Diethyl ketone triperoxide: thermal decomposition reaction in chlorobenzene solution and its application as initiator of polymerization

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ABSTRACT: The kinetics of the thermal decomposition reaction of diethyl ketone triperoxide (3,3,6,6,9,9-hexaethyl-1,2,4,5,7,8-hexaoxacyclononane, DEKT) in chlorobenzene solution were studied in the temperature range 99.0–148.0 °C and at initial concentrations of $(1.65–4.97) \times 10^{-2}$ M. The thermolysis of DEKT follows a first-order kinetic law up to at least ca 80% triperoxide conversion. The activation parameter values for the initial O—O bond rupture in chlorobenzene $(\Delta H^{\ddagger} = 134.6 \pm 1.7 \, \mathrm{kJ \, mol^{-1}}; \ \Delta S^{\ddagger} = 4.2 \pm 3.8 \, \mathrm{J \, mol^{-1} \, K^{-1}})$ and the reaction products observed support a stepwise reaction mechanism which includes as a first step the unimolecular homolytic cleavage of one peroxidic bond of the DEKT molecule giving rise to a biradical as intermediate. Additionally, the results obtained were compared with those obtained in toluene, toluene–styrene (50%, v/v) and chlorobenzene–styrene (50%, v/v) solution, showing that the decomposition reaction is strongly solvent dependant. Further, the biradical intermediate obtained in all cases was used to initiate styrene polymerization. It was demonstrated that DEKT can effectively act as initiator in styrene polymerization and its performance is similar to that presented by a multifunctional initiator giving rise to high molecular weight polystyrene at a high reaction rate. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: cyclic organic peroxide; diethyl ketone triperoxide; hexaoxacyclononane; solution kinetics; multifunctional initiator; cyclic peroxide initiator; styrene polymerization; polystyrene

INTRODUCTION

Most commercial vinyl polymers such as polystyrene, polyethylene and poly(vinyl chloride) are produced industrially by means of free radical polymerization, where organic peroxides are usually used as free radical initiators. Cyclic organic di- and triperoxides can decompose thermally by homolytic cleavage of the O—O bond to give an intermediate biradical,[1–4] which in turn initiates the polymerization of vinyl monomers. The radical thus produced is incorporated into the polymer structure yielding polymeric species with embedded peroxide groups that decompose later during the polymerization process. Since the nature of the biradical formed is dependent on peroxide structures and has a profound influence on the final polymer properties, it is important to clarify the initiation mechanism of organic peroxides, in particular di- and triperoxides, which can be considered as multifunctional initiators as a consequence of the two or three active sites of the peroxide molecule. Recently, we have published[5] some results dealing with styrene polymerization in the presence of diethyl ketone triperoxide (3,3,6,6,9,9-hexaethyl-1,2,4,5,7,8-hexaoxacyclononane) (DEKT) in the bulk and in toluene solution.

In this paper, we report a study of the thermal decomposition reaction of DEKT and its application as a trifunctional initiator of styrene polymerization. The kinetic experiments were carried out in chlorobenzene, chlorobenzene–styrene (50%, v/v), toluene–styrene (50%, v/v) and styrene. The selection of chlorobenzene in particular was made taking into account its low transfer constant in a polymerization process $(C_s = 0.56 \times 10^{-4})$ and the value of half-life of the DEKT in that solvent $(t_{1/2} = 5.1 \, \mathrm{h}$ at 130 °C).

## RESULTS AND DISCUSSION

Thermal decomposition of DEKT in solution

We have shown previously[1] that there is a significant solvent effect on the kinetics and activation parameters

corresponding to the thermal decomposition reaction of DEKT in solution in benzene, toluene and benzene–2-propanol (1 : 1, v/v). The unimolecular thermal decomposition reaction of this molecule can be represented by a stepwise homolysis where the rate of ring cyclization within the solvent cage after the initial O—O bond cleavage would be a relatively fast step[6,7] [Eqn (1)]. Thus, the rate-determining step is biradical (dialcoxy radical) formation that further decomposes by either C—C, C—O or O—O bond rupture, originating different final products.

