

LIMIT OF APPLICABILITY OF THE MONOMER-ENHANCED MECHANISM FOR RADICAL GENERATION IN PERSULFATE INITIATED POLYMERIZATION OF ACRYLAMIDE

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Abstract— The limit of applicability of the monomer-enhanced mechanism as dominant mechanism ruling the initiation process of the polymerization of acrylamide (AM) initiated with potassium persulfate ($K_2S_2O_8$) has been determined. The kinetics and mechanisms for radical generation were studied in solution at very low monomer and initiator concentrations. The transition of the initiation mechanism from dominant monomer-enhanced dissociation to dominant thermal decomposition of persulfate was observed. Both mechanisms contribute equally to radical generation at $[AM] / [K_2S_2O_8] \approx 4.5$. Thermal decomposition dominates at lower $[AM]$ or higher $[K_2S_2O_8]$ and opposite variations promote the monomer-enhanced dissociation. This work also includes quantification of the rate coefficients, efficiencies and activation energies of the mentioned mechanisms, and the kinetics of AM polymerization when photochemically initiated with phenylbis(2,4,6-trimethylbenzoyl)-phosphine oxide.

Keywords— kinetics, mechanism, initiation, acrylamide, persulfate.

I. INTRODUCTION

Polyacrylamide based products are commonly used as flocculants, thickening agents, additives in water-based paints and a multitude of other applications related to solid liquid separation, fluid control and surface modification (Myagchenkov and Kurenkov, 1991). Recently, they found applications in building and food industry, cosmetics, medicine and pharmacy (Dautzenberg *et al.*, 1994; Hunkeler and Hernandez-Barajas, 1997).

Usually, polyacrylamides are synthesized through free radical polymerization of acrylamide (AM) in homogeneous or heterogeneous media using thermal, redox or photochemical initiators (Siyam, 2001; Kurenkov and Abramova, 1992). A widely used thermal initiator is potassium persulfate ($K_2S_2O_8$). Important deviations from the ideal polymerization path have been observed for the polymerization of AM initiated with $K_2S_2O_8$.

The literature describing the system AM/ $K_2S_2O_8$ is abundant. Though, frequently only experimental obser-

vations are presented without discussing or proposing neither mechanisms nor their ranges of applicability. Moreover, the majority of the literature investigated the system under conditions of industrial interests such as heterophase polymerization carried out at high monomer concentration, high polymerization rate and high conversion. These conditions are, definitely, far from those suited for the accurate identification of basic mechanisms, applicability ranges and kinetic parameters. Table 1 summarizes the values of α and β published by several authors along more than 50 years.

These parameters are the dependency orders of $[AM]$ and $[K_2S_2O_8]$, respectively in the overall polymerization rate equation. (Odian, 1970):

$$R_p = k_p [M]^\alpha \left(\frac{f_i k_i [I]}{k_t} \right)^\beta, \quad (1)$$

The overall polymerization rate (R_p) is defined as Table 1. Conditions, monomer and initiator exponents for AM polymerizations initiated with $K_2S_2O_8$.

[AM] mol l ⁻¹	[K ₂ S ₂ O ₈] 10 ⁻³ mol l ⁻¹	Temp. °K	α	β	Ref. (year)
0.09-0.88	6.28-69.9	333-348	1.49	0.45	Mahdavian <i>et al.</i> (2004)
0.50-1.10	0.90-2.60	313-338	1.35	0.50	Kang <i>et al.</i> (2004)
1.00-2.60	0.08-0.82	298	1.25	0.50	Kurenkov and Antonovich (2003)
0.47-0.76	0.41	323	1.50	-	Giz <i>et al.</i> (2001)
0.50-1.76	0.45-2.25	328	1.26	0.50	Lin (2001)
1.00-10.0	0.30-2.00	298	1.19	0.47	Chiriac (2000)
2.82-7.04	0.23-0.63	313	1.28	0.45	Stupenkova (1991)
3.35-6.70	0.25	313-333	1.34	-	Hunkeler (1991)
0.85-4.30	0.01-0.23	308-313	1.37	0.53	Kurenkov <i>et al.</i> (1987)
0.34-0.66	0.22-0.87	303	1.53	0.53	Pohl and Rodrigues (1981)
0.10-0.15	5-20	308	1.50	0.50	Singh <i>et al.</i> (1979)
0.11-0.90	5.00	303	1.20	-	Osmanov (1980)
0.56-0.14	3.00-0.75	323	1.70	0.90	Kurenkov <i>et al.</i> (1978)
3.00-9.00	2.00-10.0	283-293	1.60	0.50	Trubitsyna <i>et al.</i> (1978)
0.70-2.82	3.06-24.5	298	1.50	0.50	Geczy and Nasr (1971)
0.13-0.53	1.00-30.0	323	1.25	0.51	Friend and Alexander (1968)
0.05-1.00	0.95-4.70	303	1.07	0.50	Riggs and Rodriguez (1967a)
0.05-0.40	0.95-0.52	303-323	1.25	0.50	Riggs and Rodriguez (1967b)
0.07-0.77	2.4-9.6	304	1.50	0.50	Morgan (1946)

