

# Thermal decomposition reaction of pinacolone diperoxide: its use as radical initiator in the styrene polymerization

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**Abstract** Some commercial vinyl polymers such as polystyrene, polymethylmethacrylate and polyvinyl chloride have been synthesized through last years using new initiators, for example those with multiple active sites. Multifunctional initiators in radical polymerization of vinyl monomers allow us to obtain different behaviours during the process and changes in the properties of the final products. In this work, the kinetic study of the thermal decomposition of cyclic pinacolone diperoxide (PDP) in ethylbenzene and its use in the initiation step of the bulk free radical polymerization of styrene is reported. The activation parameters for the thermal decomposition reaction of PDP in styrene were worked out from Eyring equation ( $\Delta H^\ddagger = 26.0 \pm 1.2 \text{ kcal mol}^{-1}$ ;  $\Delta S^\ddagger = -9.5 \pm 3.0 \text{ cal mol}^{-1} \text{ K}^{-1}$ ). In addition, the evolution of molecular weights during polymerization was studied showing an increase through the process.

**Keywords** Peroxides · Polymerization · Kinetics

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## Introduction

The synthesis and chemical behaviour of cyclic organic peroxides with the O–O function included in the cycle are interesting because the peroxidic function is not only directly related to oxidative processes of other organic compounds such as alcohols [1] and hydrocarbons [2, 3] but also can have many other industrial applications such as initiators of polymerization processes or precursors for drugs.

Regarding to their use as polymerization initiators, organic peroxides in general and, cyclic organic peroxides in special, can decompose and form free radicals which can participate in the initiation reaction of different vinyl monomers at diverse production scales. Among the compounds used as initiators for the polymerization of vinyl monomers, the use of peroxidic initiators has been preferred, as they are efficient than those of azo and carbon–carbon types, since they generally have a lower number of induced decomposition reactions and are easily accessible. However, the use of monofunctional peroxy initiators presents certain limitations associated with long residence times inside the reactor as a result of the half-life times presented by these initiators [4].

On the other hand, a large problem at industrial scale during the synthesis of vinyl polymer is the inability to achieve an appropriate balance between residence time in reactor, rates of polymerization, molecular weights, polydispersities and the possibility to reach conversions close to 100%, the latter to minimise the concentration of residual monomer. In this sense, alternatives to traditional monofunctional initiators are linear bi- and multifunctional initiators that lead to a rather complex polymerization kinetics, yielding lower prepolymerization times without diminishing the final product properties [5–7]. Also different initiation strategies employing multifunctional or macro-initiator have been carried out to make the synthesis of polymeric materials more efficient [8–10].

In previous reports, it was demonstrated that several cyclic organic peroxides have application as multifunctional initiators in the styrene (S) polymerization. In this sense, the diethylketone triperoxide (3,3,6,6,9,9-hexaethyl-1,2,4,5,7,8-hexaoxacyclononane, DEKTP) was used as initiator in the S radical polymerization reaction, and depending on the reaction temperature, this initiator can decompose either by a total or a sequential mechanism yielding polymers with high molecular weights, in a lower polymerization time and with improved mechanical properties than those obtained with mono- or bifunctional classic initiators [5, 11–13].

The use of DEKTP in the bulk polymerization of S was experimentally and theoretically investigated. The study focused on temperatures from 150 to 200 °C, considering chemical initiation by both sequential and total decomposition reactions [11]. This peroxide was also used in the synthesis of high impact polystyrene (HIPS) presenting low selectivity to grafting reactions at any of the concentrations of initiator and temperatures evaluated. When it was used under temperature ramp (120–130 °C, heat rate = 2 °C min<sup>-1</sup>), the synthesis of HIPS with an adequate morphology development and impact strength in the order of 67 J m<sup>-1</sup> was possible, depending on DEKTP concentration [14].

On the other hand, DEKTP thermal decomposition reaction in ethylbenzene solution was studied under different experimental conditions [15] (with and without methyl methacrylate (MMA) addition). It was demonstrated that a higher MMA initial concentration generates an increase in the rate constant values of DEKTP decomposition reaction ( $k_d$ ).

