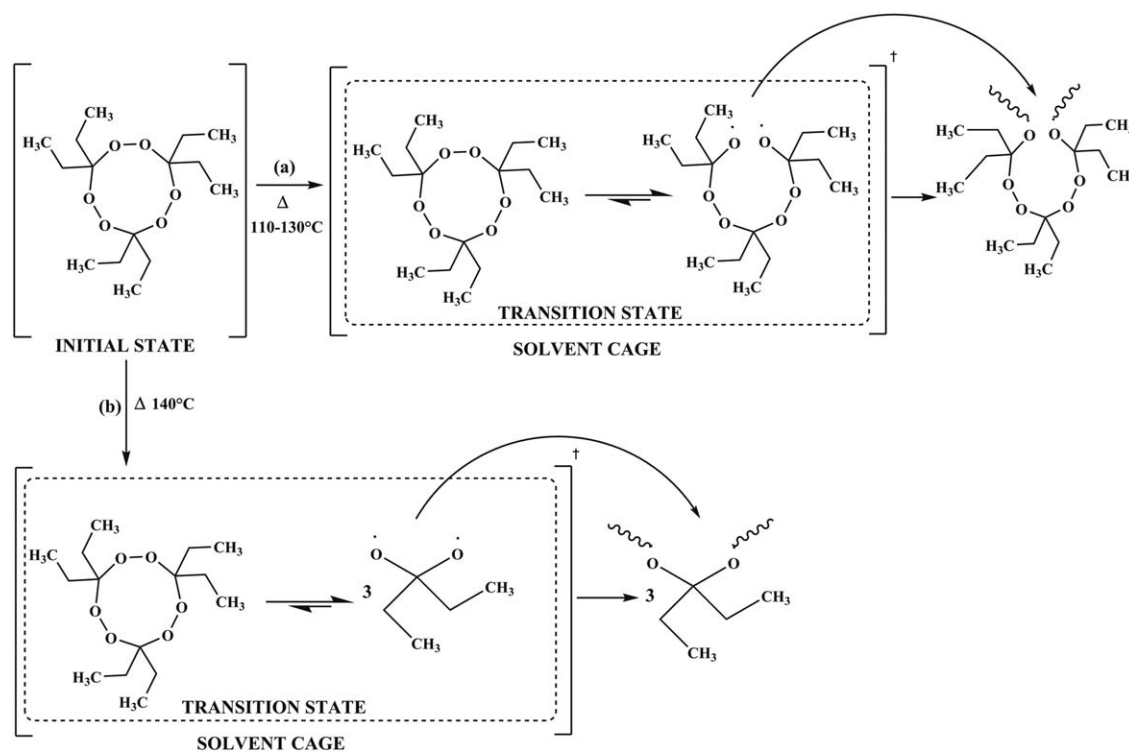
**Figure 3.** Proposed routes for the DEKTP decomposition in different monomers (MMA or St), route (a) sequential rupture and route (b) total rupture.

Table II. Activation Parameters for the Thermal Decomposition of DEKTP in Different Reaction Media

Solvent	k_d $_{130^\circ\text{C}} \times 10^5$ [s $^{-1}$]	ΔH^\ddagger [kcal mol $^{-1}$]	ΔS^\ddagger [cal mol $^{-1}$ K $^{-1}$]	ΔG^\ddagger [kcal mol $^{-1}$]
MMA	33.48	25.9 \pm 1.4	-9.1 \pm 3.5	29.5 \pm 1.4
St ¹⁸	79.5	11.5 \pm 0.4	-44.8 \pm 1.0	29.6 \pm 0.4
Ethylbenzene ¹³	1.2	37.8 \pm 1.1	12.4 \pm 2.6	32.9 \pm 1.1
Chlorobenzene ¹⁰	3.8	32.2 \pm 0.4	1.0 \pm 0.9	31.7 \pm 0.4

ΔS^\ddagger value, that resulted in non-significant variations in the ΔG^\ddagger value, as it was observed when the initiator was decomposed in different solvents (see Table II). Regarding the similarity in ΔG^\ddagger values, it could be inferred that DEKTP initiated its decomposition through the same mechanism in all the solvents, including monomers. However, different interactions mechanisms could take place. It is known that in pure organic solvents the determining step in the DEKTP decomposition mechanism is the bi-radical formation, and it seems to behave in the same way in vinyl monomers; nevertheless, sequential ruptures of O—O, C—O, and C—C bonds are different in each reaction media.

