



# Free-radical polymerization of itaconic acid in the presence of choline salts: Mechanism of persulfate decomposition



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## ABSTRACT

Kinetics of decomposition of persulfate activated by choline in aqueous solution has been studied. Additionally, the products of choline degradation were analyzed by  $^1\text{H}$  NMR spectroscopy, and betaine aldehyde was identified as the main oxidation product. Thus, radical-chain redox mechanism is postulated to explain experimental results. The mechanism was successfully verified using kinetic modeling approach. Moreover, it was found that due to formation of complex of itaconic acid and choline chloride, the salt solubility of the acid in water was increased. Finally, free-radical polymerization of itaconic acid initiated by persulfate in aqueous solution of the choline salt yielded poly(itaconic acid) with higher molecular weight and increased polydispersity.

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## 1. Introduction

Itaconic acid is an unsaturated dicarboxylic acid, structurally similar to petrochemical-derived acrylic and methacrylic acids. It can be produced in substantial quantities by means of fermentation in biotechnological processes [1]. According to the US-Department of Energy (DOE) itaconic acid ranks among the 12 most important building block chemicals from sugar [2]. The acid can be an interesting starting material for synthesis of polymers due to its dual polymerization mechanism i.e. by formation of ester bonds (polyesters) and also by free-radical mechanism (Fig. 1).

Synthesis of poly(itaconic acid) by free-radical polymerization of itaconic acid is a difficult and time-consuming process. It requires relatively large quantities of persulfate initiator ( $\sim 10\%$ mol) and proceeded competitively with side reactions e.g. chain transfer, formation of lactone and acetal leading to complicated structure of obtained polymer [3]. To limit these undesirable effects, it is important to keep the reaction temperature sufficiently low: therefore various persulfate activators which accelerate thermal decomposition of the persulfate have been proposed. To date, there have been reported a several activators i.e. N,N-dimethylethanolamine [4], disulfites [5] or hypophosphites [6]. However, numbers of activators have some significant drawbacks

including difficulty removing byproducts and reduction of molecular weights of the obtained polymers [4,7]. In fact, elaboration of a system solvent/initiator/activator that enable a fast polymerization with high molecular-weight poly(itaconic acid) still remains a challenge.

Deep eutectic solvents (DESs) are a novel family of ionic liquid-like fluids [8,9] that contain quaternary ammonium halides (most common choline chloride) and complexing agents such as hydrogen-bond donors (amides, amines, alcohols and carboxylic acids) or metal halides (e.g.  $\text{ZnCl}_2$ ,  $\text{SnCl}_2$ ,  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ). The ammonium salt is a main component of DESs and molar ratio of the salt to the complexing agent is most often 1:1 or 1:2. DESs seem to be less expensive and often biodegradable alternative to ionic liquids; thus they have recently attracted number of investigations in a field of polymeric materials synthesis [10,11]. It has been shown that radiation-initiated polymerization of methyl methacrylate in the mixtures of DMF or ethanol with  $\text{ZnCl}_2$ -choline chloride exhibits many unique features as compared with a polymerization in pure organic solvents [12]. In addition, the DES polymerization results in higher monomer conversion, higher molecular weights and multimodal molecular weight distribution of poly(methyl methacrylate). DESs containing choline chloride or other quaternary ammonium salts and monomers act as hydrogen bond donors i.e. acrylic acid or methacrylic acid were successfully polymerized by 'frontal free-radical polymerization' [13,14]. The systems demonstrated superior performance compared to regular organic solvent and even traditional ionic liquids.

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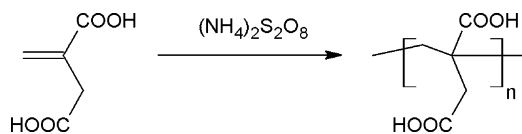


Fig. 1. Free-radical polymerization of itaconic acid.

More recently, we have reported an alternative strategy to prepare itaconic-based polymers [15]. In our approach, we have used a DES, formed by melting of itaconic acid and choline chloride, as the polymerization system. The results prove usefulness of the DES as a medium for free-radical polymerization. The preliminary comparative studies have shown that persulfate initiated copolymerization of itaconic acid is faster in the DES than in water which indicates acceleration effect induced probably by presence of choline cation. The mechanism of this phenomenon has not been explored, yet [15].

In this work, we continue our investigations of the application of choline salts as activators in free-radical polymerization of itaconic acid. We focused on aqueous solutions of the salts and propose possible explanation of the acceleration effect on the rate of the polymerization. Additionally, we demonstrated that choline salts due to its complexing properties, can be a component of solvents for itaconic acid, useful for the polymerization of itaconic acid.

## 2. Materials and methods

### 2.1. Materials

Analytical grade choline chloride (ChCl), itaconic acid (IA) and ammonium persulfate (APS) were purchased from Sigma–Aldrich (USA) and used as received. Potassium hydroxide, absolute ethanol, glacial acetic acid and phosphoric acid (85%) were obtained from POCH (Poland). In all the experiments distilled water was used.