However, despite the results with DEKTP are very promising, the synthesis and crystallisation of this initiator demands long experimental times, so in the last years, other multifunctional initiators like the cyclic pinacolone diperoxide (3,6-diterbutyl-3,6-dimethyl-1,2,4,5-tetraoxacyclohexane, PDP) has been studied. Studies concerning with the thermal decomposition reaction of this initiator in several solvents with different physicochemical properties (2-methoxyethanol, benzene, acetic acid, acetonitrile, *n*-octane, toluene, 2-propanol/benzene mixture) have been reported [16–18]. PDP was preliminarily used as initiator in the S polymerization reaction [5, 19, 20] showing that in the interval of 120–130 °C, it presents a typical multifunctional behaviour, yielding polystyrene at high reaction rate with high molecular weights. When it was used in combination with 1,1-bis(terbutylperoxy)-cyclohexane, T22E–50, as the initiation system in the S polymerization, the values of conversion and molecular weight were higher in comparison with PDP alone [5].

The synthesis of HIPS using PDP (among other peroxides) has been studied [21], and it was evidenced that PDP can give rise to materials highly reinforced, also with impact resistance values in the order of 147 J m<sup>-1</sup> with lower prepolymerization times in comparison with other initiator systems.

Also, the thermolysis of PDP in pure methyl methacrylate under different experimental conditions has been carried out [22]. In addition, S conversion during bulk polymerization employing PDP at 110 and 120 °C has been analysed by other authors [23]. However, the results of published papers have focused the attention on polymerization kinetic parameters and the macromolecular product properties and mathematical model.

The aim of this work is to study the kinetics of the thermal decomposition reaction of PDP under different experimental conditions (solution of ethylbenzene, ethylbenzene/S mixtures or S monomer; temperature an initial concentration ranges of 110–150 °C and 0.01–0.02 mol L<sup>-1</sup>, respectively).

## Experimental

### Materials

The PDP was prepared using a previously described technique [16] by pinacolone (3,3-dimethyl-2-butanone) reaction with concentrated hydrogen peroxide (Riedel-de Haën, pro-analysis grade) in acidic medium (H<sub>2</sub>SO<sub>4</sub>, Merck, pro-analysis grade). Peroxide purity (m.p.<sub>PDP</sub> 122–124 °C) was checked by gas chromatography (GC) and <sup>1</sup>H and <sup>13</sup>C NMR.

Ethylbenzene (Fluka, purum grade) and naphthalene (Mallinckrodt, pro-analysis grade) were purified according to suitable techniques [24] (naphthalene was used as

internal standard in quantitative GC analysis). S was purified by distillation under reduced pressure as reported in the literature [24].

Caution: PDP must be handled with care because it can be detonated by shock

## Kinetic methods

Pyrex glass tubes (7 cm in length  $\times$  4 mm i. d.) half-filled with the appropriate PDP solution were degassed under vacuum at  $-196\text{ }^{\circ}\text{C}$  (liquid nitrogen bath) and then sealed with a flame torch. To carry out the experiment, the ampoules were immersed in a thermostatic silicone oil bath at the desired temperature ( $\pm 0.1\text{ }^{\circ}\text{C}$ ) and removed after predetermined periods of time, stopping the reaction by cooling them in an ice-water bath ( $0\text{ }^{\circ}\text{C}$ ). The concentration of PDP remaining in the solution was determined by quantitative gas chromatography analysis in a DB-5 capillary column (5% biphenyl-95% dimethyl polysiloxane, 30 m  $\times$  0.32 mm I.D., 0.25  $\mu\text{m}$  film thickness) installed in a Konik -2000C gas chromatograph with nitrogen as the carrier gas, injection port at  $150\text{ }^{\circ}\text{C}$  in split mode, and flame ionisation detection ( $250\text{ }^{\circ}\text{C}$ ). The experiments were carried out under programmed conditions ( $100\text{ }^{\circ}\text{C}$ , 2 min,  $10\text{ }^{\circ}\text{C min}^{-1}$  and  $210\text{ }^{\circ}\text{C}$ , 15 min). Retention times of internal standard and PDP were ca. 11.2 min and 12.5 min, respectively.