To support the proposed mechanism showed in Figure 3, quantum chemical calculations were performed in both systems, DEKTP-MMA and DEKTP-St, in order to study the interaction energy at the initial molecular state.

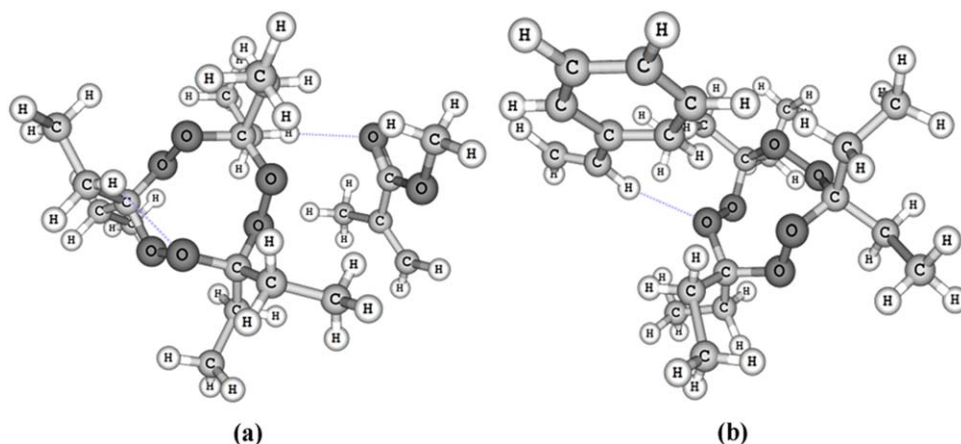
In Figure 4 it is presented the most favorable interaction for (a) DEKTP-MMA and (b) DEKTP-St systems (hydrogen bond interactions) as a result of density functional theory (DFT) calculations.

Both systems were optimized to calculate the interaction energy (E_i) at the initial molecular state (reactants still at room temperature). The E_i for the DEKTP-MMA system (-7.2 kcal mol $^{-1}$) was lower than the E_i for the DEKTP-St system (-7.0 kcal mol $^{-1}$), which means that the DEKTP-MMA system presented higher interactions. These calculated values indicate that the interactions can be characterized as physisorption in both systems, and that they are predominantly of the hydrogen bond type (2 to -10 kcal mol $^{-1}$).³⁰ Even though the system DEKTP-

MMA presented higher interactions, such interactions are strictly associated to a higher solvation at the initial molecular state.

If entropic factors are included, the values of the free energy of interaction (or Gibbs free energy) turned out to be positive for both systems, $\Delta G^\ddagger = 2.9$ for DEKTP-MMA and 3.6 kcal mol $^{-1}$ for DEKTP-St, meaning that the interaction to form the complexes DEKTP-MMA and DEKTP-St (through hydrogen bonding) under the temperature and pressure conditions at the initial molecular state, is not possible. This is in agreement with the proposed decomposition mechanism of DEKTP in the presence of the monomer (Figure 3), in which at the initial molecular state there are not interactions that allow the formation of some complexes, instead of that, there is a preferential solvation by the monomer, reaching directly the transition state.