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (1)$$
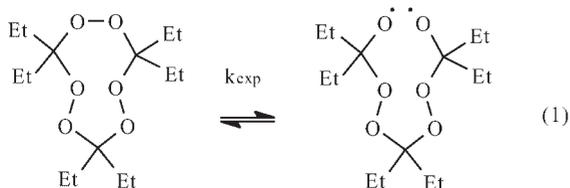
In a previous study (A. I. Cañizo, unpublished work, 2001), it was also demonstrated that the biradical decomposes thermally to form free ethyl radicals that react with the solvent, benzene or toluene, to generate different products such as ethylbenzene, biphenyl or *n*-propylbenzene and bibenzyl, respectively. In this way, this cyclic peroxide can be considered as an important source of ethyl radicals.

The thermal decomposition reaction of DEKT in chlorobenzene solution, at temperature and initial concentration ranges of 99.0–148.0 °C and (1.65–1.76) × 10^{-2} M, respectively, follows a first-order kinetic law up to at least 80% triperoxide conversion. In order to discard a radical-induced decomposition reaction as a competing mechanism, the kinetics of the DEKT thermal decomposition reaction in chlorobenzene solution were studied at 135.0 °C with a higher initial peroxide concentration (4.97 × 10^{-2} M) (Table 1). The results of the experiments show that the rate constant values are practically independent of the initial DEKT concentration. Hence it can be assumed that, under the experimental

conditions employed in this study, there are no contributions from second-order processes inducing the decomposition of the triperoxide, either at higher conversions (ca three half-lives) or at higher initial DEKT concentration. Therefore, the observed rate constant values (Table 1) can be ascribed to the unimolecular initial step of DEKT thermolysis [Eqn (1)].

The reaction products in chlorobenzene detected by gas chromatography were diethyl ketone, ethane, butane, 4,4′-dichloro-1,1′-biphenyl, 1-chloro-3-ethylbenzene, 1-chloro-4-ethylbenzene, 1-chloro-2-ethylbenzene and methyl propionate. These reaction products can be interpreted in terms of the initial O—O bond homolytic rupture to give the corresponding biradical [Eqn (1)]. This biradical can reform the DEKT molecule or undergo either a C—O, C—C or O—O bond cleavage. Quantitative analysis of 3-pentanone, generated by C—O bond ruptures, shows a molar yield of 0.27 mol per mole of DEKT decomposed. Ethyl radicals derived from C—C bond ruptures can abstract a hydrogen atom from the solvent to give ethane and other products by combination of free radicals (1-chloro-3-ethylbenzene, 1-chloro-4-ethylbenzene, butane, 4,4′-dichloro-1,1′-biphenyl). Product analysis confirms that the C—C bond rupture to give ethyl radicals makes an important contribution to the decomposition of the biradical. The presence of methyl propionate can be assumed to be a result of C—C and O—O bond ruptures coming from the former biradical [Eqn (1)] to generate a propionate radical. Oxygen and carbon dioxide probably are also formed as reaction products but the instrumental methods used made it impossible to detect them (see Experimental). At present, quantitative analysis of the reaction products is insufficient for the complete elucidation of the thermolysis mechanism of DEKT in chlorobenzene solution, and further work is in progress.

Nevertheless, the temperature effect on the rate constant values (k_{exp}) for the unimolecular reaction [Eqn (1)] can be represented by the Arrhenius equation. The

Table 1. First-order rate constants for DEKT decomposition in chlorobenzene solution

Temperature (°C)	[DEKT]^a (10^{-2} M)	k_{exp} (10^{-5} s^{-1})	Experimental points^e	DEKT conversion (%)	r^f
99.0	1.65	0.167	5	26	−0.990
118.0	1.65				
		0.925^d	9	80	−0.994
	1.76				
135.0	1.65^b	7.44^d	9	52	−0.998
	1.76^c			80	
	4.97^b	7.84	5	50	−0.988
148.0	1.65				
		28.0^c	9	78	−0.990
	1.76				

^{a} Initial DEKT concentration.
^{b} Naphthalene 0.7% as internal standard.
^{c} Decalin 0.12% as internal standard.
^{d} Average k_{exp} values with 1.65 × 10^{-2} and 1.76 × 10^{-2} M as initial DEKT concentration.
^{e} Number of experimental point obtained for the kinetic curve.
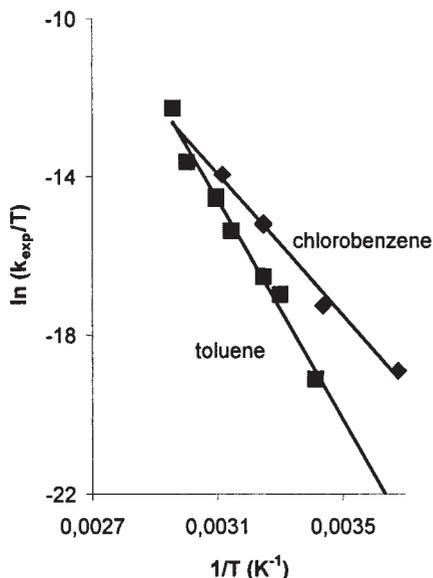^{f} r = correlation coefficient from Arrhenius equation.