The corresponding experimental pseudo-first-order rate constant values ( $k_d$ ), with 5% accuracy, were calculated from the slope of the line obtained by plotting the values of  $\ln [\text{PDP}]$  against reaction time in seconds. The corresponding activation parameters were deduced from the Eyring equation (Eq. 1) and the errors were determined using a least-means-square data treatment [25].

$$\ln\left(\frac{k_d}{T}\right) = -\frac{\Delta H^\ddagger}{R} \frac{1}{T} + \frac{\Delta S^\ddagger}{R} + \ln \frac{\kappa k_B}{h}, \quad (1)$$

where  $R$  is the gas constant,  $T$  is the absolute temperature,  $h$  is Planck's constant,  $k_B$  is the Boltzmann constant and  $\kappa$  is a constant known as the transmission coefficient and is often taken to have a value of unity and we have followed this convention above. This approach implies that those species that reached the transition state always proceeds to products and never reverts to reactants.

## Polystyrene synthesis

The synthesis of polystyrene was carried out dissolving the appropriate amount of initiator in S (Aldrich, puriss grade) and equal amounts of the resulting solution were placed into glass tubes. The cooled tubes were evacuated, sealed and kept at 110, 120 and  $130\text{ }^{\circ}\text{C}$  in a thermostated bath, for different periods of time. Conversion of thermal autoinitiated polymerization of pure S was measured under the same experimental conditions. The polymer samples were dissolved in THF (Fluka, purum grade) and this solution added drop wise over an excess of methanol in a proportion 1:10, precipitating and purifying the product. The samples were filtered, dried *in vacuo*, and the monomer conversion was measured gravimetrically.

The molecular weights were determined by gel permeation chromatography (GPC) on a Waters chromatograph (515 HPLC Pump, Refractive Index Detector 2414, Rheodyne 7725i Injector) with three Mixed-A columns Polymer Laboratories 20  $\mu\text{m}$  (PLGel). The mobile phase used was THF at a flow rate of  $1 \text{ mL min}^{-1}$  at  $25 \text{ }^\circ\text{C}$ . Narrow polystyrene standards were used to calculate the molecular weight of polymer.

## Results and discussion

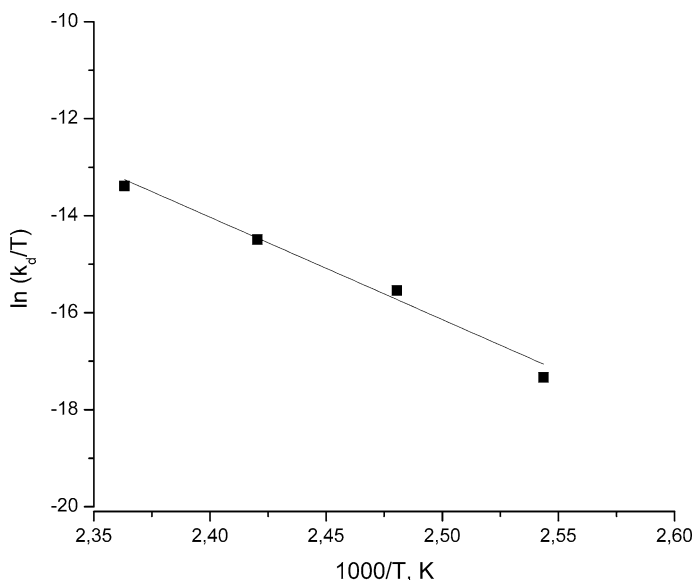
### Thermal decomposition of PDP in ethylbenzene solution

The solvent selected, ethylbenzene, is known as a “good solvent” in different polymerization processes. The experimental conditions used to study the thermal decomposition reaction of PDP in solution were such that the solvent was in great excess with respect to the peroxide. Therefore, the variation of its concentration during the reaction would be negligible and it could be considered as constant. Thus, the kinetic behaviour of the system was followed by the quantitative determination of PDP during the reaction. The kinetic data obtained in this work keep an approximately linear correlation according to a pseudo-first-order kinetic law up to at least ca. 60%.