the negative derivative of the monomer concentration with time: $-d[M]/dt$, $[M]$ and $[I]$ are the monomer and initiator concentrations (mol l^{-1}), k_p , k_i , k_t and f_i are the rate coefficients for propagation ($\text{l mol}^{-1} \text{s}^{-1}$), initiation (s^{-1}), termination ($\text{l mol}^{-1} \text{s}^{-1}$) and the dimensionless efficiency for radical generation. The temperature dependence of the rate coefficients can be expressed by an Arrhenius type relationship: $k = A e^{(-E/RT)}$. Here, A and E are the collision frequency factor (s^{-1}) and the Arrhenius activation energy (KJ mol^{-1}). In case of photopolymerization, f_i is usually called the quantum yield of the initiator, Φ . Then, k_i has to be expressed as the product of the molar absorptivity of the initiator, ϵ , (l mol cm^{-1}) and the light intensity, I_0 ($\text{mol l}^{-1} \text{s}^{-1}$).

With the exception of Mahdavian *et al.* (2004), Stupenkova *et al.* (1991) and Kurenkov *et al.* (1978), β was reported as the ideal value: 0.5 whereas α varies from its approximately ideal value: 1.07 (Riggs and Rodriguez, 1967a) to a highly deviated value: 1.70 (Kurenkov *et al.*, 1978).

The effect of AM on $\text{S}_2\text{O}_8^{2-}$ during the radical generation process is considered to be responsible for $\alpha > 1$. On the one hand, the cage-effect theory (Matheson, 1945) proposes that $\text{S}_2\text{O}_8^{2-}$ undergoes decomposition immediately followed by recombination. Primary radicals remain trapped in a cage formed by solvent and monomer molecules. Accidentally, a primary radical reacts with a cage forming monomer yielding the radical outside of the cage. The higher the monomer concentration, the higher is the concentration of cage forming monomer molecules. Consequently, the higher the probability is for a radical to escape and initiate polymerization. On the other hand, the complex theory (Gee and Rideal, 1936) proposes the formation of a reversible associated complex between AM and $\text{S}_2\text{O}_8^{2-}$ prior its dissociation in a primary radical, $\text{SO}_4^{\cdot-}$, and an initial radical, $\text{SO}_4^{\cdot-}\text{-AM}$. In this case, the higher the monomer concentration, the more AM- $\text{S}_2\text{O}_8^{2-}$ complex is formed and the higher is the production of free radicals. Although both theories are based on very different premises, they lead to an identical kinetic expression, which is generally referred as monomer-enhanced dissociation mechanism. The mechanism predicts $\alpha=1.5$ and $\beta=0.5$.

In addition, thermal decomposition of the initiator also contributes to radical generation. Thus, the initiation process has to be considered as a result of two competing effects; thermal decomposition and monomer-enhanced dissociation of the initiator. This type of initiation process is usually called as hybrid mechanism (Hunkeler, 1991). The competing mechanisms are visible in Eq. (2).

$$R_p = k_p [M] \left(\frac{f_d k_d [I] + f_a k_a [I][M]}{k_t} \right)^{1/2} \quad (2)$$

Here, k_d , k_a , f_d and f_a are the rate coefficients for thermal decomposition of $\text{S}_2\text{O}_8^{2-}$ (s^{-1}), the association coefficient of the AM- $\text{K}_2\text{S}_2\text{O}_8$ complex (s^{-1}), and the dimensionless efficiencies for radical generation through thermal decomposition of $\text{S}_2\text{O}_8^{2-}$ and AM- $\text{K}_2\text{S}_2\text{O}_8$ dissociation,

respectively. $f_a = 1$ has been mechanistically demonstrated and reported for a number of situations (Manickam *et al.*, 1979).

The hybrid mechanism predicts $1 \leq \alpha \leq 1.5$. Furthermore, it describes satisfactorily the kinetics of the polymerization of AM in emulsion, at very high monomer concentrations, $[\text{AM}] = 6.7 \text{ mol l}^{-1}$ and low initiator concentration, $[\text{K}_2\text{S}_2\text{O}_8] = 1.573 \cdot 10^{-3} \text{ mol l}^{-1}$ (Hunkeler, 1991). The extremely high monomer concentration and high monomer / initiator ratio ensures the hybrid mechanism to be governed by energetic factors since the probability that monomer and initiator approach is very high. However, as to the authors' knowledge, there is no evidence of the validity of the hybrid mechanism at very low monomer concentration and low monomer / initiator ratio. Under such conditions, frequency and energetic effects may become competitive and thus the system is expected to shift from non-ideal to ideal behavior. Actually, the polymerization of acrylic and methacrylic acids (Chapiro and Dulieu, 1977; Chapiro, 1973) which present significant deviations at high monomer concentrations, tend to "ideality" with the decrease of monomer concentration.