On the basis of reported theoretical calculations, there existed lower interactions in the DEKTP-St system in the initial molecular state, and consequently when the temperature increases, the peroxide molecules could go faster through the transition state requiring a lower energy activation, i.e., $E_{a,\text{St}} = 12203.9 \pm 379.9$ cal mol $^{-1}$, in comparison with that for the DEKTP-MMA system, i.e., $E_{a,\text{MMA}} = 26741 \pm 1414.6$ cal mol $^{-1}$. The transition state was mostly solvated as a consequence of an orientation of St molecules, that stabilized the transition state (greater interaction), originating a reduction in the energetic barrier (ΔH^\ddagger), which could be rapidly overcome to generate the intermediate bi-radical capable to initiate the polymerization in the presence of a vinyl monomer (see Figure 3). On the other hand, the

**Figure 4.** Interaction for the systems; (a) DEKTP-MMA and (b) DEKTP-St (DFT calculations).

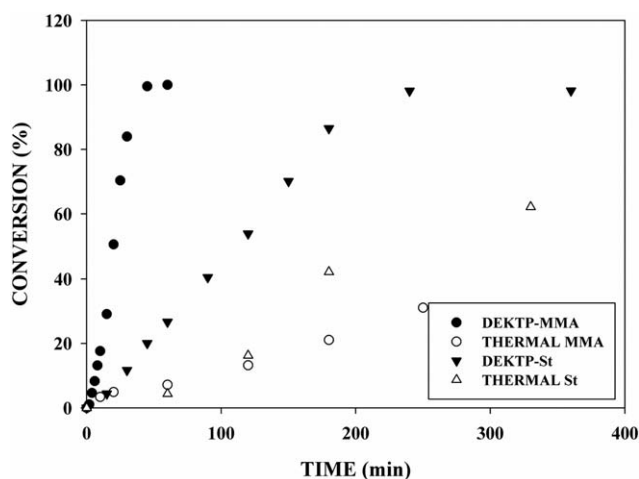


Figure 5. Conversion evolution as a function of reaction time for MMA and St polymerizations carried out at 130°C, in the presence (0.01 mol L⁻¹) and absence of DEKTP.

particularly low value of ΔS^\ddagger in the presence of St was associated with a decrease in the rotational and translational degrees of freedom of DEKTP molecules, which generated a rigid state as a consequence of higher interactions between the initiator and the monomer molecules. Consequently, the scission of the

peroxide bond was accelerated and a higher value of k_d was observed.

On the contrary, the interactions between DEKTP-MMA were higher at the initial molecular state than those at the transition state, therefore, a higher ΔS^\ddagger value was obtained for MMA in comparison with St. It is noteworthy that the re-orientation of MMA molecules around the DEKTP to stabilize the transition state is delayed, and consequently the time required to overcome the energetic barrier to form the bi-radical is longer (lower k_d) (Table II).

MMA Bulk Polymerization Using DEKTP as Initiator

Considering the obtained results during the decomposition of DEKTP in MMA, bulk polymerizations of MMA in the presence of DEKTP (0.01 mol L⁻¹) were carried out at 120 and 130°C. Bulk polymerizations of MMA and St in the presence and absence (thermal auto-initiation) of DEKTP were carried out at the same temperatures for comparison purposes. Figure 5 shows the conversion evolution as a function of reaction time, at a temperature of 130°C, for the previously mentioned polymerization reactions.

Regardless of the monomer considered, polymerization reactions initiated by DEKTP, presented higher conversions at considerably lower polymerization times in comparison with polymerizations thermally auto-initiated, demonstrating the

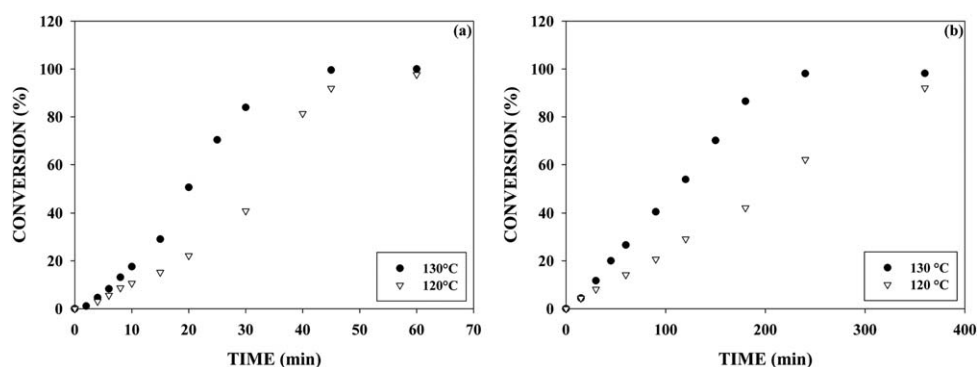


Figure 6. Conversion evolution as a function of reaction time for, (a) MMA and (b) St, bulk polymerizations initiated with DEKTP (0.01 mol L⁻¹) at 120 and 130°C.