The kinetic experiments were carried out at low concentrations of PDP ( $0.01\text{--}0.02 \text{ mol L}^{-1}$ ) in pure ethylbenzene solution, at a temperature range of  $120\text{--}150 \text{ }^\circ\text{C}$  (Table 1). The results of the experiments in ethylbenzene solution at  $120 \text{ }^\circ\text{C}$  show that the rate constant values are practically independent of the initial PDP concentration, so, induced reactions due to radicals produced during peroxide decomposition can be discarded.

**Table 1** First-order rate constant values for the thermal decomposition reaction of PDP in different reaction media, evaluated at different temperatures

Reaction medium	[PDP], $\text{mol L}^{-1}$	Temp., $^\circ\text{C}$	$k_d \times 10^5, \text{ s}^{-1}$	
Ethylbenzene	0.010	120	1.28	
		120	1.24	
		120	1.17	
	0.020	130	9.16	
		140	21.0	
		150	65.0	
Ethylbenzene/St [50:50]	0.010	110	7.02	
		120	16.0	
		130	33.0	
	0.015	130	35.0	
		0.010	130	40.0
			0.015	110
120	21.6			
Styrene	0.015	130		43.0



**Fig. 1** Eyring plot corresponding to the thermal decomposition reaction of PDP in ethylbenzene solution

On the other hand, the temperature effect on the rate constant values for the unimolecular reaction of PDP  $0.02 \text{ mol L}^{-1}$  in ethylbenzene solution can be represented by the Arrhenius equation (Eq. 1), where the errors shown are standard deviations from a least mean square data treatment and the activation energy is expressed in  $\text{kcal mol}^{-1}$ .

$$\ln k_d = (43.7 \pm 3.0) - \frac{(42800 \pm 1200)}{RT} \quad (2)$$

The corresponding activation parameters for PDP  $0.02 \text{ mol L}^{-1}$  in ethylbenzene solution can be deduced from the Eyring plot (Fig. 1), where the representation is linear ( $r = 0.983$ ) in a relatively large temperature range (ca.  $30 \text{ }^\circ\text{C}$ ).

The linearity shown in Fig. 1 suggests that the activation parameters values (Table 2) for the PDP reaction belong to a single process, which could be ascribed to its unimolecular homolysis (Scheme 1).

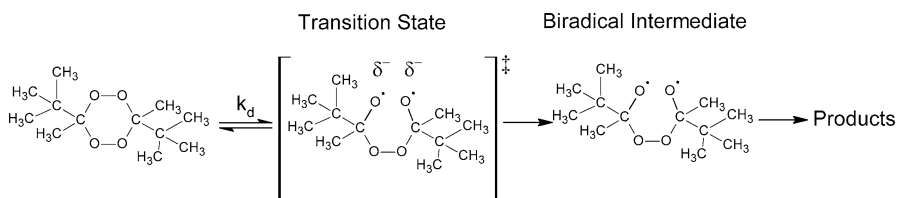
### Thermal decomposition of PDP in S containing solution

The kinetic study of the thermal decomposition of PDP in pure S was carried out in the temperature range of  $110\text{--}130 \text{ }^\circ\text{C}$ . The thermal decomposition reaction of PDP at different temperatures follows a pseudo-first-order kinetic law up to at least 50% of the cyclic diperoxide conversion. The peroxide initial concentration variation from  $0.01$  to  $0.015 \text{ mol L}^{-1}$  does not affect the rate constant value which is in reasonable agreement within the typical experimental error of this kind of experiments.  $k_d$  values increase with temperature (Table 1) as it was expected.

**Table 2** Kinetic and activation parameters of the thermal decomposition reaction of PDP in different reaction media

Solvent	$\Delta H^\ddagger$ , kcal mol <sup>-1</sup>	$\Delta S^\ddagger$ , cal mol <sup>-1</sup> K <sup>-1</sup>	$\Delta G^{\ddagger a}$ , kcal mol <sup>-1</sup>	$k_d \times 10^5$ , s <sup>-1</sup> (130 °C)
Ethylbenzene	41.9 ± 1.2	25.5 ± 3.0	31.4 ± 1.2	9.16
Ethylbenzene/styrene [50:50]	23.7 ± 1.6	-16.3 ± 4.0	30.0 ± 1.6	35.0
Styrene	26.0 ± 1.2	-9.5 ± 3.0	29.9 ± 1.2	43.0
2-Methoxyethanol [16]	43.8 ± 1.0	31.9 ± 2.6	30.7 ± 1.0	11.0
Acetonitrile [18]	34.6 ± 0.6	10.8 ± 1.5	30.1 ± 0.6	3.88