It is worth mentioning that some authors have explained the deviation of α from its ideal value assuming that the presence of AM could influence medium properties (Seabrook *et al.*, 2005) such as pH (Cabaness *et al.*, 1971; Currie *et al.*, 1965; Pascal *et al.*, 1990), solvent quality (Gromov *et al.*, 1980) and ionic strength of the polymerization medium (Pascal *et al.*, 1993) causing variations in k_p . Later, the variation of k_p were experimentally interpreted as a deviation of α . The effects were also explained by electrostatic interactions between monomers and terminal units of growing radicals, protonation of AM at low pH and hydrolysis of the amide group at high pH (Pascal *et al.*, 1993). Changes in the flexibility, configuration, mobility and reactivity of growing radicals, changes in the nature of solvation shells and complex formation between the reacting species and solvent molecules were proposed (Pascal *et al.*, 1993). Finally, favorable molecular orientation, high local monomer concentration in the proximity of the radical centre and dimerization of AM by H-bond formation were suggested (Gromov *et al.*, 1980; Pascal *et al.*, 1993). The experimental conditions of this study were selected in such a way that these effects resulted minimized or even avoided. Thus, exclusively information about the initiation mechanism should become significant.

The goal of the present study is to establish the limit or range of applicability of the hybrid mechanism for the polymerization of AM in solution initiated with $\text{K}_2\text{S}_2\text{O}_8$.

II. METHODS

A. Materials

White crystals of ultra pure AM, four times recrystallized purchased from Axon Lab, Switzerland, $\text{K}_2\text{S}_2\text{O}_8$ puriss. > 99%, purchased from Fluka Chemie, Switzerland.

land and an aqueous dispersion of phenylbis(2,4,6-trimethylbenzoyl)-phosphine oxide ($C_{26}H_{27}O_3P$) purchased from Ciba Specialty Chemicals, Switzerland were selected as monomer, thermal and photochemical initiators respectively. ϵ and Φ of $C_{26}H_{27}O_3P$ were reported as $7900 \text{ l mol}^{-1} \text{ cm}^{-1}$ and 0.40, respectively in a previous work (Rintoul and Wandrey, 2007). The water had Millipore quality ($18.2 \text{ MOhm cm}^{-1}$) and HPLC grade acetonitrile purchased from Axon Lab, Switzerland was used to precipitate the polymer in the withdrawn samples.

B. Polymer Synthesis

Syntheses were performed in a 100 ml glass reactor equipped with a stirrer, condenser, gas inlet and a heating/cooling jacket. A thermostat adjusted the reaction temperature within 1°K . Oxygen was removed from the initial monomer solution prior to the polymerization by purging with high purity N_2 ($O_2 < 2 \text{ ppm}$) purchased from AirLiquide, Switzerland, during 30 min at 273°K . Afterwards, the temperature was increased to activate the thermal decomposition of $K_2S_2O_8$ and to initiate the polymerizations. The reactions were performed isothermally. An UV lamp was immersed in the reactor to carry out photopolymerizations. The lamp had a primary output at 254 nm and $540 \text{ erg s}^{-1} \text{ cm}^{-2}$ of intensity at the surface of the lamp ($I_0 = 5.16 \cdot 10^{-8} \text{ mol l}^{-1} \text{ s}^{-1}$). Samples of $0.1 - 0.2 \text{ g}$ were withdrawn each 5 min during $20 \pm 5 \text{ s}$ during the first hour of reaction to obtain highly reliable curves. The polymerizations were allowed to progress up to 2 hours of reaction time. A final sample was analyzed to get information about the limiting conversion.

C. Experimental Conditions

The effects related to pH, temperature, and solvents hypothesized by some authors as responsible for the non-ideal behavior of the AM/ $K_2S_2O_8$ system were minimized or avoided by preparing aqueous monomer solutions at $\text{pH} = 4$ to ensure electrochemical neutrality of AM and growing radicals (Cabaness *et al.*, 1971; Currie *et al.*, 1965; Pascal *et al.*, 1990) and polymerizing between $303 - 323^\circ\text{K}$ to expect the absence of H-bond effects (Gromov *et al.*, 1980; Pascal *et al.*, 1993; Rintoul and Wandrey, 2007). Solvent effects and ionic strength are not considered by using pure water and highly diluted monomer and initiator solutions.

The first series of experiments were performed in order to prove that thermal decomposition of $K_2S_2O_8$ (series 1a) and $C_{26}H_{27}O_3P$ (series 1b) were insignificant during the degassing process. In series 1a, an AM/ $K_2S_2O_8$ solution was maintained at the degassing temperature (273°K) during 60 min under permanent N_2 flow. In series 1b, an AM/ $C_{26}H_{27}O_3P$ solution was maintained 60 min at 313°K , under permanent N_2 flow without lighting the UV lamp. Furthermore, the possibility of monomer photolysis was evaluated (series 1c). Here, an initiator-free AM solution was illuminated with

UV light during 380 min. Samples were withdrawn from the reactor to measure the monomer concentration

Table 2. Summary of experimental conditions.

