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ORIGINAL PAPER

Thermal decomposition of 3,3,6,6,9,9-hexaethyl-1,2,4,5,7,8-hexaoxacyclononane in solution and its use in methyl methacrylate polymerization

Gastón P. Barreto · Gladys N. Eyler

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Abstract The kinetics of the thermal decomposition reaction of diethylketone triperoxide (3,3,6,6,9,9-hexaethyl-1,2,4,5,7,8-hexaoxacyclononane, DEKTP) in ethylbenzene solution were studied in the temperature range of 120.0–150.0 °C and at an initial concentration range of 0.01–0.10 M. This peroxide was used as a new initiator in methyl methacrylate (MMA) polymerization process at high temperatures (110.0–140.0 °C) in ethylbenzene solution. The effects of initiator concentration and reaction temperature on the polymerization rate were investigated in detail. Thus, activation parameters of the solution polymerization process ($\Delta E_d^* = 83.3$ kJ mol^{-1} and $\Delta E_p^* - \Delta E_t^*/2 = 54.0$ kJ mol^{-1}) will be obtained. DEKTP can effectively act as initiator in MMA polymerization and its performance is similar to that presented by a multifunctional initiator resulting in high-molecular weight polymethylmethacrylate with a high reaction rate.

Keywords Cyclic organic peroxide · Solution polymerization · Methyl methacrylate

Introduction

Cyclic organic peroxides have acquired great importance through the years because of the unusual reactivity of the O–O bond linkage, whose decomposition in free radicals make them applicable in polymerization, an essential operation in the production of synthetic polymers.

G. P. Barreto (✉) · G. N. Eyler
Laboratorio de Química, Dpto. Ingeniería Química, Facultad de Ingeniería, Universidad Nacional
del Centro de la Provincia de Buenos Aires, Avda. del Valle 5737, B7400JWI Olavarría,
Buenos Aires, Argentina
e-mail: gbarreto@fio.unicen.edu.ar

In recent years, there has been a great interest in the use of multifunctional initiators in radical polymerization of vinyl monomers. The benefits of these initiators include increased polymerization rate and the production of molecular weights that are either identical in magnitude or higher than those obtained from mono-functional initiators [1–4].

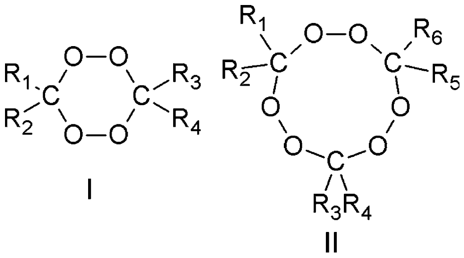
In previous research, solvent effect analyses of thermal decomposition reactions of cyclic peroxides of substituted 1,2,4,5-tetraoxacyclohexane and 1,2,4,5,7,8-hexaoxacyclononane families (I and II respectively, Scheme 1) have been evaluated [5–7]. On the other hand, it has been demonstrated that these cyclic diperoxides and triperoxides are good initiators of polymerization.

Most papers focus their attention on polymerization kinetic parameters and product properties and there is little information about initiator kinetic and decomposition mechanism behavior.

It has been studied that the ozonolysis products of tetramethylethene (3,3,6,6-tetramethyl-1,2,4,5-tetraoxacyclohexane, structure I where $R_1 = R_2 = R_3 = R_4 = –CH_3$, DADP; 3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexaoxacyclononane, structure II where $R_1 = R_2 = R_3 = R_4 = R_5 = R_6 = –CH_3$, and other oligomers of the acetone carbonyl oxide) generate radicals which are useful in the polymerization of vinyl monomers such as methyl methacrylate (MMA) [8].

When 3,6,9-triethyl-3,6,9-trimethyl-1,2,4,5,7,8-hexaoxacyclononane (structure I where $R_1 = R_3 = R_5 = –CH_3$ and $R_2 = R_4 = R_6 = –CH_2CH_3$) was employed as initiator in styrene (sty) bulk polymerization process [3], it was possible to produce polymers with higher molecular weights and narrower molecular weight polydispersity at a higher rate. The same results were found when the initiators used for sty polymerization were 3,6-di-t-butyl-3,6-dimethyl-1,2,4,5-tetraoxacyclohexane (structure I where $R_1 = R_3 = –CH_3$ and $R_2 = R_4 = –C(CH_3)_3$, PDP) and 3,3,6,6,9,9-hexaethyl-1,2,4,5,7,8-hexaoxacyclononane (structure II where $R_1 = R_2 = R_3 = R_4 = R_5 = R_6 = –CH_2CH_3$, DEKTP) [4]. Two possible routes for decomposition and initiation have been proposed for cyclic peroxides.