<sup>a</sup> Calculated at the average temperature of the experimental range for each reaction media

**Scheme 1** Proposed initial step thermal decomposition reaction for PDP in ethylbenzene solution

The rate constant value at 130 °C for the thermolysis of PDP in ethylbenzene/styrene mixture (50:50) is 3.8 times higher than the  $k_d$  in ethylbenzene solution and lower than the  $k_d$  in pure *S*.

It is evident that solvent effects are closely related to the nature and extent of solute–solvent interactions developed locally in the immediate environment of the solute. When the thermolysis reaction is evaluated in pure *S*, the  $k_d$  reaches the highest value, probably by the interaction between the biradical initially formed (Scheme 2) and the *S* molecules (which are excellent radical scavengers). This reaction between monomer and initial biradical produces a shift in the equilibrium of biradical formation (Scheme 1) generating an increase in the rate of its production.

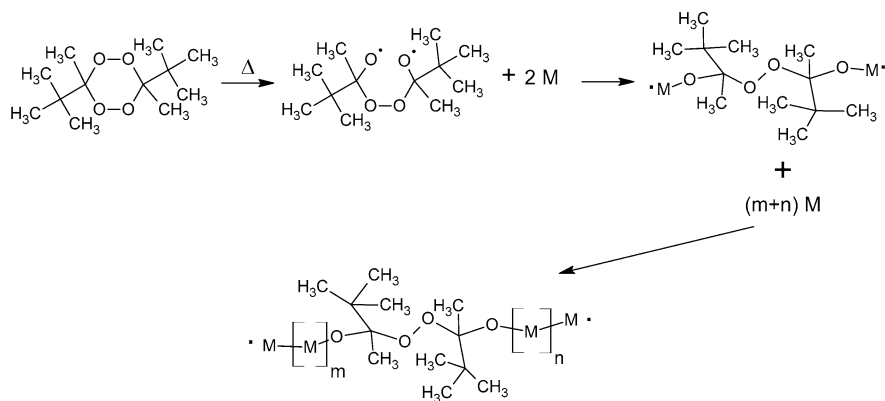
The interaction monomer/biradical generates primary growing radicals which favour the subsequent addition of a large number of monomer units, resulting in the production of polymeric species.

The temperature effect on the rate constant values ( $k_d$ ) for the unimolecular reaction in the pure styrene can be represented by the Arrhenius equation:

$$\ln k_d (s^{-1}) = (25.71 \pm 3.00) - \frac{(26753 \pm 1200)}{RT} \quad (3)$$

The activation parameters of PDP thermolysis in ethylbenzene with and without *S* can be compared with those values reported for the thermal decomposition in other solvents (Table 2).

The activation parameter values ( $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ ) of the PDP thermal reaction in *S* are lower than those observed for several organic solvents. The data analysis of