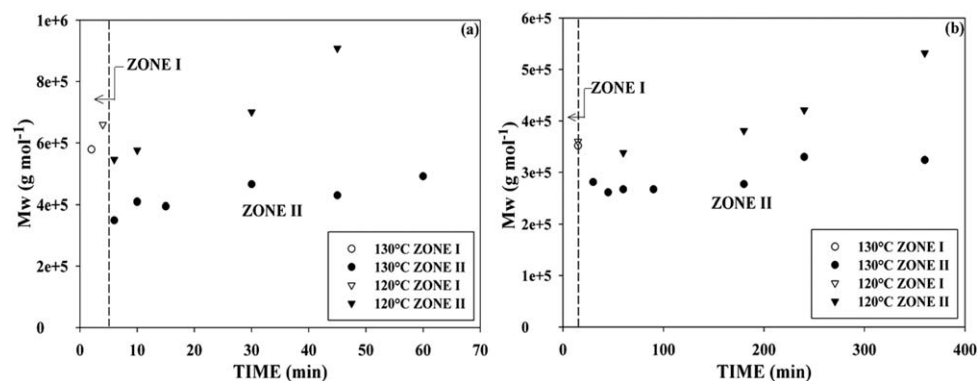


Figure 7. Weight-average molecular weight as a function of reaction time for, (a) MMA and (b) St, bulk polymerizations initiated with DEKTP (0.01 mol L⁻¹) at 120 and 130°C.

Table III. Polymerization Rate Values Calculated for St and MMA Polymerizations Initiated with DEKTP at 120 and 130°C

T [°C]	$R_{p,St} \times 10^4$ [mol L ⁻¹ s ⁻¹]	$R_{p,MMA} \times 10^4$ [mol L ⁻¹ s ⁻¹]
130	6.546	33.655
120	4.460	21.613

organic triperoxide capability to initiate MMA and St polymerizations. For instance, 11% conversion of MMA was approximately reached in 60 minutes for auto-initiation while in the presence of DEKTP as the initiator a monomer conversion close to 100% was achieved.

On the other hand, conversion values for MMA polymerizations initiated with DEKTP were higher than those for St, at 30 minutes of reaction, MMA presented *ca.* 93% of conversion meanwhile at the same time St showed only 12%. The faster MMA polymerization was explained by its higher propagation rate constant (k_p) in comparison with that for St ($k_{p,MMA} = 0.513 \times 10^3$ and $k_{p,St} = 0.165 \times 10^3$ L mol⁻¹ s⁻¹, at 60°C).³¹

Figure 6 shows the temperature effect on the conversion evolution for (a) MMA and (b) St bulk polymerizations carried out in the presence of DEKTP. Temperatures evaluated were 120 and 130°C, and it could be clearly observed for both monomers that conversion increased with temperature, as expected, due to a faster DEKTP decomposition and a higher concentration of radicals in the reaction medium at 130°C.

Figure 7 shows the temperature effect on the weight-average molecular weight for (a) MMA and (b) St bulk polymerizations carried out in the presence of DEKTP as the initiator. As it was expected for free-radical polymerizations initiated with peroxy compounds, lower molecular weights were obtained as temperature increased, regardless of the polymerized monomer. Elevated molecular weights observed at 120°C in both cases were also associated with diffusional restrictions of polymeric chains affected by the increase in reaction viscosity, thus reducing termination reactions and yielding larger polymeric chains.