In last years, different studies have been carried out in this laboratory focusing on kinetics studies of the thermal decomposition of some cyclic organic peroxides during radical polymerization of sty. This monomer has a high incidence of self-initiated thermal polymerization in the temperature range of 100–150 °C in the polymerization process when carried out using cyclic organic peroxides as initiators. However, for MMA, thermal polymerization self-initiated is lower than for sty at experimental working temperatures.



Scheme 1 Structures of cyclic organic peroxides

The aim of this study is to investigate the thermal decomposition of DEKTP in ethylbenzene (a good solvent in different industrial polymerization processes), and evaluate the DEKTP use as a trifunctional initiator for MMA radical polymerization in ethylbenzene solution. Preliminary results of this study were published [9].

Experimental

Materials

DEKTP was prepared following methods described in the literature [10]. Synthesis: 5.6 mL (50 mmol) of 3-pentanone was added drop wise (15–20 drops per minute) to a stirring mixture of 4.6 mL (56 mmol) of hydrogen peroxide (30%) and 10.4 mL of sulfuric acid (70% v/v) at −15 to 20 °C. After a 3-h reaction, the mixture was extracted with purified light petroleum ether (3 × 25 mL). The organic layer was freed of excess hydrogen peroxide with saturated ammonium chloride (3 × 10 mL) and water washings (3 × 10 mL) and then dried over anhydrous sodium sulfate for ca. 24 h. The solution was evaporated at room temperature and the residue was left ca. 20 h in a desiccator. The white solid obtained was recrystallized twice from boiling methyl alcohol and its purity was checked by gas chromatography (GC). *Caution*: DEKTP must be handled with care because it can be detonated by shock.

Ethylbenzene (Fluka, purum grade) was shaken with concentrated H_2SO_4 until a fresh portion of acid remained colorless, then washed with aqueous 10% NaOH, followed by distilled water until neutral. Then it was dried with sodium and fractionally distilled from sodium. MMA (Fluka, purum grade) was washed with 10% sodium hydroxide solution and then with distilled water several times to remove inhibitor. It was dried over anhydrous Na_2SO_4 and distilled under reduced pressure. Methanol (Anal Quim, PA grade) for polymer precipitation was treated with Na_2–EDTA, filtered, and dried over anhydrous $CaCl_2$. Then it was distilled before use.

Polymerization experiments

Solution polymerization of MMA in the presence of DEKTP was carried out at a temperature range between 110 and 140 °C. The monomer concentration employed was 1 M and the DEKTP concentration range from 0.005 to 0.1 M. Pyrex glass ampoules (0.1 m length × 0.006 m external diameter) were filled with prepared solutions, degassed under vacuum at −196 °C and then sealed with a flame torch. The ampoules were immersed in a thermostat silicone oil bath and taken out after required period times. The reaction was stopped by cooling to 0 °C. The conversions of DEKTP and MMA were determined by quantitative GC analysis.

Bulk polymerization of MMA was carried out in bigger ampoules (0.1 m × 0.01 m internal diameter) following the same procedure for their degassing and sealing. The polymeric products were precipitated adding dropwise over methanol, filtered, and dried under vacuum at room temperature. Monomer conversions were determined by gravimetric procedure.

Analytical techniques

GC analyses were performed on a Konik KNK 2000 C with a 30 m 0.32 mm i.d., 0.25 μm film thickness, DB-5 (5% biphenyl, 95% dimethylpolysiloxane) capillary column. Nitrogen was used as carrier gas at a constant pressure of 23.5 psig at the head of the column. The linear velocity through the column was 29.4 cm s^{-1} at 60 °C. The injector operated in the split mode at 150 °C, flame ionization detector at 250 °C, with nitrogen as the make-up gas (30 mL min^{-1}). The oven temperature was maintained at 80 °C for 5 min then programed at 20 °C min^{-1} to 160 °C for 10 min.

