Catalysis Today xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

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

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ARTICLE INFO

Article history:
Received 15 March 2014
Received in revised form 29 May 2014
Accepted 11 July 2014
Available online xxx

Keywords:
Radical chain reactions
Kinetic modeling
Choline oxidation
Reaction mechanism
Redox polymerization
Ionic liquids

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}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.

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 (~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. $ZnCl_2$, $SnCl_2$, $CrCl_3{\cdot}6H_2O$). 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 $ZnCl_2$-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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http://dx.doi.org/10.1016/j.cattod.2014.07.021
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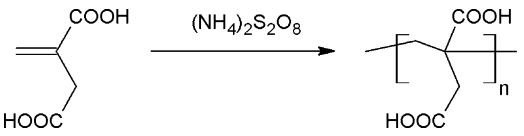

Fig. 1. Free-radical polymerization of itaconic acid.

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 inducted 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 °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 (H_3PO_4, CH_3COOH, itaconic acid) yielded salts: choline monohydrophosphate (Ch_2HPO_4), choline acetate (ChAc), choline hydrogenitaconate (ChHIA) and choline itaconate (Ch_2IA). 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 ± 0.1 °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 Ch_2HPO_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 D_2O solution at 75 ± 0.1 °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, ^1H 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 °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 $NaNO_3$ 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:

$$S_2O_8^{2-} \rightarrow 2SO_4^{\bullet -}$$

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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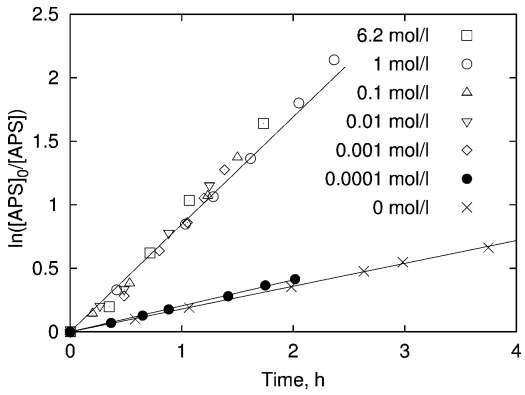

Fig. 2. The first order decomposition plot for initial concentration 0.01 mol/L APS at 75 °C in the presence of different concentration of ChCl.

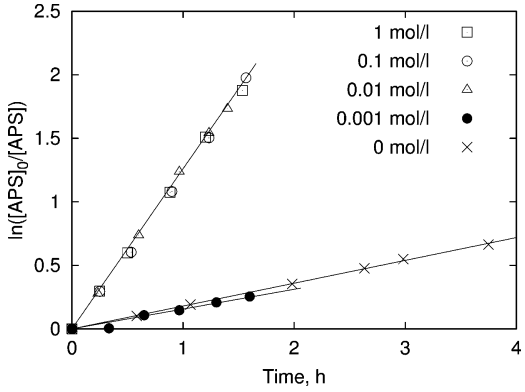

Fig. 3. The first order decomposition plot for initial concentration 0.01 mol/L APS at 75 °C in the presence of different concentration of ChAc.

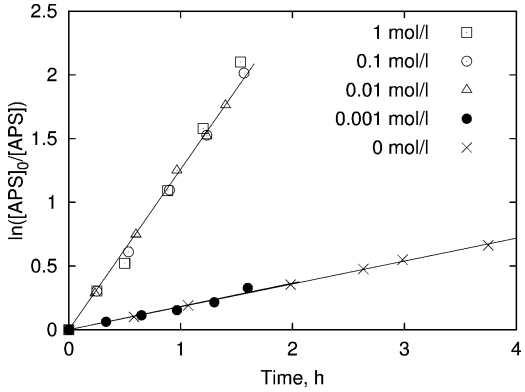

Fig. 4. The first order decomposition plot for initial concentration 0.01 mol/L APS at 75 °C in the presence of different concentration of Ch_2HPO_4.