The molecular weights observed in Zone I [Figure 7(a,b)] were associated with species that resulted from the combination of growing primarily radicals [Figure 3, route (a)] giving rise to

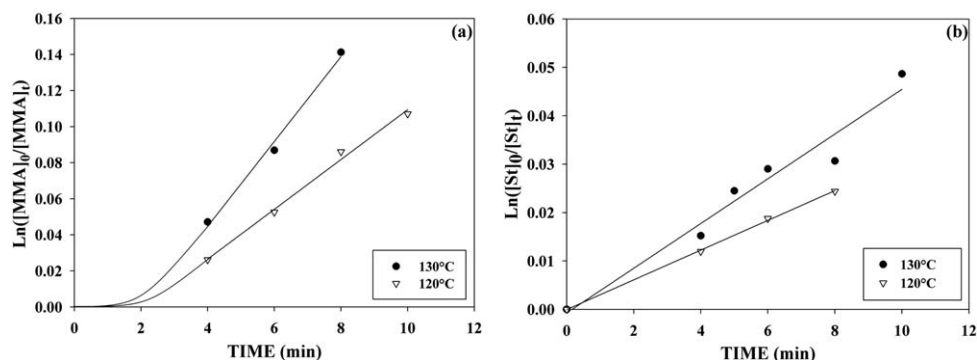
species with two undecomposed O—O bonds within their inner structures that subsequently could decompose and re-initiate new polymeric chains. After this initial behavior, molecular weights presented a tendency to increase (Zone II) with polymerization time in both monomers, being this behavior more noticeable at 120°C and comparable with those reported for polymerization reactions initiated with multi-functional linear initiators,¹⁰ where in the polymerization course several cycles of initiation-propagation-termination reactions took place, allowing for the growth of molecular weights with conversion. In contrast, in a free-radical polymerization initiated by monofunctional initiators, the molecular weights remained without significant changes during the polymerization process.

Comparing the two regions in the molecular weight evolution (Zones I and II) in Figure 7(a) for MMA and 7(b) for St, it could be observed by one hand, that molecular weights were in both zones, higher in the case of MMA. On the other hand, the difference in molecular weights at the two evaluated temperatures, in the two regions, were also higher in the MMA case. These behaviors could be associated to the solution viscosity that limited the diffusion rates of large polymer chains within the solution. This inability to manoeuvre limited the termination step, increasing the ratio of propagation rate to termination rate.³¹

Simultaneously, in order to determine the polymerization rate (R_p) several experiments at low monomer conversions (lower than 15%) were carried out for both monomers. This conversion region is characterized by a good mobility of growing chains and low contribution of termination reactions compared to propagation reactions. For both monomers, MMA and St, the R_p values increased with temperature (Table III).

When the temperature was increased by 10°C, the effect of temperature on R_p was slightly higher in MMA [Figure 8(a)] than in St [Figure 8(b)], being 1.56 for MMA and 1.47 for St, respectively. On the other hand, the polymerization rate was accelerated up to *ca.* 5 times in MMA explained by its higher k_p .

It should be emphasized that in the case of MMA polymerization [Figure 8(b)], an induction period is observed at the two evaluated temperatures, contrary to the case of St polymerization. Although this behavior has been previously observed,^{32,33} it has never been explained before. However, taking into account the k_d values (*ca.* $k_{d,MMA} = 33.48 \times 10^{-5}$ s⁻¹ and $k_{d,St} =$

**Figure 8.** Ln([monomer]₀/[monomer]_t) as a function of reaction time for, (a) MMA and (b) St, bulk polymerizations initiated with DEKTP (0.01 mol L⁻¹) at 120 and 130°C, data from Reference 18.