### 2.2. Preparation of choline salts

Equimolar amount of choline chloride and KOH were dissolved separately in absolute ethanol, and then the solutions were mixed together with stirring and cooled to  $-25\text{ }^{\circ}\text{C}$  for 24 h. Precipitated KCl was separated by filtration through a sintered funnel. The obtained choline hydroxide solutions were neutralized by appropriate amount of acids ( $\text{H}_3\text{PO}_4$ ,  $\text{CH}_3\text{COOH}$ , itaconic acid) yielded salts: choline monohydrophosphate ( $\text{Ch}_2\text{HPO}_4$ ), choline acetate (ChAc), choline hydrogenitaconate (ChHIA) and choline itaconate ( $\text{Ch}_2\text{IA}$ ). Ethanol and water were removed from the salt solutions under vacuum using a rotary evaporator.

### 2.3. Kinetics experiments

The reactions of decomposition of ammonium persulfate were studied in unbuffered aqueous solution at  $75 \pm 0.1\text{ }^{\circ}\text{C}$  in borosilicate glass vials heated in a thermostated aluminum block. All the experiments were performed for persulfate initial concentration of 0.01 mol/L with varied concentrations of choline salts ranged from 0.0001 to 6.2 mol/L for ChCl and 0.001–1 mol/L for ChAc and  $\text{Ch}_2\text{HPO}_4$ . The decomposition process was monitored by the determination of APS concentration using a spectrophotometric method [16]. In additional experiments, it has been confirmed that choline salt do not interfere with persulfate analysis.

### 2.4. Kinetic modeling

On the basis of the postulated reaction mechanism, a system first-order ordinary differential equations describing changes of

concentration each chemical compounds was made. The numerical integration of the system and estimation of rate constants were performed by using computational program Dynafit [17]. The experimental data describing persulfate concentration vs. decomposition time for different initial concentrations of choline salts were fitted to the model by non-linear least-square regression method based on the Levenberg–Marquardt algorithm.

### 2.5. Degradation experiment

The reaction of decomposition of persulfate was conducted in unbuffered  $\text{D}_2\text{O}$  solution at  $75 \pm 0.1\text{ }^{\circ}\text{C}$  in borosilicate glass vial heated in a thermostated aluminum block. Mixture of initially 0.1 mol/L ChCl and 0.01 mol/L APS was heated for 2 h. After cooling to room temperature,  $^1\text{H}$  NMR spectra of the solution was taken (Varian Mercury VX-300).

### 2.6. Determination of itaconic acid solubility

The solubility of itaconic acid in water or choline chloride solution was estimated using visual dynamic method. Experiments were carried out in a glass vial (7 mL) placed in a thermostatic block equipped with a magnetic stirrer. Itaconic acid in portions of 50 mg was slowly added to a vigorously mixed solution until saturated solutions were obtained. The measurement was repeated two times and average value was taken.

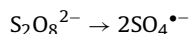
### 2.7. Synthesis of poly(itaconic acid)

Mixture of 25 mL of freshly distilled water, 5.20 g itaconic acid (40 mmol), appropriate amount of choline chloride (0.91 g–4 mmol or 9.1 g–40 mmol) and 0.456 g ammonium persulfate (2 mmol) was heated for 96 h at  $55\text{ }^{\circ}\text{C}$  in a stoppered Erlenmeyer flask in circulating oven. Next, the solution was dialyzed through cellulose membrane (MWCO 1000 Da) against distilled water to remove low-molecular weight products, and finally lyophilized. Yield of polymerization was calculated as a ratio of weight of the starting monomer and weight of the obtained polymer. Molecular weight distribution of poly(itaconic acid) was determined using gel permeation chromatography (Phenomenex Poly-Sep-P Linear column, eluent 0.1 M  $\text{NaNO}_3$  1 mL/min, RI detector). Polyethylene glycols standards were used for calibration.

## 3. Results and discussion

### 3.1. Kinetics of choline-activated persulfate decomposition

The thermal decomposition of persulfate in water is commonly written as:



However, it is well known that the process is quite complex and the mechanism depends on changes in pH, presence of metal ions or organic reducing agents, which can form a redox couple with persulfate and thus catalyze the decomposition [18,19]. Additionally, the thermal dissociation of persulfates can be activated by vinyl monomers, polymeric latexes or surfactants [20–24].

Recent studies suggest that presence of choline chloride could accelerate polymerization of itaconic acid initiated by persulfates [15]. A possible reason may be increasing rate of the initiator decomposition by the salt. It is well known [25], that under the steady state assumption, rate of free-radical polymerization is directly proportional to square root of an initiator decomposition rate constant. In other words, speeding up the initiation process/decomposition rate enhances polymerizations.

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