To investigate the effect of choline on persulfate activation, reactions of thermal decomposition of APS in unbuffered aqueous solutions of various choline salts at varying concentrations were conducted (Figs. 2–4). In all the cases, the data are consistent with the expected first-order decomposition kinetics with respect to persulfate concentration [19]. Determined values of decomposition rate coefficients are listed in Table 1. These data clearly showed that the presence of the choline salt has 2-fold effect on the reaction rates depending on the salt concentration. In diluted solutions, the decomposition rate is close to non-activated reaction. In contrast, above a certain value, the rate constant of disappearance of APS increases and the coefficient is independent on the concentration of the choline salt. The rate enhancement in the presence

Table 1
The rate constants determined for the thermal decomposition of ammonium persulfate ($[APS]_0$ = 0.01 mol/L) at 75 °C in aqueous solutions of various choline salts at different concentrations.

Choline salt	Salt concentrations, mol/L	$10^5 \cdot k_d$, L/s
ChCl	0.0001	5.8
ChCl	0.001–1.0	24.0
Ch_2HPO_4	0.001	4.9
Ch_2HPO_4	0.01–1.0	35.0
ChAc	0.001	4.5
ChAc	0.01–1.0	35.0
None	–	5.0

Table 2
^1H NMR shifts (D_2O) for products of degradation or oxidation of choline chloride in various processes.

Product	Method of choline chloride decomposition
Betaine: δ: 3.25 CH_3, 3.88 N-CH_2 ref. [27]	A, B, C
Betaine aldehyde hydrate: δ: 3.23 CH_3, 3.42 N-CH_2, 5.56 C<u>H</u>-$(OH)_2$ ref. [27]	B
Trimethylamine: δ: 2.94 CH_3 ref. [28]	C, D, E
Acetaldehyde: δ: 1.48 CH_3 ref. [28]	C, D, E
Acetic acid: δ: 1.95 CH_3 ref. [28]	C
N,N-dimethylaminoethanol: δ: 2.27 CH_3, 2.46 N-CH_2-, C<u>H</u>$_2$-OH 3.61 ref. [29]	D

A – oxidation by $KMnO_4$ ref. [30]; B – enzymatic oxidation by choline oxidase ref. [31]; C – oxidation by hydrogen peroxide refs. [28,32]; D – electrochemical decomposition ref. [33]; E – radiolysis by γ-radiation ref. [34].

of choline chloride (~5-fold) is lower than for choline acetate and choline hydrogenphosphate (~7-fold). Moreover, the minimal catalytic concentration of the choline chloride is a value between 0.001 and 0.0001 mol/L and is lower than those values for choline acetate and choline hydrogen phosphate (the value between 0.01 and 0.001 mol/L).

3.2. Products of choline degradation by persulfate

Identification of the products formed during choline-activated decomposition of persulfate is essential before attempting to formulate a mechanism of the reaction. Therefore, a mixture of 0.1 mol/L choline chloride and initially 0.01 mol/L $(NH_4)S_2O_8$ in D_2O was heated at 75 °C for 2 h and the solution was analyzed using ^1H NMR spectroscopy. Additional experiments proved that under these conditions more than 75% of persulfate decomposed, which means that ~7% of initial amount of the salt undergoes oxidation (or other transformations) if choline reacts with persulfate and these products should be detectable by ^1H NMR.

The ^1H NMR spectrum of choline chloride in D_2O (Fig. 5A) shows three signals (labeled a–c): at 3.20 ppm (CH_3-), 3.51 ppm (N-CH_2) and 4.06 ppm (CH_2-OH), whereas peaks in low intensity around methyl singlet are ^{13}C satellites (d) whereas several new signals appeared (labeled e–j) in ^1H NMR spectrum of the solution after reaction (Fig. 5B). The chemical shifts were compared to those of possible products of choline chloride decomposition (Table 2): betaine, betaine aldehyde, trimethylamine, acetaldehyde, acetic acid and N,N-dimethylaminoethanol (Fig. 6). Peaks e (at 3.23 ppm, overlapped with signal a), f (overlapped with signal d) and g could be assigned to betaine aldehyde. There are no peaks in the 3.8–3.9 ppm region characteristic for methylene group of betaine, thus, ^1H NMR data suggest that under the experiment