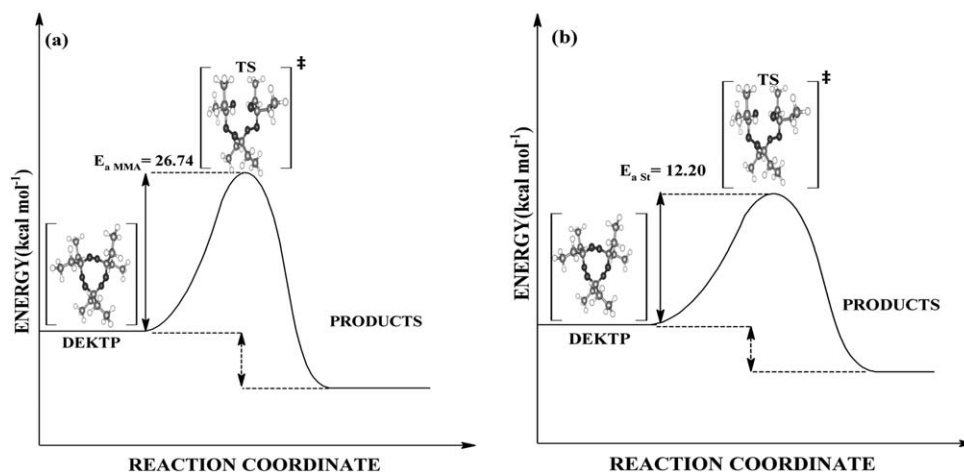


Figure 9. Scheme of energy as a function of reaction coordinate for DEKTP initiator in (a) MMA and (b) St.

$79.5 \times 10^{-5} \text{ s}^{-1}$ at 130°C), it could be assumed that the induction period in MMA was the result of a higher energetic demand by the initiator to dissociate and generate the intermediate bi-radicals (according to the DEKTP-MMA interaction system, in which the interaction was higher at the initial molecular state) than at the transition state, which in turn required a greater energy to go through the energetic barrier and to diffuse out of the solvent cage to initiate the polymerization. The behavior of the DEKTP initiator with the evolution of the polymerization (reaction coordinate) for both MMA and St polymerization is represented in Figure 9. In both cases, the initiator was initially solvated by the monomer molecules (MMA or St), the geometry optimization was performed to obtain the initiator-monomer interaction with the DFT method in the initial molecular state taking into account that the solvation (interaction) was different depending on the monomer involved, as it was previously described. Therefore, the energy required for the DEKTP-MMA solvated system to reach the transition state (TS) was almost twice as high as that required for the DEKTP-St solvated system. Once the bi-radicals were generated out of the solvent cage, they were trapped by monomer molecules, shifting the dissociation of the DEKTP to the right.

CONCLUSIONS

The thermal decomposition reaction of DEKTP in MMA followed a pseudo-first order kinetic law up to at least 52% of cyclic triperoxide conversion. The decomposition rate constant of DEKTP in MMA was calculated to be 2.4 times lower than in St; nevertheless activation parameters were higher. The occurrence of different interaction mechanisms DEKTP-monomers could account for such behaviors. Theoretical calculations and experimental kinetic data supported the proposed DEKTP decomposition and polymerization initiation mechanisms.

In the systems DEKTP/vinyl monomers, besides the solvent polar character, other factors like monomer reactivity and interactions solute-solvent have to be taken into account to explain the calculated decomposition rate constant values. The differences observed in the decomposition rate constants for DEKTP-MMA and DEKTP-St systems were explained by quantum

chemical calculations, in terms of solvation in the initial molecular state. It was also demonstrated that the energy required for the DEKTP-MMA solvated system to reach the transition state was almost twice as high as that required for the DEKTP-St solvated system.

Bulk polymerizations of MMA carried out in the presence of DEKTP as the initiator evidenced polymerization rate values approximate five times higher than those observed for DEKTP-St system, which was associated to the higher propagation rate constant of MMA.

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REFERENCES

- Choi, K. Y.; Lei, G. D. *AIChE J.* **1987**, *33*, 2067.
- Choi, K. Y.; Liang, W. R.; Lei, G. D. *J. Appl. Polym. Sci.* **1988**, *35*, 1547.
- Villalobos, M. A.; Hamielec, A. E.; Wood, P. E. *J. Appl. Polym. Sci.* **1991**, *42*, 629.
- Yoon, W. J.; Choi, K. Y. *J. Appl. Polym. Sci.* **1992**, *46*, 1353.
- Sheng, W.; Shan, G.; Weng, Z.; Pan, Z. *Polymer* **2005**, *46*, 10553.
- Eyler, G. N.; Cañizo, A. I.; Alvarez, E. E.; Cafferata, L. F. R. *An. Asoc. Quím. Argent* **1994**, *82*, 175.
- Eyler, G. N.; Cañizo, A. I.; Nesprías, R. K. *Quim. Nova.* **2002**, *25*, 364.
- Eyler, G. N. *J. Phys. Org. Chem.* **2006**, *19*, 776.