Figure 1. Eyring plot corresponding to the thermal decomposition reaction of DEKT in chlorobenzene and toluene solution

corresponding activation parameters can be deduced from the Eyring plot (Fig. 1) and the kinetic data for the thermal decomposition reaction of DEKT in toluene solution obtained in previous studies (Ref. 1 and A. I. Cañizo, unpublished work, 2001) were included. The representation in Fig. 1 is linear ($r = 0.996$) over a relatively wide temperature range (ca 49 °C), which suggests that the activation parameters (Table 2) belong to a single process, which corresponds to the unimolecular homolysis of the DEKT molecule [Eqn (1)]. The errors shown in Table 2 are standard deviations from a least mean squares treatment[8,9] of the kinetic data.

The marked solvent effect observed[1] on the unimolecular decomposition reaction of the DEKT molecule is confirmed once again with the results obtained in other polar solvents such as chlorobenzene and solvent–styrene mixtures. In neat solvent both activation parameters (enthalpy and entropy of activation) decrease when the solvent polarity increases (Table 2); this effect is the 'compensation effect'. The initial state of the DEKT molecule, and also the corresponding activated complex, is solvated to different extents depending on the solvating power of the solvent used. In this case we postulate the existence of a rather dipolar activation complex in comparison with the initial state. As a consequence of differential solvation, in more polar solvents the reaction is accelerated (k_{exp} in chlorobenzene is three times higher than that in toluene) because of higher solvation of the activation complex. A more highly ordered activated complex results because of the presence of some kind of association with the solvent molecule resulting in a more rigid species. Therefore, the observed activation entropy values are lower in polar solvents, reflecting the decrease in the degrees of freedom of the molecules.

On the other hand, when the thermal decomposition reaction of DEKT was carried out in styrene–chlorobenzene or styrene–toluene mixtures (Table 2), it could be observed that the reactivity of DEKT in the presence of styrene is higher when the organic solvent is toluene, in contract to the behavior observed in neat solvents. Again, it is evident that solvent effects are closely related to the nature and extent of solute–solvent interactions developed locally in the immediate vicinity of the solutes. When the same decomposition reaction is evaluated in pure styrene, the rate constant (k_{exp}) reaches the highest value, probably owing to the fast reaction that takes place between the biradical initially formed [Eqn (1)] and styrene molecules, which are excellent radical scavengers. The multifunctional character of the initiator makes the polymerization reaction rate increase as a consequence of successive initiation–propagation–termination reactions during the course of the polymerization process. In this scenario, polymerization of styrene in the presence of DEKT is analyzed on the basis of the initial step previously proposed that includes the presence of a biradical initiating species (Scheme 1).

## Polymerization of styrene in the presence of DEKT

The effect of solvent on the monomer conversion and polymer molecular weight was studied using DEKT as initiator and the behavior of this cyclic peroxide in styrene solution polymerization was also evaluated. The temperature employed was 130 °C because at this temperature and in toluene solution, it was previously

Table 2. Kinetic and activation parameters for DEKT thermal decomposition in different solvents

Solvent	$t_{1/2}$ (h)	$k_{exp}^{130\,°C}$ (10^{-5} s^{-1})	R_p (10^{-3} mol l^{-1} s^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})[a,b]	$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})[a,b]
Styrene	0.13	153	7.5	n.a.	n.a.
Styrene–toluene (50%, v/v)	0.34	56.5	7.2	n.a.	n.a.
Toluene[1]	14.8	1.3	n.a.	203.6 ± 6.3 (48.7)	169.3 ± 14.2 (40.5)
Styrene–chlorobenzene (50%, v/v)	0.41	46.8	3.8	n.a.	n.a.
Chlorobenzene	5.1	3.8	n.a.	134.6 ± 1.7 (32.2)	4.2 ± 3.8 (1.0)