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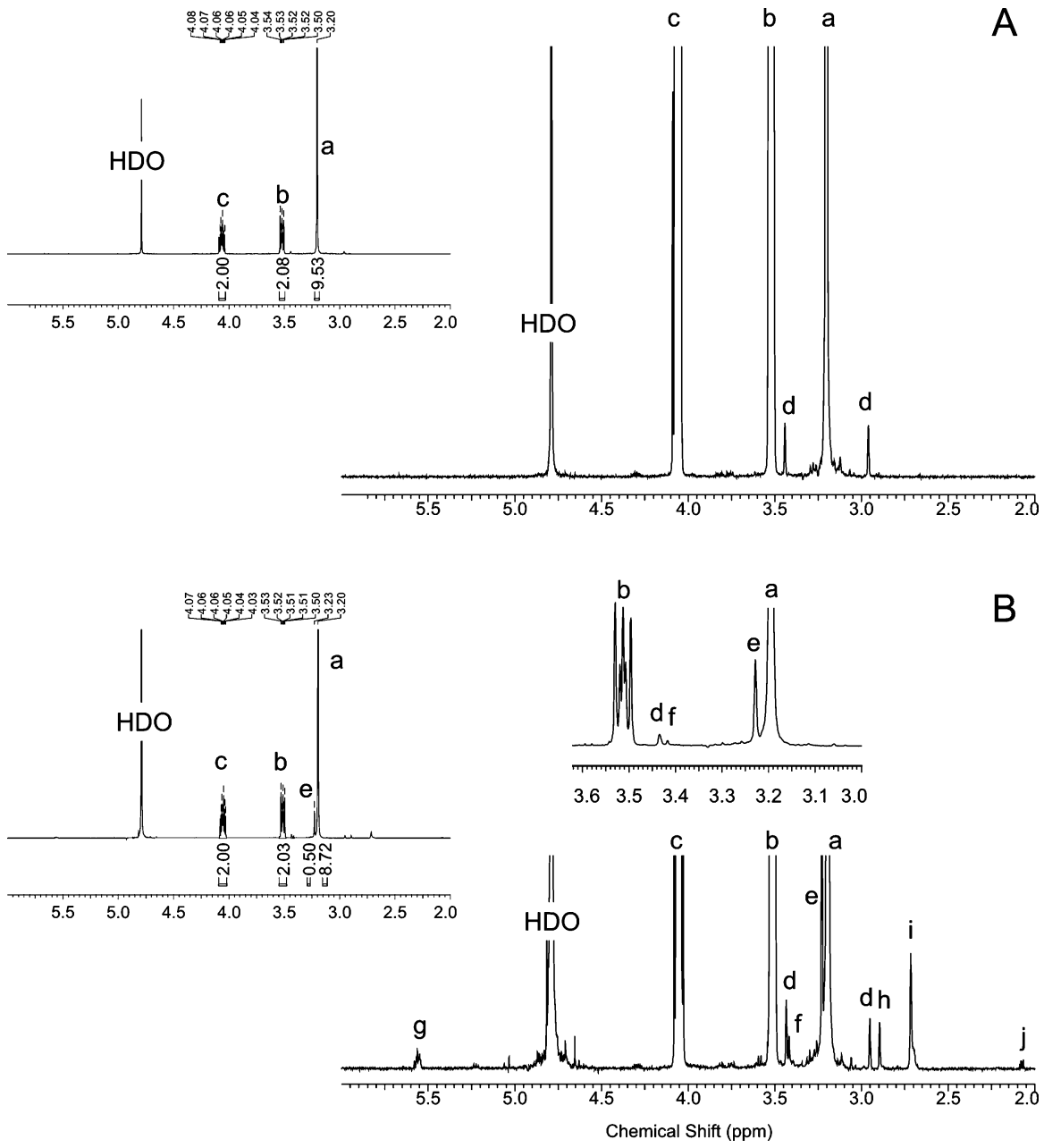

Fig. 5. ^{1}H NMR spectra of (A) 0.1 mol/L choline chloride in D_2O; (B) 0.1 mol/L choline chloride and initially 0.01 mol/L $(NH_4)S_2O_8$ in D_2O after heating at 75 °C for 2 h.