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

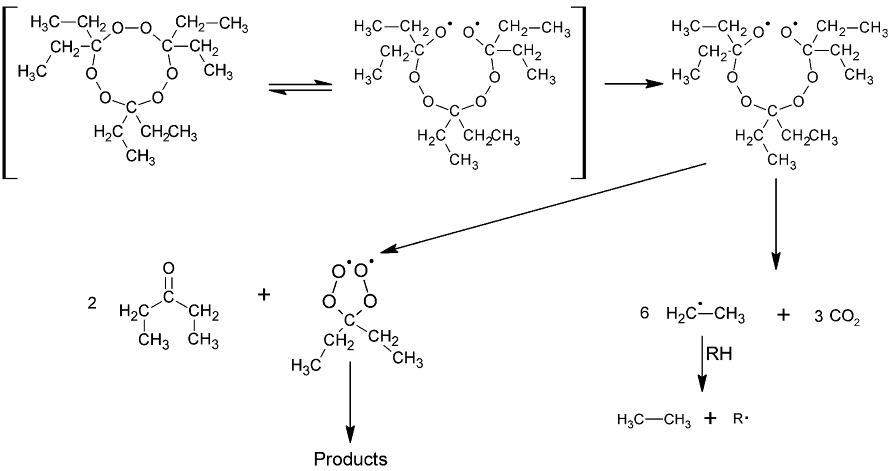
The reaction products were determined by GC–MS analysis in a Rtx-5MS capillary column (5% biphenyl–95%dimethyl polysiloxane, 30 m, 0.25 mm i.d., 0.25 μm film thickness), installed in a Thermo Quest Trace 2000 CG model gas chromatograph with helium as carrier gas (0.5 mL min^{-1}) and injection port at 150 °C in split mode (split ratio: 1:33, split flow: 33 mL/min). The detection was carried out with a Finnigan Polaris Ion trap MS with transfer line at 275 °C and ion source at 200 °C. The experiments were carried out under the same programed temperature conditions as in the quantitative GC analysis.

Results and discussion

DEKTP thermal decomposition in ethylbenzene solution

It is recognized that DEKTP decomposes thermally in solution by homolytic cleavage of one O–O bond to generate an intermediate biradical that can then decompose by C–O and C–C bond scissions [6, 7, 11] (Scheme 2).

The thermolysis of DEKTP 0.01 M follows a first-order kinetic law (Fig. 1) up to at least 65% peroxide conversions at all temperatures (120.0–150.0 °C). In order to discard a radical-induced reaction as a competing mechanism, the kinetic of the DEKTP thermal decomposition reaction at 130.0 °C was studied with higher initial peroxide concentrations ($k_{d,[DEKTP]=0.01\ M} = 1.20 \times 10^{-5}\ s^{-1}$, $k_{d,[DEKTP]=0.05\ M} = 1.21 \times 10^{-5}\ s^{-1}$, and $k_{d,[DEKTP]=0.1\ M} = 1.63 \times 10^{-5}\ s^{-1}$). The results show that the rate constant values slightly change. So, it can be assumed that, under the experimental conditions employed in this study ([DEKTP] $\cong$ 0.01 M), there are no contributions from second-order processes inducing the decomposition of the triperoxide. However, there are reactants like DADP whose empirical rate constant of decomposition increases with an increase in the peroxide concentration in solution [12]. Therefore, the observed rate constant values can be ascribed to the unimolecular initial step of DEKTP thermolysis.



Scheme 2 DEKTP thermal decomposition

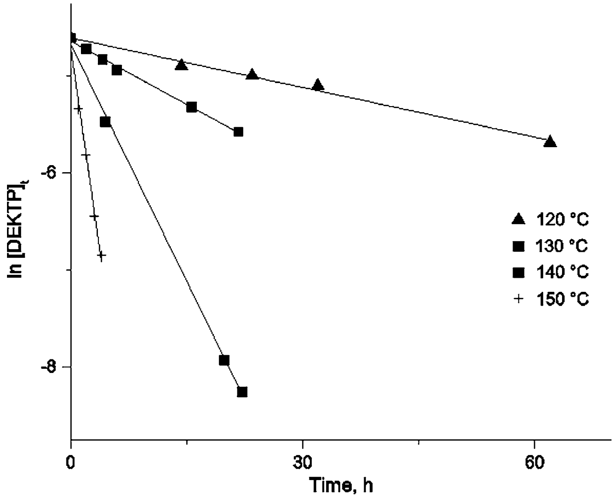


Fig. 1 Kinetic plots for DEKTP thermal decomposition in ethylbenzene solution at different temperatures