N°	[AM] mol l^{-1}	[initiator] mol l^{-1}	Temp $^\circ\text{K}$
1a	0.2	$[K_2S_2O_8] = 3.2 \cdot 10^{-2}$	273
1b	0.2	$[C_{26}H_{27}O_3P] = 10^{-6}$	313
1c	0.2	$[C_{26}H_{27}O_3P] = 0$	313
1d	0.2	$[K_2S_2O_8] = 3.2 \cdot 10^{-3}$	313
2	$0.05 \leq [AM] \leq 0.3$	$[C_{26}H_{27}O_3P] = 10^{-6}$	313
3	$0.05 \leq [AM] \leq 0.3$	$[K_2S_2O_8] = 1.6 \cdot 10^{-3}$	313
4	$0.05 \leq [AM] \leq 0.3$	$[K_2S_2O_8] = 3.2 \cdot 10^{-2}$	313
5	0.2	$1.6 \cdot 10^{-3} \leq [K_2S_2O_8] \leq 3.2 \cdot 10^{-2}$	313
6	0.2	$[K_2S_2O_8] = 3.2 \cdot 10^{-2}$	$303 \leq T \leq 323$

Series 1a-c: Exclusion of side effects; Series 1d: Experimental reproducibility; Series 2-4: Influence of monomer concentration; Series 5: Influence of initiator concentration; Series 6: Influence of temperature.

and to determine if polymerization occurred. Series 1d served to ensure experimental reproducibility. Here, the same polymerization was repeated three times.

Series 2, 3 and 4 constitute the most important experiments to identify the effect of [AM] on Rp. For this purpose photo and thermal polymerizations of AM at different monomer concentrations and initiation mechanisms were performed. Series 5, served to obtain information about the influence of $[K_2S_2O_8]$ on the Rp. The effect of temperature was studied in series 6. Table 2 lists the conditions of all experiments performed.

D. Determination of Residual Monomer Concentrations and Polymerization Rates

The residual monomer concentration of withdrawn samples served for determining the conversion (P) and for calculating Rp according to a detailed procedure (Rintoul and Wandrey, 2005). Most of conversion curves presented linearity ($R^2 > 0.99$) until, at least, 20 min of reaction time. However, the best fitting was achieved by exponential decay regressions (always presenting $R^2 > 0.999$). Then, Rp at the early stages of polymerization were calculated as the negative derivative of the exponential decay regressions of residual monomer concentration vs. reaction time plots. Limiting conversion values (P_∞) were approached at 2 hours of reaction time.

The residual monomer concentration was determined using a HPLC system composed of L-7110 Merk-Hitachi pump (Hitachi, Japan) and SP6 Gynkotec UV detector (Gynkotec, Germany) operating at a wavelength of 197 nm . The stationary and mobile phases were LiChrosphere 100 RP-18 from Merk, Germany and 5 wt% acetonitrile aqueous solution with a flow rate of 1 ml min^{-1} . The samples were first mixed with 4 ml of acetonitrile to precipitate and isolate the polymer from the solution. The residual monomer remains in solution. Subsequently, $20 \mu\text{l}$ of the supernatant were injected into the HPLC for analysis. The HPLC system was calibrated using AM standard solutions in the concentration range of $7 \cdot 10^{-4}$ to $7 \cdot 10^{-3} \text{ mol l}^{-1}$. The standard solutions were prepared by sequential dilutions of 1 mol l^{-1} stock solution of AM. The peak area served as calibration parameter. Figure 1 shows a typical calibration curve.

III. RESULTS

A. Prerequisites, Reproducibility and Residual Monomer Concentration versus Time Plots

No polymerization was evidenced for series 1a-c. Contrarily, the three polymerizations of series 1d progressed near by linearly ($R^2 > 0.99$) until approximately 30 min of reaction. A short induction time was present for some polymerizations as those presented exemplary in Fig. 2. Induction times were not taken into account for R_p calculations. Differences of less than 5.5% were found between the residual monomer concentrations at the corresponding time values. Furthermore, the slope $-d[AM]/dt$ values presented differences of less than 3% demonstrating good experimental reproducibility.

It was observed that R_p increases with the monomer concentration (series 2-4), initiator concentration (series 5) and temperature (series 6). The R_p of series 2 to 6 were calculated and plotted vs. the reaction parameter under study in Figs. 3 to 5.

B. The Monomer Exponent

The logarithmic plots of R_p vs. $[AM]$ for series 2 to 4 are presented in Fig. 3 according to: $\log(R_p) = \alpha [AM] + b$. The slopes of the linear regressions ($R^2 > 0.99$) directly yield α which was obtained as 1.00, 1.34 and 1.33 for series 2, 3, and 4 and the intercept values, b , were obtained as -3.13 , -3.61 and -3.77 , respectively.

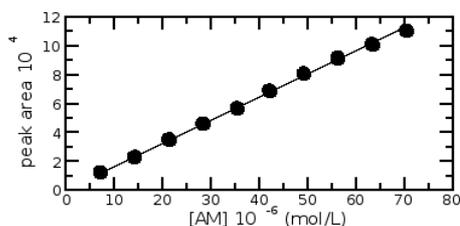


Figure 1. HPLC calibration curve for AM at room temperature (298 °K). Linear regression: Peak area = 0.158 [AM] + 0.117. $R^2 = 0.9991$.