**Scheme 2** *S* addition to initial biradical formed from PDP thermal decomposition (*M* monomer molecule)

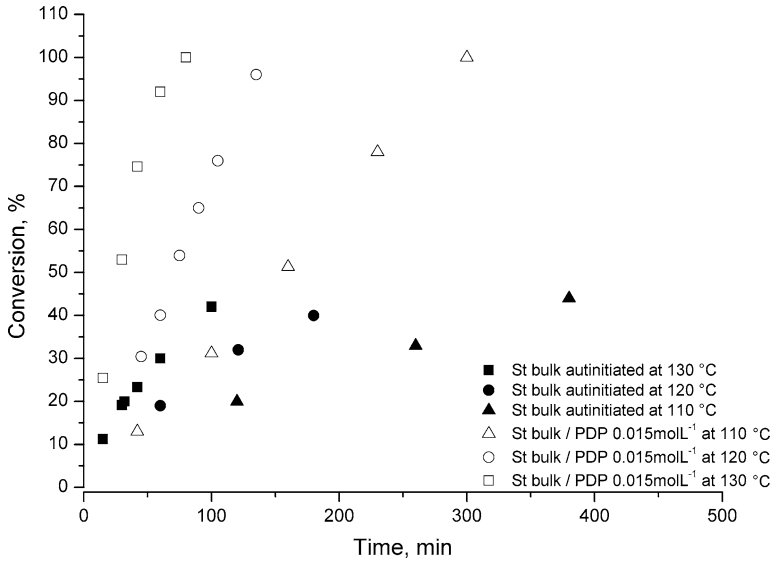
the activation parameters in organic solvents and in monomer shows that a change in  $\Delta H^\ddagger$  is accompanied by a change in the corresponding  $\Delta S^\ddagger$  values which results in non-significant variations of the  $\Delta G^\ddagger$  values (calculated at the average temperature of the experimental range for each reaction media) as it was observed when the initiator is decomposed in pure solvents. The similarity in  $\Delta G^\ddagger$  values allows postulating that the PDP initiates its decomposition through the same mechanism in all the media but very different interaction mechanisms can be taking into account. The determining step of the mechanism is the biradical formation (Scheme 1) which is the common step in pure solvents and in the vinyl monomer; but sequential ruptures of O–O, C–O and C–C bonds are different in each reaction media. The same behaviour has been observed when DEKTP is employed as initiator in the polymerization of the same monomer [12, 26].

### Bulk polymerization of *S* employing PDP as initiator

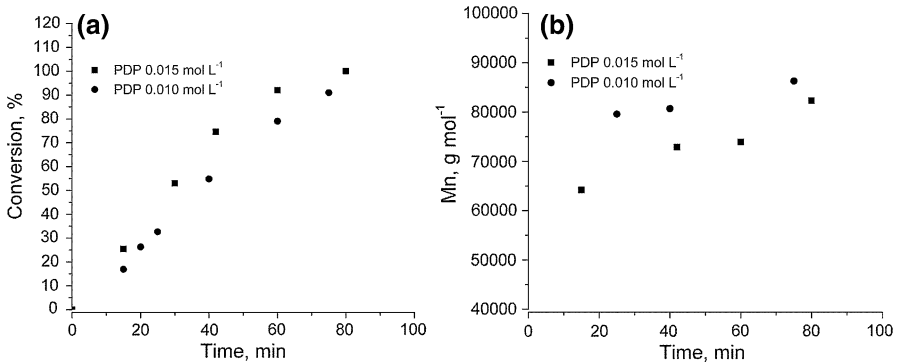
Bulk polymerizations of *S* in the presence of PDP ( $0.015 \text{ mol L}^{-1}$ ) were carried out at 110, 120 and 130 °C. The monomer conversion and molecular weights evolution were studied. Bulk autoinitiated polymerizations of *S* (in the absence of initiator) were also carried out at the same temperatures only for comparison purposes.

In Fig. 2, it can be observed that the presence of PDP in the case of bulk systems largely affects the conversion of monomer rate, resulting in conversions higher at the same reaction times with respect to thermal autoinitiated process for all temperatures. For example, when reaction time is 60 min at 130 °C, conversion of *S* in the case of thermal polymerization is about 30%, whereas in the presence of PDP, this value rises to 92%. These results can be compared with those obtained for the DEKTP thermolysis in *S* solution [12]. Whether the polymerization takes place in solvent–*S* mixtures or in bulk, DEKTP efficiently initiates the polymerization of the monomer. Moreover, the polymerization rates in bulk or solution are higher than those obtained for the autoinitiated process showing the same behaviour as in PDP systems studied in this work.