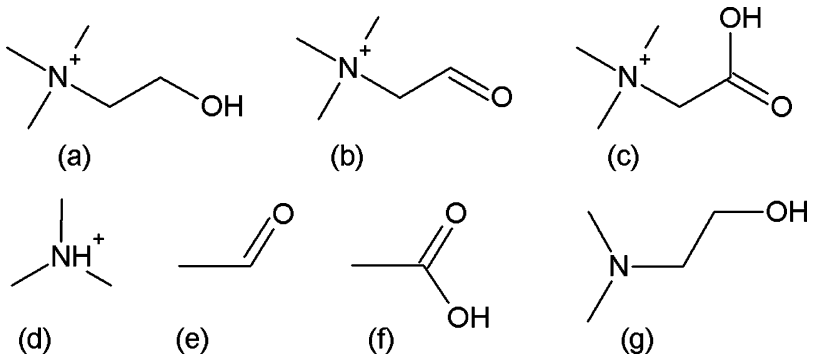

Fig. 6. The structures of choline (a) and its possible decomposition/oxidation products: betaine aldehyde (b), betaine (c), trimethylamine (d), acetaldehyde (e), acetic acid (f) and N,N-dimethylaminoethanol (g).

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conditions choline oxidize to betaine aldehyde rather than oxidize to betaine. Chemical shift of singlet (h) corresponds probably to trimethylamine, whereas peak (j) may confirm presence of acetic acid or its ammonium salt. Detection of trimethylamine and acetic acid indicate cleavage of N–C bond of choline, which results in formation of the amine and acetaldehyde oxidized to acetic acid. Absence of a signal characteristic for acetaldehyde at 1.49 ppm might be explained by evaporation of the aldehyde from reaction mixture (b.p. 20 °C) followed by fast oxidation of the residue aldehyde to the acid. Relatively intense signal (i) might belong to dimethylamine, but the presence of amine is difficult to explain at this stage of the investigations. Due to low intensity of signals of products of choline decomposition, it is not possible to evaluate ^{1}H NMR data quantitatively. However, taking into account high integral intensity of methyl signal of betaine aldehyde (e) in respect to methyl signal of trimethyamine (h), it seems most probable that the aldehyde is the main product of choline decomposition. This finding suggests that oxidation of choline to betaine aldehyde and simultaneously reduction of persulfate to sulfate is a major path of choline chloride–persulfate reaction in aqueous solution. The proposed redox mechanism is similar to that postulated for oxidation of aliphatic alcohols by persulfates [19,26]. It should be noted that the presence of trimethylamine and acetate derivatives in the reaction mixture might suggest additional radical-chain reactions. It is also not clear why betaine aldehyde does not undergo oxidation to betaine under the experimental conditions. These issues need further studies.

3.3. Mechanism of choline-activated persulfate decomposition

Zero-order kinetics of thermal decomposition of persulfate with respect to an ammonium salt has been postulated for cationic surface-active agents [22]. The study included aqueous solutions of *n*-butyltrimethyl-, *n*-butyltriethyl- and *n*-octyltriethylammonium chlorides in the concentrations ranged from 0.01 to 0.1 mol/L. To explain the results, transfer-catalyzed mechanism consistent with general understanding of persulfate chemistry [18,19] was proposed, but chemical structure of the reaction intermediates was not investigated [22]. This mechanism was later postulated for the persulfate decomposition in the presence of methyl metacrylate, styrene and saturated analogues of these monomers [20]. On the basis of our experimental results, in accordance with literature data [19,22,26,32], we proposed the mechanism of choline-activated chain-radical decomposition of persulfate (Fig. 7). The initiation step is homolytic scission of persulfate (Eq. 1). The reaction is the slowest, uncatalyzed and undergoes under action of UV light or temperature. The propagation steps are given by Eqs. (2–4). The last is most important, because of hydrogen-transfer step in which choline is oxidized by persulfate to betaine aldehyde and also sulfate radical is generated. This step is slower than the steps 2, 3, 5 and 6 but much faster than the step 1. The sulfate radical produced in the step 4 reacts likely with choline radical-cations in termination step (Eq. 5) and yields betaine aldehyde. The termination occurs also by fast disproportionation of two choline radical-cations (Eq. 6) as was proposed for persulfate oxidation of alcohols [26]. Hydrogen abstraction in the step 3 at the α-carbon is consistent with the EPR studies for the oxidation of β-amino alcohols (including choline) in Ti^{3+}-H_2O_2 system [32].