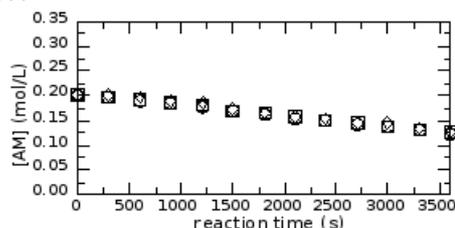


Figure 2. Experimental reproducibility. $[AM] = 0.2 \text{ mol l}^{-1}$; $[K_2S_2O_8] = 3.2 \cdot 10^{-3} \text{ mol l}^{-1}$; $T = 313 \text{ °K}$. $R_p = 2.33 \cdot 10^{-5}$ (\square); $2.40 \cdot 10^{-5}$ (\circ); $2.29 \cdot 10^{-5}$ (\triangle) $\text{mol l}^{-1} \text{ s}^{-1}$.

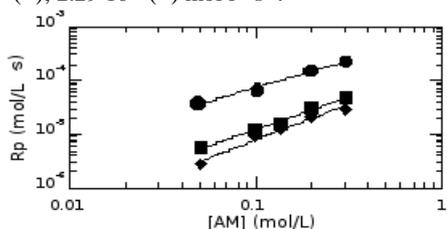


Figure 3. R_p vs. $[AM]$ for photochemically (series 2) and thermally initiated (series 3 and 4) polymerizations. $[C_{26}H_{27}O_3P] = 10^{-6} \text{ mol l}^{-1}$ (\bullet); $[K_2S_2O_8] = 1.6 \cdot 10^{-3} \text{ mol l}^{-1}$ (\blacklozenge) and $3.2 \cdot 10^{-2} \text{ mol l}^{-1}$ (\blacksquare); $T = 313 \text{ °K}$.

C. The $k_p/k_t^{1/2}$ Ratio

The ideal value, $\alpha = 1$, obtained for series 2 permitted to express R_p as a function of the batch composition according to Eq. (1) adapted to the photopolymerization-case where the photoinitiator does not suffer of monomer-enhanced dissociation. From this equation the intercept of the linear regression, $b = -3.13$, of series 2 can be expressed as:

$$b = \frac{1}{2} \log(\Phi \varepsilon I_0 [C_{26}H_{27}O_3P]) + \log\left(\frac{k_p}{k_t^{1/2}}\right), \quad (3)$$

The $k_p/k_t^{1/2}$ ratio was calculated as 58 after introducing the values for b , Φ , ε , I_0 and $[C_{26}H_{27}O_3P]$ into Eq. (3). Propagation and termination steps are considered as independent of the initiation step. Therefore, the $k_p/k_t^{1/2}$ ratio obtained for photochemically initiated polymerizations may be valid for polymerizations using $K_2S_2O_8$ as initiator.

D. The Thermal Decomposition Rate Coefficient

The dead-end polymerization technique (Tobolsky *et al.*, 1960; Bohme and Tobolsky, 1966; Gobran *et al.*, 1960) was used to calculate k_d . The technique can be expressed as Eq. (4) where P and P_∞ are the actual and limiting conversion values.

$$-2 \ln\left(1 - \frac{\ln(1-P)}{\ln(1-P_\infty)}\right) = k_d t, \quad (4)$$

The value of k_d was obtained as the slope when the left side of Eq. (4) was plotted vs. the reaction time. The experimentally obtained P_∞ and the calculated k_d values for series 3 to 6 are presented in Table 3.

E. The AM- $K_2S_2O_8$ Association Constant and The Efficiency for Thermal Decomposition

k_a and f_d were calculated employing Eq. (5). Equation (5) was obtained rearranging Eq. (2). The left side was calculated introducing the corresponding values of R_p , $k_p/k_t^{1/2}$, $[AM]$ and $[K_2S_2O_8]$. Subsequently, it was plotted against $[AM]$ and fitted with a linear regression. k_a and f_d resulted from the slope and intercept of the linear regression. Here, it was assumed $f_a = 1$ as previously demonstrated by Hunkeler (1991) and Pascal *et al.*, (1990).

$$\left(\frac{R_p}{\frac{k_p}{k_t^{1/2}} [AM] [K_2S_2O_8]^{1/2}}\right)^2 = f_d k_d + k_a [AM], \quad (5)$$

Results from series 3 yielded $f_d = 3.7 \cdot 10^{-4}$ and $k_a = 1.16 \cdot 10^{-6} \text{ l mol}^{-1} \text{ s}^{-1}$ and for series 4 it was $f_d = 4.8 \cdot 10^{-4}$ and $k_a = 1.04 \cdot 10^{-6} \text{ l mol}^{-1} \text{ s}^{-1}$.

F. The Initiator Exponent

The logarithmic plot of R_p vs. $[K_2S_2O_8]$ is presented in Fig. 4. $\beta = 0.38$ for $K_2S_2O_8$ was obtained as the slope of the linear regression ($R^2 > 0.99$).