The rate constant of the thermal decomposition reaction increases with an increase in the solvent polarity [from ethylbenzene to chlorobenzene; i.e. $k_{\mathrm{chlorobenzene}}/k_{\mathrm{ethylbenzene}}$ (at 130 °C) = 3.17] (Table 1). On the other hand, the activation parameter values $\Delta H^{\#}$ and $\Delta S^{\#}$ corresponding to the homolytic dissociation of the O–O bond of DEKTP decrease with the solvent polarity increase. Both parameter values for ethylbenzene are higher than for chlorobenzene.

The temperature effect on the dissociation rate constant values for the unimolecular reaction can be represented by the Arrhenius equation

Table 1 Activation parameters for DEKTP 0.01 M thermal dissociation in different reaction media

Reaction media	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (J mol^{-1} K^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})	$k_{\mathrm{d},\ 130\ ^\circ\mathrm{C}}$ × 10^5 (s^{-1})	References
Ethylbenzene	158.2 ± 4.6[a]	51.9 ± 10.9[a]	137.7 ± 4.6[a]	1.2	This work
Chlorobenzene	134.6 ± 1.7[a]	4.2 ± 3.8[a]	132.9 ± 4.6[a]	3.8	[11]
Ethylbenzene/ MMA 0.1 M	–	–	–	1.3	This work
Ethylbenzene/ MMA 1 M	79.9 ± 1.7[a]	−137.3 ± 4.2[a]	134.8 ± 1.7[a]	2.3	This work
Ethylbenzene/ sty 0.15 M	–	–	–	1.2	Cerna et al. (2010, unpublished)
Styrene	48.1 ± 1.7[a]	−187.5 ± 4.6[a]	123.9 ± 1.7[a]	79.5	Cerna et al. (2010, unpublished)

[a] Standard deviations from a least mean square treatment of the kinetic data

$$\ln k_{\mathrm{d}} = (37.0 \pm 2.6) - (161.4 \pm 1.1)\frac{1}{RT}$$

The corresponding activation parameters can be deduced from the Eyring plot (Fig. 2). The representation corresponding to ethylbenzene solution systems in Fig. 2 is linear ($r = 0.9959$) over a relatively wide temperature range (ca. 30 °C), suggesting that the activation parameters (Table 1) belong to a single process, which corresponds to the unimolecular homolysis of the DEKTP molecule (Scheme 2).

It has been studied that the products obtained from thermal decomposition of DEKTP in solution (Table 2) can be interpreted in terms of initial O–O bond

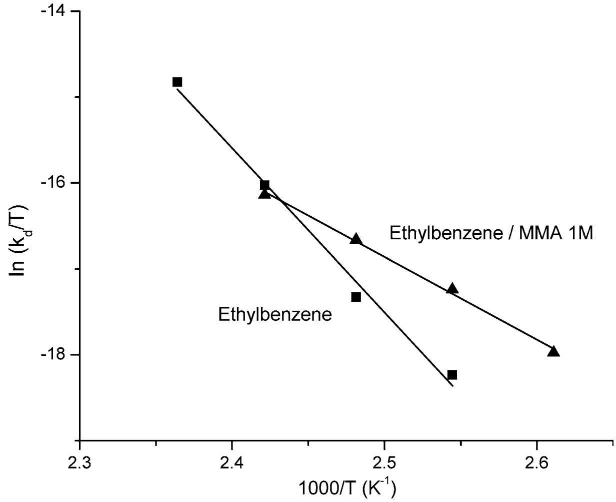


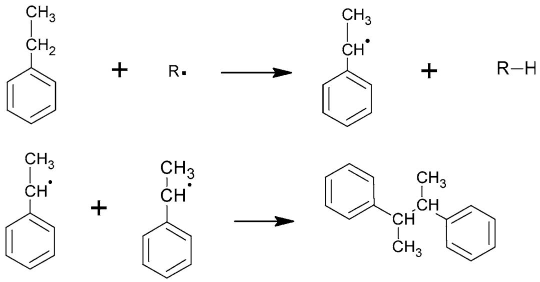
Fig. 2 Eyring equation plots for the unimolecular thermal decomposition reaction of DEKTP in ethylbenzene solution and in the presence of MMA