[a] Standard deviation from a least mean squares data treatment.
[b] In parentheses, activation parameters expressed in kcal mol^{-1} or cal mol^{-1} K^{-1}, respectively (1 kcal = 4.184 kJ).
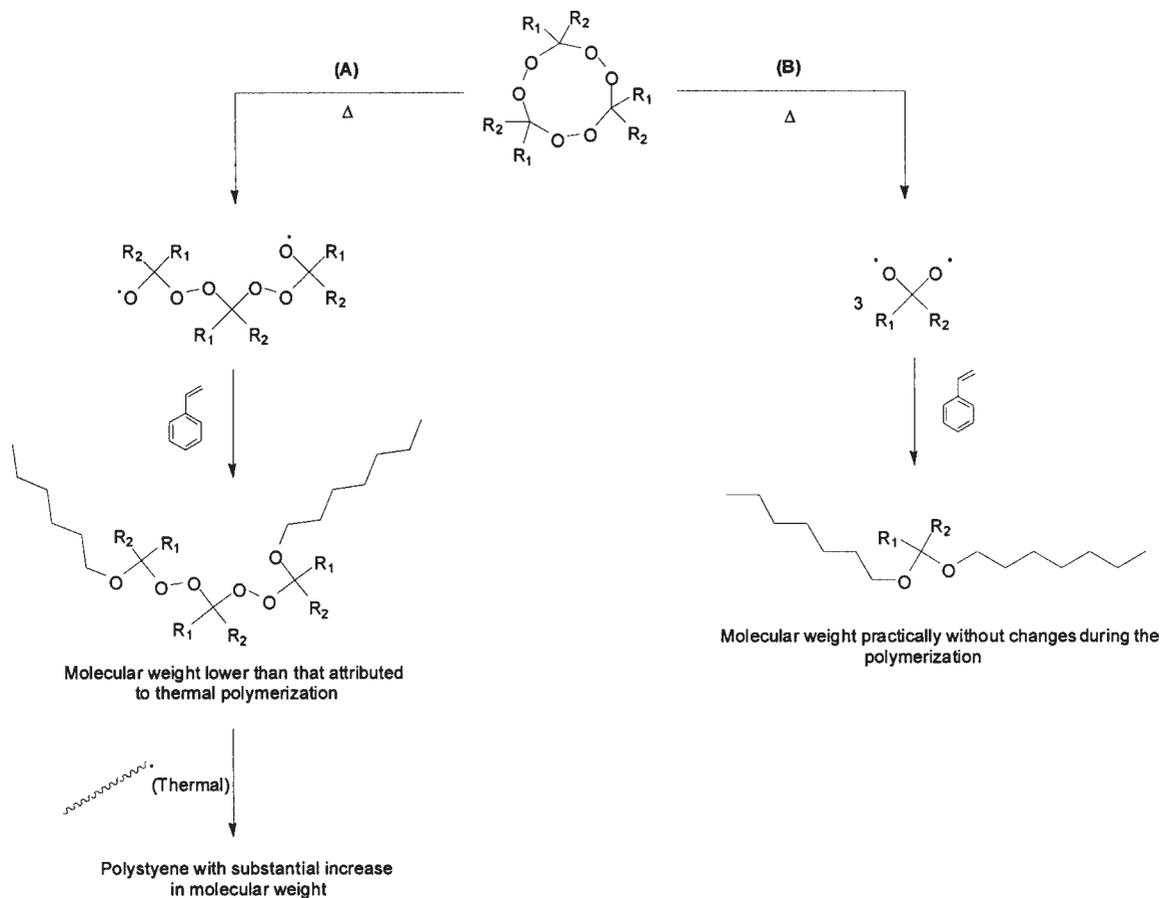
Scheme 1. Different routes proposed for the decomposition of DEKT and characteristics of the polymers obtained

demonstrated that this initiator can act as a multifunctional initiator.[5] One of the potential advantages of using multifunctional initiators, such as that proposed in this study, is that a high polymer molecular weight and a high polymerization rate can be obtained simultaneously by controlling the initiator decomposition rate through optimal reactor temperature programming, leading to better control of the radical concentration through sequential decomposition of labile groups (Scheme 1, route A) of different thermal stabilities. For free radical polymerization with monofunctional initiators, the reaction rate depends on the initiator concentration and the polymerization is of order 0.5 with respect to initiator concentration. The presence of additional labile groups in multifunctional initiators makes the polymerization kinetics very complicated, because labile groups such as peroxide become redistributed repeatedly in the growing and inactive polymers and they are engaged in further initiation, propagation, chain transfer and termination reactions during the course of polymerization.