This proposed kinetic model is based on the six elementary steps. The reactions 3, 5 and 6 are very fast, so the rate constants k_3, k_5 and k_6 are a few orders of magnitude greater than k_1, k_2 and k_4 [19,35]. However, k_2 and k_4 are in the same order, and are much larger than k_1. Value of k_1 was determined experimentally in non-activated persulfate decomposition experiment, whereas for estimation of k_4 kinetic modeling approach was applied. Simulation software Dynafit [17] was used to fit experimental concentration–time data to the proposed kinetic model. It should be stressed that accurate values of k_2, k_3, k_5 and k_6 are not needed to be known, because any value higher a few orders of magnitude than k_1 gives good results and do not influence significantly on the estimated value of k_4. Fitting procedure was used to experimental data of ChCl, ChAc and Ch_2HPO_4 activated decomposition of persulfate. The results of the numeric calculation are listed in Table 3. As expected from macrokinetic studies (Table 1), estimated values of k_4 for decomposition of persulfate activated by ChAc and Ch_2HPO_4 are similar and greater than for the ChCl-mediated reaction. However, oxidation–reduction step (Eq. 4) is a bimolecular reaction between choline cation-radical and persulfate anion, and it is not clear why the rate of this step depends on the type of a choline salt used in the experiment. It may suggest that chemical structure of the anion or indirectly pH of the reaction mixture can influence the reactivity of choline cation-radical through certain ionic interactions on the quaternary nitrogen atom.

Table 3
Rate constants values used for kinetic modeling of choline-activated persulfate decomposition in the presence of various choline salts.

Rate constant	ChCl	ChAc	Ch_2HPO_4
k_1, L/s[a]	5×10^{-5}	5×10^{-5}	5×10^{-5}
k_2, L/(mol s)[b]	10^3	10^3	10^3
k_3, L/(mol s)[c]	10^5	10^5	10^5
k_4, L/(mol s)[d]	104	168	170
k_5, L/(mol s)[c]	10^5	10^5	10^5
k_6, L/(mol s)[c]	10^5	10^5	10^5

[a] Determined for uncatalyzed persulfate decomposition.
[b] Ref. [35] reaction 2.20.
[c] Typical value of rate constant for very fast radical reactions.
[d] Rate constant derived from the fits of kinetic model to the experimental data.

Finally, based on the kinetic model and know values of rates constant (Table 3) progress the curves were calculated for persulfate decomposition in aqueous solution of various choline salts (ChCl, ChAc and Ch_2HPO_4) at different concentration levels (Figs. S1–S4 in the supplementary material). In general, the fits are very good. Only a significant lack of fit could be observed in the experiments when initial concentration of the choline salt is lower than the initial concentration of persulfate, especially for ChCl-activated system (Fig. S2). In this case, choline undergoes oxidation to betaine aldehyde at ~10% conversion of persulfate and radical reactions (Eqs. 2–6) are thus terminated, so decomposition of persulfate is suppressed to the homolytic scission (Eq. 1) and therefore overall decomposition rate dropt. In contrast, experimental results (Fig. S2 and Table 1) indicate that such low concentration of choline chloride (0.001 mol/L) showed an activation effect. This phenomenon could not be explained by the proposed mechanism and needs further studies. Taking into account the presence of trimethylamine and other choline decomposition products, it is quite probable that postulated mechanism (Fig. 7) is more complex. There is also possible that some of the products might initiate additional radical-chain reactions which participate in the decomposition of persulfate, and thus cause the increase of overall decomposition rate. For example, we have found that the rate constant of persulfate decomposition in the presence of trimethylamine hydrochloride (0.1 mol/L in unbuffered aqueous solution) at 75 °C is 5.5×10^{-5} L/s, whereas for betaine hydrochloride in the same experimental conditions the overall rate constant is as high as 49×10^{-5} L/s.