9. Eyler, G. N.; Mateo, C. M.; Alvarez, E. E.; Cañizo, A. I. *J. Org. Chem.* **2000**, *65*, 2319.
10. Cañizo, A. I.; Eyler, G. N.; Morales, G.; Cerna, J. R. *J. Phys. Org. Chem.* **2004**, *17*, 215.
11. Cañizo, A. I.; Eyler, G. N.; Mateo, C. M.; Alvarez, E. E.; Nesprías, R. K. *Heterocycle* **2004**, *63*, 2231.
12. Cañizo, A. I.; Eyler, G. N. *Rev. Latinoamer. Quim.* **2005**, *33*, 103.
13. Barreto, G. P.; Eyler, G. N. *Polym. Bull.* **2011**, *67*, 1.
14. Bellamy, J. J. *Forensic Sci.* **1999**, *44*, 603.
15. Dubnikova, F.; Kosloff, R.; Almog, J.; Zeiri, Y.; Boese, R.; Itzhaky, H.; Alt, A.; Kernan, E. *J. Am. Chem. Soc.* **2005**, *127*, 1146.
16. Barreto, G. P.; Alvarez, E. E.; Eyler, G. N.; Cañizo, A. I.; Allegretti, P. E. *Aus. J. Chem.* **2014**, *67*, 881.
17. Cerna, J. R.; Morales, G.; Eyler, G. N.; Cañizo, A. I. *J. Appl. Polym. Sci.* **2002**, *83*, 1.
18. Cerna, J. R. *Uso de Peróxidos Cíclicos Multifuncionales como Iniciadores de la Polimerización del Estireno*. Ph. D. Thesis, CIQA, México, **2002**.
19. Cafferata, L. F. R.; Eyler, G. N.; Svartman, E. L.; Cañizo, A. I.; Alvarez, E. *J. Org. Chem.* **1991**, *56*, 411.
20. Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yázyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian, Inc.: Wallingford, CT*, **2009**.
21. Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1992**, *46*, 6671.
22. Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.
23. Perdew, J. P.; Kurth, S.; Zupan, A.; Blaha, P. *Phys. Rev. Lett.* **1999**, *82*, 2544.
24. Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.
25. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104154104.
26. Grimme, S.; Ehrlich, S.; Goerigk, L. *J. Comp. Chem.* **2011**, *32*, 1456.
27. Iglesias, M.; Eyler, N.; Cañizo, A. *J. Phys. Org. Chem.* **2009**, *22*, 96.
28. Barreto, G. P. *Termólisis de Triperóxido Cíclico de Dietilcetona: Estudios Cinéticos en Solución y su Uso como Iniciador en Polimerizaciones Radicalarias*. PhD Thesis. Universidad Nacional de la Plata, Argentina, **2008**.
29. Cañizo, A. I. *Trends Org. Chem.* **2006**, *11*, 55.
30. Koch, W.; Holthausen, M. C. *Hydrogen Bonds and Weakly Bound Systems, in A Chemist's Guide to Density Functional Theory*, Wiley-VCH, Verlag GmbH: Cambridge, UK, **2001**; Chapter 12, pp 217–238.
31. Odian, G. *Radical Chain Polymerization, Principles of Polymerization*, John Wiley & Sons: New York, **2004**; Chapter 3, p 198.
32. Scoriah, M. J.; Dhib, R.; Penlidis, A. *J. Macromol. Sci., Part A: Polym. Chem.* **2005**, *42*, 403.
33. Scoriah, M. J.; Dhib, R.; Penlidis, A. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 5647.