From Fig. 2, it can be seen that whether the polymerization takes place in bulk or in solvent–styrene mixtures, the initiator efficiently initiates the polymerization of styrene if curves b, c and d are compared with curve a, which corresponds to the autoinitiated polymerization.

Moreover, the polymerization rates in bulk or solution are higher than that obtained for the spontaneous process.

Nevertheless, when the conversion values and, in consequence, the polymerization rates in chlorobenzene and toluene are compared, it can be observed that conversion is lower in chlorobenzene than toluene (Fig. 2). This behavior is in accord with the observed half-lives of DEKT in each solvent ($t_{1/2} = 14.8\,h$ in toluene and $5.1\,h$ in chlorobenzene) and is reflected in an increase in the polymerization rate (R_p) in toluene–styrene mixtures (Table 2).

When the evolution of molecular weight with polymerization time is considered (Fig. 3), there is clear evidence that supports the solvent participation in the initiating step. The molecular weight of the polymers obtained in chlorobenzene are of the order of $1.7 \times 10^5\,g\,mol^{-1}$ with a polydispersity index (M_w/M_n) of <2, values which are slightly higher than those obtained in the presence of toluene.

With respect to the bulk polymerization, the conversion values reached are greater than those in toluene or chlorobenzene, as expected in a mass polymerization process. Otherwise, the molecular weight values present a singular behavior, as can be observed from Fig. 3 where molecular weight increases with polymerization time in a
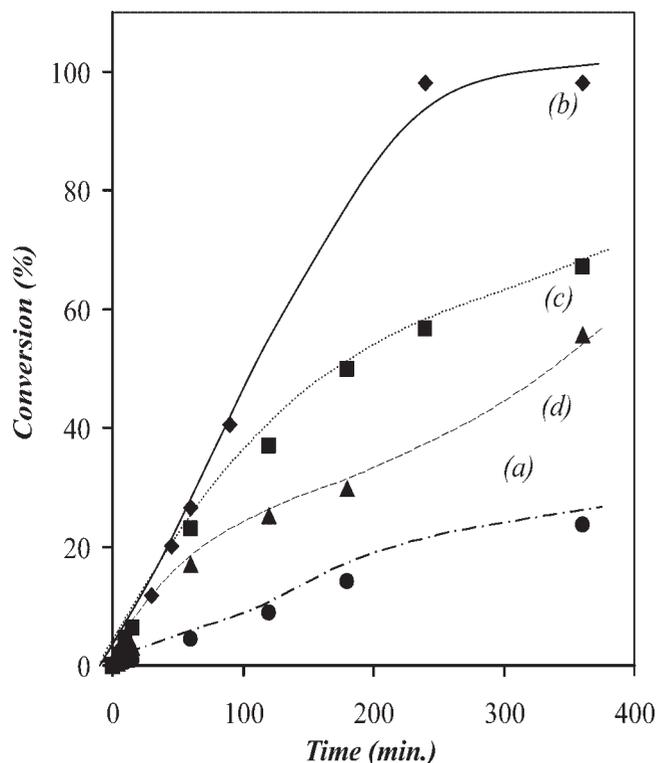
Figure 2. Evolution of conversion as a function of polymerization time for (a) thermal, (b) bulk, (c) toluene and (d) chlorobenzene polymerization of styrene using DEKT as initiator
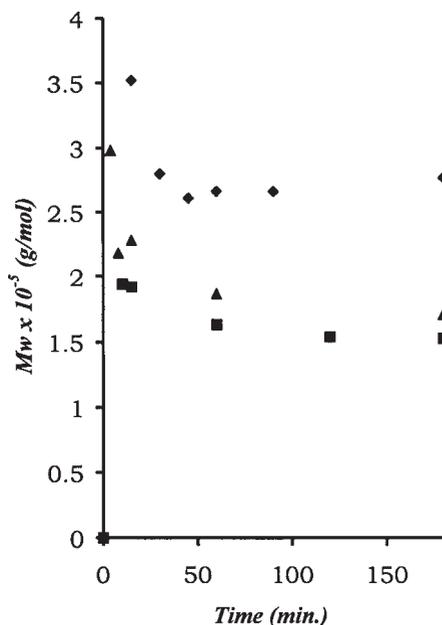