3.4. Polymerization of itaconic acid in aqueous choline chloride solution

Itaconic acid which was melted with choline chloride in 1:1–1:2 molar ratio form liquid systems (DES) at room temperature [15], which could indicate strong intermolecular interactions between

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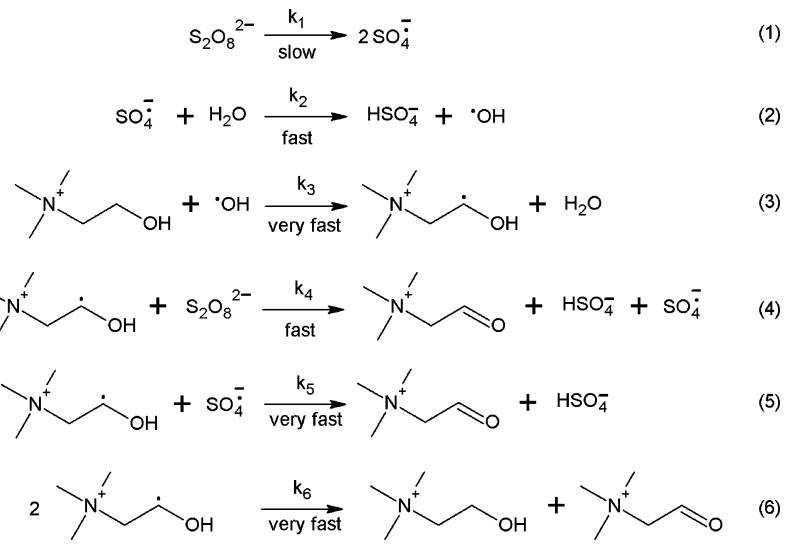

Fig. 7. Proposed mechanism of choline-activated radical-chain redox decomposition of persulfate.

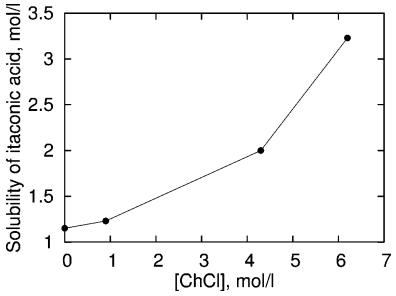

Fig. 8. Increasing solubility of itaconic acid in aqueous solutions of choline chloride at different concentrations (up to saturated ChCl–H_2O system).

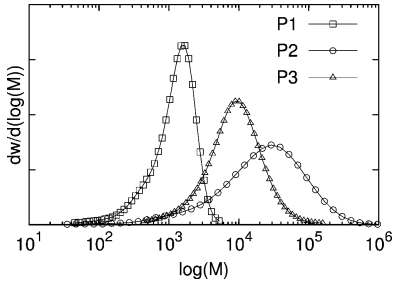

Fig. 9. Comparison of the molecular weight distribution of poly(itaconic acid) synthesized by a standard method (P1) with polymers prepared in presence of ChCl (P2, P3). The parameters for each experiment were listed in Table 5.

Table 4
Concentration of itaconic species in various liquid mediums.

Medium	IA, mol/L
H_2O	1.15[a]
6.2 M $ChCl_{aq}$ ($ChCl{\cdot}2H_2O$)	3.23[a]
Ch_2IA (IL)	4.10
$ChCl{\cdot}H_2IA$ (DES)	4.21
ChHIA (IL)	5.62

[a] Concentration of saturated itaconic acid solution at 35 °C.

the melted components. This inspired us to study choline-based systems containing itaconic acid as useful polymerization media. We have found that presence of choline salts (e.g. choline chloride) in water increase solubility of itaconic acid by the factor of 3 (Fig. 8). This effect is strongest for saturated choline chloride–water system, where the weight concentration of the salt is ca. 80%. Quaternary ammonium salts are able to associate with protic compounds e.g. carboxylic acids *via* hydrogen bonding, ion-pair formation and solvation [36–39], which might explain improved solubility of itaconic acid in water–choline chloride system.

Additionally, we have found that salts obtained by partial or full neutralization of itaconic acid by choline, namely choline hydrogenitaconate or choline itaconate, are liquid at room temperature, so they can be called "ionic liquids" (IL). It is interesting to compare total concentration of itaconic species (both neutral and dissociated) for mentioned systems (Table 4).