Table 2 Main products of the thermolysis of DEKTP in solution at 150.0 °C (molar yields)

Solvent	Product	References
Benzene	DEK (0.12), ethylbenzene (0.31), biphenyl (0.32), ethane[a], butane[a]	[10]
Toluene	DEK (0.06), bibenzyl (0.95), *n*-propylbenzene (0.48), ethane[a], butane[a], benzyl alcohol[a], benzaldehyde[a], 1-methyl-4-(phenylmethyl)-benzene[a].	[10]
Ethylbenzene	2,3-Diphenylbutane[a] 1,3-Diphenylbutane[a] 1-Phenyl-1-phenylethylethane[a] Ethane[a]	This work

[a] Qualitative identification

Scheme 3 Mechanism formation of 2,3-diphenylbutane



homolysis, which can be followed by either C–O bond cleavage, producing diethylketone, and a diperoxy radical (3,3-diyldioxy-pentane), or C–C bond cleavage, resulting mainly in ethyl radicals. These in turn can abstract a hydrogen atom from solvent to give ethane and radicals derived from the solvent [7]. In ethylbenzene solution the most abundant product found was 2,3-diphenylbutane, agreeing with a hydrogen abstraction from solvent and subsequent radicals combination (Scheme 3).

DEKTP thermal decomposition in ethylbenzene with the addition of MMA

The effect of MMA addition on DEKTP dissociation rate was studied adding different monomer initial concentrations to ethylbenzene solutions at 130 °C. As can be seen in Table 3, the addition of MMA affects the dissociation rate of DEKTP so that a higher MMA initial concentration generates an increase in DEKTP dissociation rate constant (k_d in ethylbenzene with the addition of MMA 1 M is two times higher than that in neat ethylbenzene), which corresponds to the determinant kinetic step in the initiation of MMA solution polymerization.

However, when the MMA concentration is 0.1 M, the rate constant value is similar to the one obtained in neat solvent. These results can be compared with those reported for the sty monomer [11]. In this case, when low concentrations of sty are employed, variations in the values of the rate constant are not observed (Table 1).

The activation energy values (ΔE_d*) of the decomposition reaction in ethylbenzene decrease when the decomposition takes place in the presence of MMA 1 M

Table 3 Effect of MMA initial concentration on DEKTP dissociation rate constants at 130 °C

$[DEKTP]_0$ (mol L^{-1})	$[MMA]_0$ (mol L^{-1})	$k_d \times 10^5$ (s^{-1})
0.01	0.035	1.29
	0.1	1.30
	0.5	1.45
	1	2.34
0.05	0.05	1.42
	0.27	1.57
	0.5	1.77

Table 4 Apparent polymerization constant values of MMA 1 M and dissociation rate constants of the initiator using different initial concentrations of DEKTP at different temperatures

Temperature (°C)	[DEKTP] (mol L^{-1})	$k_d \times 10^5$ (s^{-1})	k_{ap} x 10^4, $L^{1/2}$ $mol^{-1/2}$ s^{-1}	Conversion (%)
110	0.01	0.60	6.7	32.45
	0.1		10.3	21.17
120	0.01	1.28	8.7	27.02
	0.05		7.3	16.91
	0.1		9.2	35.57
130	0.01	2.34	12.9	37.77
	0.05		14.0	31.18
	0.1		15.4	45.58
140	0.01	4.03	18.1	30.12

(Tables 4 and 5). When DEKTP thermal decomposition is carried out in pure ethylbenzene the ΔE_d* is 161.4 kJ mol^{-1}, while in the presence of MMA 1 M the value that is obtained is 83.3 kJ mol^{-1}. The differences found show the importance of determining kinetic parameters of initiator during the polymerization process instead of employing reported data on different pure solvents.