Figure 3. Evolution of M_{w} as a function of time for styrene polymerization in different solvents: ◆, bulk; ■, toluene; ▲, chlorobenzene

bulk process. This last situation is typical of a polymerization reaction initiated by a multifunctional initiator where in the course of the polymerization several cycles of initiation–propagation–termination reactions take place, allowing the conversion and molecular weights to increase simultaneously, contrary to a 'classical' radical process where an increase in conversion, due to an increase in radical concentration, leads to a decrease in molecular weight of the final products. Moreover, the high molecular weights observed in the first step of the polymerization are associated with species that result from the combination of growing primarily radicals giving rise to species with two O—O bonds within their structures that subsequently can decompose and initiate new chains. The intermediate species formed from the beginning of the reaction has recently been isolated by G. Morales and co-workers (to be published). This fact supports the postulated mechanism where the unimolecular homolysis of peroxide is the rate-determining step and the existence of that biradical species is responsible for the initiation step in polymerization reactions as described above.

CONCLUSIONS

The thermolysis of DEKT in chlorobenzene solution follows a first-order kinetic law up to at least ca 80% triperoxide conversion.

Under the experimental conditions described here, a radical-induced decomposition reaction as a competing mechanism with the decomposition of DEKT may be dismissed, so the activation parameters correspond to the unimolecular thermal decomposition reaction of the DEKT molecule.

Analysis of the reaction products is insufficient to elucidate the real mechanism of the thermolysis of the diethylketone triperoxide, but studies are in progress to clarify it.

DEKT can effectively act as an initiator in styrene polymerization and its performance is similar to that presented by a multifunctional initiator leading to polymers with high molecular weight at a high reaction rate compared monofunctional initiated polymerization.

Values of the conversion and molecular weight of the polymers obtained strongly depend on the solvent used and the polymerization conditions. It was observed that the DEKT initiator efficiency decreases in chlorobenzene.

EXPERIMENTAL

Materials. DEKT was prepared by methods described elsewhere[10,11] and its purity was checked by GC, FTIR (KBr), ^{13}C NMR, ^{1}H NMR and TLC. **Caution**: DEKT must be handled with care because it can be detonated by shock. Chlorobenzene (Mallinckrodt, AR grade) was purified by standard techniques[12] (b.p. 132–133 °C). Sublimed naphthalene (Mallinckrodt, AR grade) or decalin was employed as an internal standard in quantitative

determinations of DEKT concentration and the 3-pentanone concentration was determined by GC. Styrene (Aldrich) was distilled over sodium under vacuum and kept in refrigeration until use.[13]

Kinetic methods. Pyrex glass ampoules (10 cm long × 6 mm o.d.) half filled with DEKT solution and spiked with naphthalene or decalin as an internal standard were thoroughly degassed under vacuum at −196 °C and then sealed with a flame torch. To perform the runs, the ampoules (5–8 at each temperature) were immersed in a thermostated silicone oil-bath (± 0.1 °C) and withdrawn after predetermined times. The reaction was stopped by cooling to 0 °C. The concentrations of DEKT remaining in the solution and the reaction products were determined by quantitative GC analysis in a 3% SE-30 column (silicone gum rubber stationary phase on Chromosorb-W, 1/8 in o.d. stainless steel) installed in a Konik-2000 C gas chromatograph with nitrogen as carrier gas and flame ionization detection. The reaction products were identified by GC–MS analysis.

The corresponding first-order rate constants were calculated from the slope of the line obtained by plotting the values of ln[DEKT] aganist reaction time. The corresponding activation parameters were deduced from the Eyring equation and the errors were determined using a least mean squares data treatment.[8,9]

Polymerization experiments. The syntheses of different polystyrenes were carried out by dissolving the appropriate amount of DEKT in styrene–chlorobenzene (50%, v/v) and equal amounts of the resulting solution were placed in glass tubes. The tubes were evacuated, sealed and kept at 130 °C for 4, 6, 8, 10, 15, 60, 120, 180 and 360 min. The conversion in the pure thermal polymerization of styrene was measured under the same experimental conditions. Experiments in bulk were also evaluated for comparison with the results obtained in solution polymerization. After the predetermined poly-merization time, the polymer samples were dissolved in THF and precipitated by adding excess methanol, dried *in vacuo* and the monomer conversion was measured gravimetrically. The molecular weight and molecular weight distribution of polystyrene were determined by GPC using THF as a solvent.

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