In all cases, the concentration is higher than for saturated aqueous system and comparable or higher than for alcohols which are know as good itaconic acid solvents (solubility of IA ranged from 1 to 3 mol/L [40]). Moreover, both choline itaconates and choline chloride – itaconic acid DES, enable to achieve the initial concentration of itaconic acid in the range of values typical for bulk monomers (e.g. styrene or methacrylic acid ~8–9 mol/L). It is well know that to increase free-radical polymerization rate the initial monomer concentration should be increased [25]; therefore, it is important to conduct the process in an appropriate solvent. Taking into account the activation effect of choline salts on decomposition of the initiator and solubility enhancement of the monomer, it could be stated that choline-based solvents (Table 4) seem to be good candidates as a media for free-radical polymerization of itaconic acid. Here, we would like to report preliminary results of polymerization of itaconic acid in aqueous solutions of choline chloride. Results concerning the others systems, namely choline chloride dihydrate, ChHIA, Ch_2IA and choline chloride – itaconic acid DES, will be published separately.

To investigate effect of choline chloride on polymerization of itaconic acid, the yield of reactions and molecular weight of poly(itaconic acid) were compared (Table 5). All polymers were obtained in a similar good yield ranged from 50 to 62%. It means that presence of choline salt does not influence substantially the polymerization yields under such reaction conditions.

Analyzing molecular weights of poly(itaconic acid) samples (Table 5), we found the choline effect clearly evidenced. Polymer P1 prepared by a standard method in aqueous solution, has significantly lower molecular weight than P2 and P3. Thus, the presence of choline chloride resulted in the formation poly(itaconic acid) with higher molecular weights and broader molecular weight distributions (Fig. 9). The observed increase of polydispersity

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Table 5
Reaction conditions, yield and molecular weight of poly(itaconic acid) obtained at 55 °C after 48 h of polymerization. Number average molecular weight (M_n), weight average molecular weight (Mw) and polydispersity index (PDI) = M_w/M_n calculated from GPC data.

Polymer	$[IA]_0$, mol/L	$[APS]_0$, mol/L	[ChCl], mol/L	Yield, %	M_n, g/mol	M_w, g/mol	PDI
P1	1.6	0.08	0	62	800	1400	1.8
P2	1.6	0.08	0.16	55	4400	46,000	10.5
P3	1.6	0.08	1.6	50	5400	13,000	2.4

might be explained by induction by radicals generated in choline salt–persulfate system and side reactions causing formation of branched polymers. The choice of appropriate polymerization parameters includes temperature and $[APS]_0/[ChCl]_0$ ratio seems to be crucial to limit undesired branching processes on one hand, and simultaneously to obtain poly(itaconic acid) with high molecular weight on the other hand.

4. Conclusions

In summary, to better understand free-radical polymerization processes in deep eutectic solvents, the effects of choline interactions with an initiator and a monomer were studied. We have examined mechanism of persulfate initiated polymerization of itaconic acid in aqueous solution in the presence of choline chloride. The choline salts activate decomposition of persulfate thus enhance initiation step of free-radical polymerization. ^{1}H NMR studies of products of choline salts-activated persulfate decomposition indicate that betaine aldehyde is the main (but not the only) product of choline oxidation. Choline and persulfate form most likely a redox couple and radical-chain redox mechanism can be one of possible explanation of acceleration effect of choline on the decomposition of persulfate. Additionally, our studies shown that the presence of choline increases solubility of itaconic acid in water and allows synthesis of poly(itaconic acid) with higher molecular weight but also with higher polydispersity. It is probable that free radicals generated as transient intermediates in the course of redox initiation cause branching of the polymer which explain observed broadening of molecular weight distributions and result in more complex chemical structure of poly(itaconic acid).

The presented mechanistic studies on choline salts-activated decomposition of persulfates are important to understand the initiation step kinetics of free-radical polymerization in aqueous solutions of choline salts and also in choline-based deep eutectic solvents, where DES serve as a solvent of monomer and also acts as redox activator of persulfate initiator. The results may be useful to elaborate mechanism, chemical structure and properties of polymers prepared by redox initiated free-radical polymerization in both deep eutectic solvents and also in choline, and other quaternary ammonium ionic liquids. The identification of products of choline oxidation could help to explain chemical structure of end-groups of macromolecules and also possible mechanisms of branching. Better understanding of mechanisms of quaternary ammonium-activated decomposition of persufates (or perhaps other peroxo initiators) should result in developing novel DESs and ILs act both as solvents and as accelerators in redox-initiated free-radical polymerization.

Acknowledgments

COST Action CM0903 (UBIOCHEM) is gratefully acknowledged.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cattod.2014.07.021.

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