G. The Arrhenius Parameters

The values for the overall frequency factor, $A_p = 1.56 \cdot 10^6 \text{ s}^{-1}$, overall activation energy, $E_p = 53.77 \text{ KJ mol}^{-1}$,

Table 3. Limiting conversion (P_∞) and dissociation constant of $\text{K}_2\text{S}_2\text{O}_8$ (k_d).

Series 3. $[\text{K}_2\text{S}_2\text{O}_8] = 1.6 \cdot 10^{-3} \text{ mol l}^{-1}$; $T = 313^\circ\text{K}$			
	$[\text{AM}] \text{ mol l}^{-1}$	P_∞	$k_d \cdot 10^4 \text{ s}^{-1}$
3.1	0.05	0.34	4.09
3.2	0.10	0.54	3.92
3.3	0.13	0.48	3.76
3.4	0.20	0.58	3.81
3.5	0.30	0.58	3.95
Series 4. $[\text{K}_2\text{S}_2\text{O}_8] = 3.2 \cdot 10^{-2} \text{ mol l}^{-1}$; $T = 313^\circ\text{K}$			
	$[\text{AM}] \text{ mol l}^{-1}$	P_∞	$k_d \cdot 10^4 \text{ s}^{-1}$
4.1	0.05	0.47	4.61
4.2	0.10	0.60	3.72
4.3	0.13	0.63	3.72
4.4	0.20	0.69	3.51
4.5	0.30	0.70	3.01
Series 5. $[\text{AM}] = 0.2 \text{ mol l}^{-1}$; $T = 313^\circ\text{K}$			
	$[\text{K}_2\text{S}_2\text{O}_8] \cdot 10^3 \text{ mol l}^{-1}$	P_∞	$k_d \cdot 10^4 \text{ s}^{-1}$
5.1	1.8	0.58	3.71
5.2	3.8	0.67	3.76
5.3	6.7	0.74	3.93
5.4	11.0	0.81	3.84
5.5	18.0	0.88	3.68
5.6	32.0	0.95	3.87
Series 6. $[\text{AM}] = 0.2 \text{ mol l}^{-1}$; $[\text{K}_2\text{S}_2\text{O}_8] = 3.2 \cdot 10^{-2} \text{ mol l}^{-1}$			
	Temp $^\circ\text{K}$	P_∞	$k_d \cdot 10^4 \text{ s}^{-1}$
6.1	303	0.41	1.16
6.2	308	0.52	2.31
6.3	313	0.69	3.12
6.4	318	0.88	3.50
6.5	323	0.99	3.54

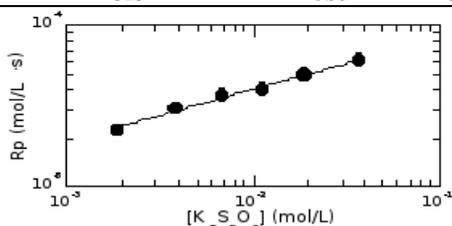


Figure 4. R_p vs. $[\text{K}_2\text{S}_2\text{O}_8]$ (series 5). $[\text{AM}] = 0.2 \text{ mol l}^{-1}$; $T = 313^\circ\text{K}$.

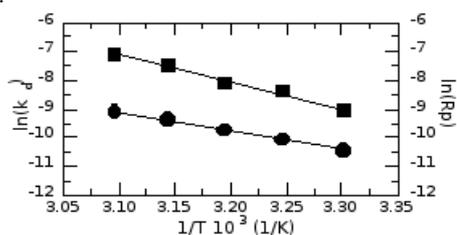


Figure 5. $\ln(k_d)$ (■) and $\ln(R_p)$ (●) vs. T^{-1} plots. $[\text{AM}] = 0.2 \text{ mol l}^{-1}$; $[\text{K}_2\text{S}_2\text{O}_8] = 3.2 \cdot 10^{-2} \text{ mol l}^{-1}$.

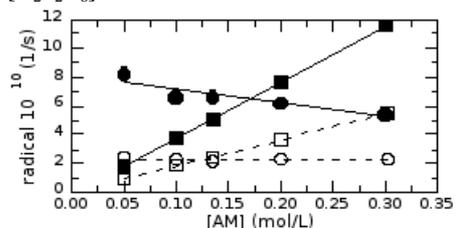


Figure 6. Rate of radical generation by thermal decomposition of $\text{K}_2\text{S}_2\text{O}_8$ (circles) and monomer-enhanced dissociation of $\text{AM-K}_2\text{S}_2\text{O}_8$ complex (squares) vs. $[\text{AM}]$. $[\text{K}_2\text{S}_2\text{O}_8] = 3.7 \cdot 10^{-2} \text{ mol l}^{-1}$ (full symbols) and $1.6 \cdot 10^{-3} \text{ mol l}^{-1}$ (empty symbols), $T = 313^\circ\text{K}$.

the initiator decomposition frequency factor, $A_d = 4.42 \cdot 10^9 \text{ s}^{-1}$ and the activation energy for the thermal decomposition of $\text{K}_2\text{S}_2\text{O}_8$, $E_d = 78.62 \text{ KJ mol}^{-1}$ were determined according to the Arrhenius equation. The natural logarithms of R_p and k_d obtained for series 6 were plotted vs. T^{-1} as presented in Fig. 5.