The addition of MMA causes a decrease in the activation parameters (enthalpy and entropy of activation) (Table 1). In this case, the initial state of DEKTP molecule, and also the corresponding activated complex, is solvated to different extents depending on the solvating power of the solvent (or solvent mix) used. As a consequence of differential solvation, in more polar media the decomposition reaction is accelerated because of higher solvation of the activated complex. Therefore, the observed decrease in activation entropy could be explained by the existence of a more highly ordered activated complex because of the presence of interactions with MMA molecules resulting in a more stable species.

When the reaction is carried out in pure sty [11], DEKTP reactivity increases 66 times, and smaller values of both enthalpy and entropy of activation are observed compared with those obtained for DEKTP decomposition in pure ethylbenzene (Table 1).

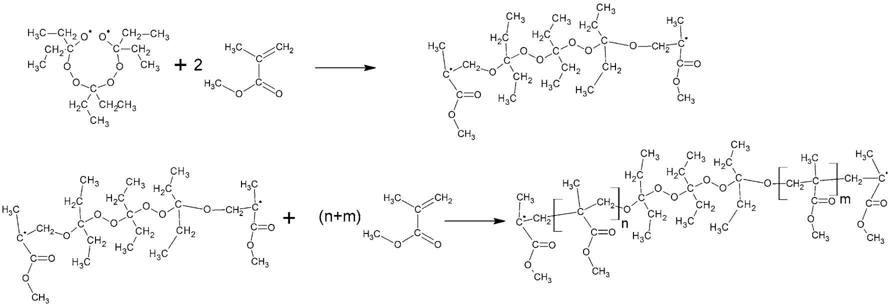
On the other hand, the results obtained from the analysis of products by GC/MS showed that the most abundant product identified for DEKTP decomposition in pure ethylbenzene (2,3-diphenylbutane) is not present when MMA is added. This

Table 5 Values of ΔE_d* and $\Delta E_p^* - \Delta E_t^*/2$ obtained for the studied system (DEKTP 0.01 M/MMA 1 M in ethylbenzene) and other relevant data in the literature

Solvent	Initiator	ΔE_d* (kJ mol^{-1})	$\Delta E_p^* - \Delta E_t^*/2$ (kJ mol^{-1})	ΔE* (kJ mol^{-1})	References
Ethylbenzene	DEKTP	83.3	12.5	54.0	This work
Benzene	DMDM[a]	–	11.3	–	[13]
Benzene	AIBN[b]	123.4	15.1	76.6	[13]
Dioxane	AIBN	–	14.2	–	[14]

[a] *p*,*p*′-dimethoxydiphenyldiazomethane

[b] 2,2′-Azobisisobutyronitrile



Scheme 4 MMA addition to initial biradical formed from DEKTP thermal decomposition

supports the fact that the radicals formed initially do not participate in the hydrogen abstraction to solvent but react with the MMA, possibly producing the primary radical of polymerization process (Scheme 4).

Solution polymerization of MMA employing DEKTP as initiator

Ethylbenzene solution polymerization of MMA 1 M experiments were carried out employing different concentrations of DEKTP (0.005, 0.01, 0.05, and 0.1 M). In Fig. 3 the representations from which apparent polymerization constants (k_{ap}) values were determined for the different initial concentrations of DEKTP employed are shown. At lower DEKTP concentrations (0.005 and 0.01 M) there seems to be no variations in MMA polymerization rate, but increases over 0.01 M in the initial concentration of initiator cause higher polymerization rates. Similar results were found when the initial concentration of MMA was 0.5 M.

Based on the kinetics expression:

$$R_p = k_p \left(\frac{fk_d}{k_t}\right)^{\frac{1}{2}} [M][I]^{\frac{1}{2}}$$

where $k_{ap} = k_p \left(\frac{fk_d[I]}{k_t}\right)^{\frac{1}{2}}$ is the overall rate constant, f the initiator efficiency, and $[M]$ and $[I]$ are monomer and initiator concentrations, respectively, the order with respect to $[I]$ must be near to 0.5. This reaction order was determined for two

