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] / [$K_2S_2O_8$] ≈ 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 observations 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):

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

The overall polymerization rate (Rp) is defined as

Table 1. Conditions, monomer and initiator exponents for AM polymerizations initiated with $K_2S_2O_8$.

[AM] mol l^{-1}	[$K_2S_2O_8$] 10^3 mol l^{-1}	Temp. ºK	α	β	Ref. (year)
0.09-0.88	6.28-69.9	333-348	1.49	0.45	Mahdavian *et al.* (2004)
0.50-1.10	0.90-2.60	313-338	1.35	0.50	Kang *et al.* (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 et al. (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 et al. (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 *et al.* (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 et al. (1978)
3.00-9.00	2.00-10.0	283-293	1.60	0.50	Trubitsyna *et al.* (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)