H. Thermal Decomposition vs. Monomer Enhanced Dissociation Analysis

Finally, the rates of radical generation by thermal decomposition and monomer-enhanced dissociation processes as function of monomer and initiator concentrations are presented in Fig. 6. The rate of radical generation due to thermal decomposition and monomer-enhanced dissociation were calculated according to Eq. (2):

$$f_d k_d [\text{K}_2\text{S}_2\text{O}_8] \text{ and } f_a k_a [\text{K}_2\text{S}_2\text{O}_8] [\text{AM}], \text{ respectively.}$$

Figure 6 shows that the contribution of radicals yielded to the reaction medium via thermal decomposition slightly decreases with the increment of the $[\text{AM}]$. Contrary, the contribution due to monomer-enhanced dissociation clearly increases with $[\text{AM}]$. Moreover, the radical contribution corresponding to thermal decomposition and monomer-enhanced dissociation mechanisms crossover at $[\text{AM}] = 0.17 \text{ mol l}^{-1}$ and 0.12 mol l^{-1} when polymerizations were carried out at $[\text{AM}]/[\text{K}_2\text{S}_2\text{O}_8]$ within the range 31-187 and 1.56-9.38, respectively.

IV DISCUSSION

A. Comparison Between Own Results and Literature Data

Table 4 presents own results and literature data. In the present contribution, the maximum monomer / initiator ratio is 187. Only, Mahdavian *et al.* (2004), Singh *et al.* (1979), Osmanov *et al.* (1980) and possibly Morgan (1946) with maximum monomer / initiator ratios about 140, 30, 180 and 320, respectively can be considered within the range used in the present contribution. However, the other reaction conditions and the subjects of the papers were not the same as those applied here. Mahdavian *et al.* (2004) studied the rate coefficients at high conversion, Singh *et al.* (1979) investigated the influence of Ag^+ and Cu^{++} ions on the polymerization rate of AM, Osmanov *et al.* (1980) determined the $k_p/k_t^{1/2}$ ratio and the very old article of Morgan (1946) is related to the influence of pH and AgNO_3 on persulfate decomposition. Therefore, the comparison between own and literature data is relative since little is known about the system under low monomer / initiator ratio. However, the comparison may be useful to have an idea of magnitude orders and general perspective of the system.

In general good agreement between the obtained $k_p/k_t^{1/2}$ ratio, the frequency factor A_d and the activation energy E_d for the thermal decomposition of $\text{K}_2\text{S}_2\text{O}_8$ and those from the literature was observed. The obtained $k_p/k_t^{1/2}$ ratio, was slightly higher than that reported in the literature (Currie *et al.*, 1965; Rintoul and Wandrey, 2007; Seabrook *et al.*, 2005). The reason could be the extremely low monomer concentration used in the present study. In fact, k_p was found to increase from $3.83 \cdot 10^4$ to $5.53 \cdot 10^4$ when the $[\text{AM}]$ decreased from 2.81 to 0.32 mol l^{-1} (Seabrook *et al.*, 2005). Therefore higher k_p ,

Table 4. Comparison between own and literature parameters.

Parameter	This work	Literature data	Ref. (year)
$[AM]/[K_2S_2O_8]$	187		See Table 1
$k_p/k_t^{1/2}$	58	20-60	Currie (1965) Rintoul and Wandrey (2007) Seabrook <i>et al.</i> (2005)
α	1.34 1.33		See Table 1
β	0.38		See Table 1
A_d	$4.42 \cdot 10^9 \text{ s}^{-1}$	10^9 s^{-1} 10^{14} s^{-1}	Stearn <i>et al.</i> (1940) Hussain and Gupta (1977)
E_d	78.6 KJ mol^{-1}	83.4 KJ mol^{-1}	Rasmussen <i>et al.</i> (1983)
f_d	$3.7 \cdot 10^{-4}$ $4.8 \cdot 10^{-4}$	0.024	Hussain and Gupta (1977)
k_a	$1.2 \cdot 10^{-6} \text{ l mol}^{-1} \text{ s}^{-1}$ $1.0 \cdot 10^{-6} \text{ l mol}^{-1} \text{ s}^{-1}$	$5 \cdot 10^{-7} \text{ l mol}^{-1} \text{ s}^{-1}$	Hunkeler (1991)
A_p	$1.56 \cdot 10^6 \text{ s}^{-1}$	10^5 - 10^8 s^{-1}	Riggs and Rodriguez (1967b)
E_p	53.7 KJ mol^{-1}	45.1 KJ mol^{-1}	Lin (2001)

and consequently higher $k_p/k_t^{1/2}$, can be expected at $[AM] < 0.3 \text{ mol l}^{-1}$.