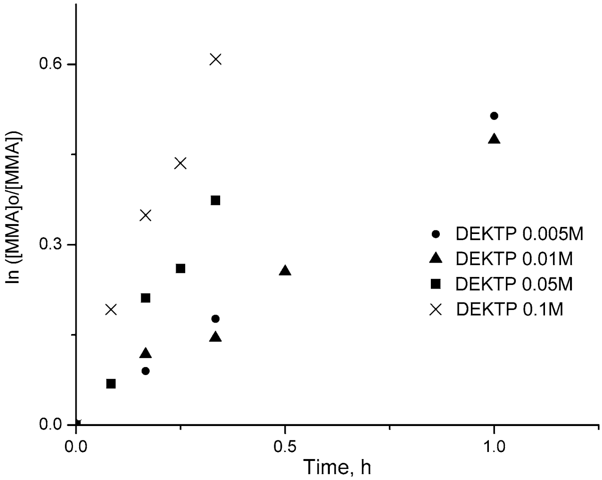


Fig. 3 Conversion for solution polymerization of MMA 1 M with various DEKTP initial concentrations at 130 °C

polymerization temperatures so they are 0.502 at 120 °C and 0.573 at 130 °C. Both show that the polymerization rate is proportional to $[I]^{1/2}$ according to the kinetic model employed.

Activation energy of polymerization

Both the apparent polymerization constants (k_{ap}) and the dissociation constants of initiator (k_d) were determined simultaneously at different temperatures (Table 4). The kinetic study of the initiator decomposition in the medium where polymerization takes place is very important because most of the kinetic data available for initiators are those calculated in different neat solvents and not in the presence of monomer.

These simultaneous determinations allow the calculation of activation energies of both the initial stage and the overall process of polymerization according to the following Arrhenius expression

$$k_p\left(\frac{k_d}{k_t}\right)^{\frac{1}{2}} = A_p\left(\frac{A_d}{A_t}\right)^{\frac{1}{2}}\exp\left(-\frac{\Delta E_p^* + \frac{\Delta E_d^*}{2} - \frac{\Delta E_t^*}{2}}{RT}\right)$$

where k_d, k_p, and k_t are the rate constants of initiation, propagation, and termination, respectively; A_d, A_p, and A_t are the pre-exponential factors of each step reaction; ΔE_d^*, ΔE_p^*, and ΔE_t^* are the activation energies of each step reaction and R is the universal gas constant.

The activation parameter usually reported is $\Delta E_p^* - \Delta E_t^*/2$, which corresponds to a difference between the propagation activation energy and half of the termination activation energy. Table 5 shows the values of ΔE_d^* and $\Delta E_p^* - \Delta E_t^*/2$ obtained for the studied system and other relevant data in the literature. The value determined for

$\Delta E_p^* - \Delta E_t^*/2$ in the polymerization system studied is comparable to those found in the literature for the same monomer in solvents such as benzene or dioxane. This similarity in the activation parameter suggests a mechanism of polymerization with energetic characteristics analogous to the processes studied by other authors [13, 14].

MMA bulk polymerization using DEKTP as initiator

The bulk polymerization of MMA employing an initial concentration of DEKTP 0.01 M at 130 °C was carried out in order to make a comparison with data obtained in solution polymerization and with thermal self-initiated polymerization of MMA at the same temperature.

In Fig. 4, it can be observed that the presence of DEKTP in the case of a bulk system largely affects the conversion of monomer rate, resulting in conversions 10 times higher at the same reaction times with respect to thermal process. For example, when reaction time is 20 min, conversion of MMA in the case of thermal polymerization is about 5%, whereas in the presence of DEKTP, this value rises to 50%. These results can be compared with those obtained for the DEKTP thermolysis in sty solution [11]. It can be seen that whether the polymerization takes place in solvent–sty 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 self-initiated process showing the same behavior as in our systems.

The evolution of molecular weights with conversion monomer has also been studied. As shown in Fig. 5, the molecular weight values present a singular behavior, which increase with polymerization time representing a common