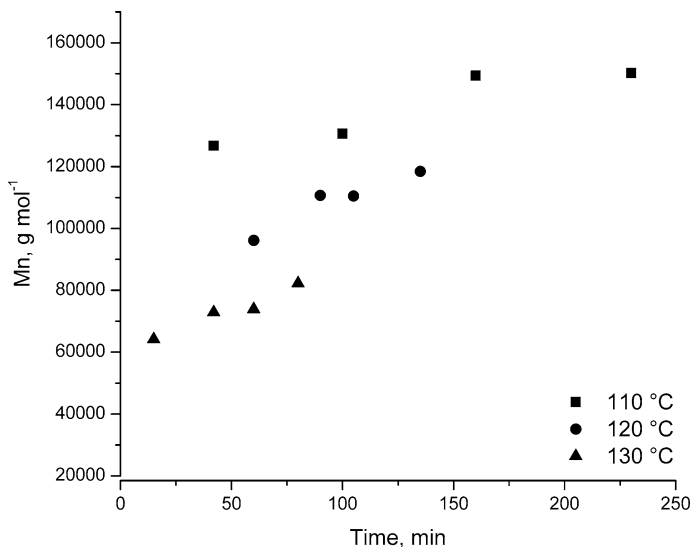
**Fig. 2** Evolution of conversion as a function of reaction time for *S* bulk polymerizations initiated with PDP 0.015 mol L<sup>-1</sup> and without initiator at the temperature range of 110–130 °C



**Fig. 3** Effect of initiator concentration at 130 °C on **a** *S* conversion and **b** average number molecular weights (*M<sub>n</sub>*)

As it is expected for typical radical polymerizations, an increase in initiator concentration from 0.010 to 0.015 mol L<sup>-1</sup> generates a higher polymerization rate (Fig. 3a), allowing us to obtain greater conversions of monomer at the same reaction times. However, the higher content of initiator generates a larger number of radicals responsible for the polymerization initiation, which produces a detrimental in molecular weights of the final products (Fig. 3b).

Figure 4 shows the temperature effect on the number average molecular weight behaviour for *S* bulk polymerizations carried out in the presence of PDP. As it is expected for free radical polymerizations initiated with peroxidic compounds, lower molecular weights are obtained as temperature increases. The results show growing



**Fig. 4** The effect of the polymerization time on the  $M_n$  ( $PDP = 0.015 \text{ mol L}^{-1}$ ) at different temperatures

molecular weights during polymerization reaction at all temperatures. At an initial stage, the species are formed from the combination of growing primary radicals (Scheme 2) giving rise to species with one O–O bond within their structures that subsequently can decompose and re-initiate new polymeric chains. After this initial behaviour, molecular weights increase with polymerization times comparable with those reported for polymerization reactions initiated with DEKTP initiator [12, 15], where in the course of the polymerization several cycles of initiation–propagation–termination reactions take place, allowing the molecular weights to grow simultaneously. Other authors have demonstrated the same results at 110 and 120 °C and a comprehensive mathematical model was presented, simulating the evolution of all chemical species in the course of bulk polymerization [23]. On the other hand, in a conventional radical polymerization, the molecular weights remained without changes during the polymerization process. Also, a constant polydispersity index along the polymerization process at all reaction temperatures was observed. The values in the range between 1.7 and 1.8 showed a low dispersion, and in all cases, they were lower than those obtained for self-initiated process (ca. 2.0).

## Conclusions

The thermolysis reaction of PDP in ethylbenzene solution with and without S addition was studied at different experimental conditions. The reaction follows a pseudo-first-order kinetic law up to at least ca. 60% of diperoxide conversion. At the initial concentrations of the initiator studied, a radical-induced decomposition reaction of PDP may be dismissed.

The addition of S monomer affects the rate constant values, so higher S initial concentration generates an increase in  $k_d$ . The addition of S causes a decrease in the activation parameters ( $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ ). The PDP molecule and also the corresponding transition state can be solvated to different extents when the monomer is present or not, so the increment in  $k_d$  values can be justified attending to a radical trapping mechanism, shifting the equilibrium of the initial decomposition step to the product formation (Scheme 1).

The observed decrease in activation entropy could be explained by the more highly ordered transition state attending to a more efficient solvation by the S in the solvent cage.

Using PDP as initiator in bulk polymerization of S leads to total conversions of monomer in short periods of time (80 min at 130 °C), and the molecular weights increase through the process, which could be explained assuming a gradual decomposition of the bifunctional initiator.

The results presented and analysed in this work allow us to complement the studies focused on the production and characterization of S-based polymeric materials. A complete kinetic and mechanistic study of bifunctional initiator decomposition during the radical polymerization process allows us to obtain important quantitative data that can be used to simulate industrial processes.

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