f_d resulted one order of magnitude lower than the values found by Baer *et al.* (1972) and Hussain and Gupta (1977). However, very low initiator efficiencies were observed for persulfate-based initiators due to the formation of cage products. Furthermore, an additional decrease in the initiator efficiency is expected when the $[AM]/[K_2S_2O_8]$ ratio decreases due to higher probability for radical transfer to the initiator, which also results in initiator wastage. In fact, the decrease of the initiator efficiency with the increase of the initiator concentration may be the cause for the apparent non-ideal initiator exponent, $\beta = 0.38$.

k_a resulted 2 times higher than $k_a = 5.28 \cdot 10^{-7} \text{ l mol}^{-1} \text{ s}^{-1}$ obtained by Hunkeler (1991). Such a difference may be due to the very low monomer/initiator ratio used here compared to Hunkeler's work. The overall frequency factor, A_p , resulted within the range proposed by Riggs and Rodriguez, (1967b) and the activation energy, E_p , agreed well with the values found by Lin, (2001).

The reaction order of $[AM]$ for polymerizations initiated with $K_2S_2O_8$ deviated significantly from unity ($\alpha = 1.34$ and 1.33). Such deviation is coincident with the results presented in Table 1 and specially those obtained by Hunkeler (1991) and Kurenkov *et al.* (1987) with $\alpha = 1.34$ and 1.37 , respectively.

B. The Hybrid Mechanism at Low Monomer Concentration

β deviated significantly from its ideal value in case of initiation with $K_2S_2O_8$ while it reverted to ideality in case of initiation with $C_{26}H_{27}O_3P$ which certainly does not interact with AM during the photochemical dissociation process. Therefore, the deviation of β was evidently caused by monomeric influences on the rate of

initiation. It suggests that the monomer participates actively in the initiator decomposition process. This effect may contribute to the support of the hybrid mechanism for persulfate-initiated AM polymerizations even at such low monomer concentration unlike the cited condition suggest ideal behavior.

Comparing the values obtained for $k_d = 3.8 \cdot 10^{-4}$ and $k_a = 1.16 \cdot 10^{-6} \text{ l mol}^{-1} \text{ s}^{-1}$ presented in Tables 3 and 4 it is clear that thermal decomposition of $K_2S_2O_8$ occurs a hundred times faster than the dissociation of the AM- $K_2S_2O_8$ complex. However, the very low efficiency of $K_2S_2O_8$, $f_d = 3.7 \cdot 10^{-4}$, decreases substantially the contribution of thermally generated radicals to the initiation of polymerization. Thus, both initiation mechanisms become competitive. The radical generation via monomer-enhanced dissociation of the initiator yields two free radicals, a free primary radical and a radical, that has already add the first monomer unit. Thus, the radicals do not form cage products justifying $f_a = 1$ (Manickam *et al.*, 1979).

The crossover for the thermal and monomer-enhanced contributions for radical generation shown in Fig. 6 shifted to lower $[AM]$ when the $[AM]/[K_2S_2O_8]$ ratio was increased. This effect may indicate that polymerizations carried out at very high $[AM]/[K_2S_2O_8]$ such as those performed industrially are dominated by the monomer-enhanced mechanism. Moreover, under industrial conditions, it is usual to find more than 10^4 monomers per each initiator molecule, thus the probability of formation of monomer-initiator associates is very high. Contrary, the probability of finding a non-associated initiator molecule able to undergo thermal decomposition would be very low. Only at very low monomer and initiator concentrations the radical contribution due to thermal dissociation is higher than the contribution due to monomer-enhanced decomposition. This effect demonstrates that AM and $K_2S_2O_8$ tend to associate and therefore, only at highly diluted systems they may occur as single molecules.

V. CONCLUSIONS

The hybrid mechanism describes satisfactorily the kinetics of the polymerization of AM initiated with $K_2S_2O_8$ at very low monomer concentrations. Taking into account other studies carried out at higher monomer concentrations, it can be concluded that the hybrid mechanism rules the polymerization in the range of AM concentrations from 0.05 mol l^{-1} until its solubility limit.

The formation of a persulfate-AM complex is suggested as explanation for the deviations from the ideal monomer exponent found in persulfate-initiated polymerizations of AM. The kinetics of dissociation and subsequent release of radicals to the polymerization medium of such complex is slower than the corresponding kinetics for thermal decomposition and radical release of non-associated persulfate. However, it occurs with much higher efficiency. Therefore, the overall initiation rate is the result of both, thermal decomposition and monomer-enhanced dissociation processes supporting

the idea of the hybrid mechanism.

The rate of radical generation by thermal decomposition and monomer-enhanced dissociation contribute equally to the initiation of polymerization when $[AM] / [K_2S_2O_8] \approx 4.5$ for polymerizations carried out at 313 K. At $[AM] = 0.05 \text{ mol l}^{-1}$ thermal decomposition dominates since about 80% of the radicals are generated by thermal decomposition. Contrary, 54% of the radicals are generated by monomer-enhanced dissociation at $[AM] = 0.3 \text{ mol l}^{-1}$. It lets expect the initiation process of polymerizations at very high $[AM] / [K_2S_2O_8]$ such as those performed under industrial conditions to be ruled mainly by the kinetics of the monomer-enhanced mechanism.

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