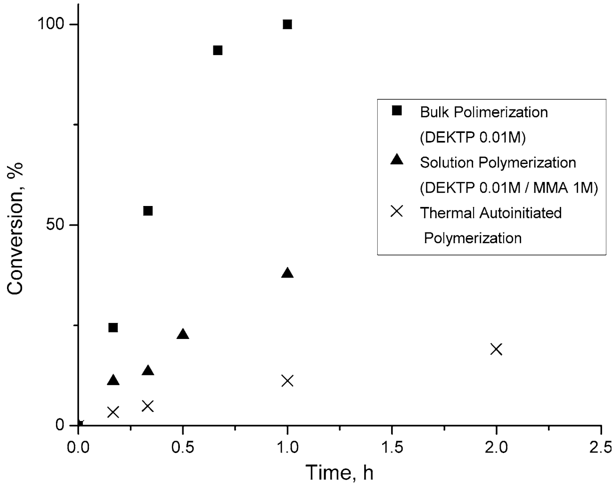


Fig. 4 Conversion evolution of MMA in different reaction media at 130 °C

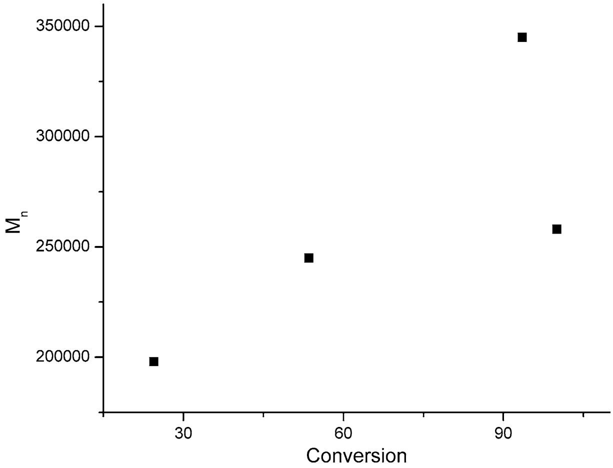


Fig. 5 M_n evolution with MMA conversion for MMA bulk polymerization at 130 °C employing DEKTP 0.01 M

polymerization process initiated by a multifunctional initiator [2, 11]. At ca. 90% conversion of MMA is reached polymeric products with values of M_n ca. 3.45×10^5 g mol^{-1}. This M_n variation suggests that growing polymer chains continue adding monomer units through the process due to the sequential decomposition of peroxide groups present in chains.

The decrease in M_n after reaching the maximum conversion of MMA can be attributed to the scission of active sites derived from DEKTP contained in polymer chains (Scheme 4). This effect can be considered as another tool that would justify the existence of O–O bonds in the polymeric products obtained. These results are consistent with the sequential decomposition of DEKTP raised for the polymerization of sty [11], where a gradual decomposition of the three functions was proposed. However, a larger study about polymeric products would be necessary in order to elucidate the behavior of DEKTP in bulk polymerization of MMA, which exceeds the objectives of this work.

Conclusions

The thermal decomposition reaction of DEKTP in ethylbenzene solution with and without MMA addition was studied at different temperatures. The reaction follows a pseudo-first-order kinetic law up to at least ca. 65% of triperoxide conversion. At the initial concentrations of the initiator studied, a radical-induced decomposition reaction of DEKTP may be dismissed.

The addition of MMA monomer affects the decomposition rate constant of DEKTP so that a higher MMA initial concentration generates an increase in k_d.

In all cases, the k_d values and the activation parameters (enthalpy and entropy of activation) for the DEKTP reaction belong to a single process, which could be its unimolecular homolysis with biradical formation in the rate-determining step.

The addition of MMA causes a decrease in the activation parameters (enthalpy and entropy of activation; Table 1). So, the initial step of DEKTP molecule, and also the corresponding activated complex, is solvated to different extents depending on the solvating power of the pure solvent (or solvents mix) used. By differential solvation, in more polar media, the decomposition reaction is accelerated because of higher solvation of the activated complex. The observed decrease in activation entropy could be explained by the existence of a more highly ordered activated complex.

The activation energy (ΔE_d*) related to the DEKTP decomposition decreases to a half when MMA is added to DEKTP solution in ethylbenzene. This fact shows the importance of determining kinetic and thermodynamic parameters for the initiator during the polymerization process to use, for example, in mathematical model constructions. Most authors use kinetic data available for initiators in different neat solvents and not in the presence of monomer.

The apparent rate constant of MMA polymerization (k_{ap}) in ethylbenzene solution increases when DEKTP is used as initiator, so higher monomer conversions are obtained at the same time intervals in comparison with the thermal autoinitiated process.

Using DEKTP as initiator in bulk polymerization of MMA leads to total conversions of monomer in short periods of time (50 min at 130 °C), and the molecular weights increase through the process, which could be explained assuming a gradual decomposition of the initiator.

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