

Synthesis of Hydrogels by Polymerization of Itaconic Acid–Choline Chloride Deep Eutectic Solvent

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ABSTRACT: Itaconic acid (IA)–choline chloride (CC) deep eutectic solvents (DES) were prepared and characterized by NMR, TGA, and DSC. Poly(itaconic acid–*co*–bisacrylamide) hydrogels were synthesized by *in situ* polymerization–crosslinking of the DES. For comparison, the hydrogels were also prepared in water under the same process conditions, that is, temperature, time, initial concentration of the monomer, the initiator, and *N,N*–methylenebisacrylamide (BAA) as the cross-linking agent. Chemical structure of the polymers was proved by elemental analysis and FTIR. The values of insoluble gel fraction and water swelling of obtained hydrogels suggest that polymers prepared in DES have higher cross-link density. Preliminary comparative studies of polymerization of IA in water and in DES medium indicated higher polymerization rate resulting from the presence of the choline salt, what might explain properties of the hydrogels prepared in DES. This study shows that DES can be used both as a solvent and catalyst in free-radical polymerization processes. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40608.

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INTRODUCTION

Deep eutectic solvents are a new family of ionic fluids¹; they are two-component mixtures of a quaternary ammonium halides with complexing agents such as hydrogen-bond donors (amides, amines, alcohols, and carboxylic acids) or anhydrous (ZnCl₂, SnCl₂) or hydrated metal halides (e.g., CrCl₃·6H₂O).² The freezing point depression in the mixtures results from lowering of the lattice energy of the ammonium salt by the charge delocalization *via* formation of the halide anion–the complexing agent supramolecular complexes. Choline chloride (2-hydroxyethyltrimethyl ammonium chloride, vitamin B4), is a most often used as ammonium component of DESs. The choline chloride (CC) is less expensive than most ionic liquids and has a very low toxicity for humans and environment (CC is applied as a food additive). The salt is nonflammable and can be considered as thermally stable. Unfortunately, CC has a high melting point ~300°C; therefore, it is itself is not useful as a room-temperature ionic liquid.

DESs are now of growing interest in many fields of research because of some advantages over traditional ionic liquids.¹ First of all, DESs are cheap, often biodegradable, nontoxic, and based on renewable chemicals. Second, synthesis of DESs is simply

(mixing and melting two components), with 100% atom economic, does not require purification step. These make their large-scale use feasible. DESs have been proposed as alternative solvents attractive for electrodeposition of metals and alloys, in electropolishing, and processes such as electrowinning of metals from complex oxide matrices.^{3,4} DESs have gained much attention given their capability to induce textural properties in a number of inorganic materials.⁵ Mixtures of glycerol and CC have been found as effective extraction media for glycerol from biodiesel product mixtures.^{6,7} Additionally, owing to their nontoxic nature, biodegradability, and low cost, DESs have been applied as alternative solvents in enzyme-catalyzed reactions.⁸ However, papers concerning application of DESs in polymer synthesis is limited and very recently has been excellently reviewed.⁹ Resorcinol^{10,11} or resorcinol-3-hydroxypyridine¹² based DESs have been polymerized with formaldehyde resulted in formation of gels. It was demonstrated that DESs played multiple role: they are solvents and structure-directing agents allowed preparation of hierarchical porous carbon monoliths after carbonization of the gels. The versatility of the DES assisted approach was also demonstrated by the fabrication of carbon-composites containing carbon nanotubes exhibiting porous structures by using *para*-toluene sulfonic acid-based DES.¹³

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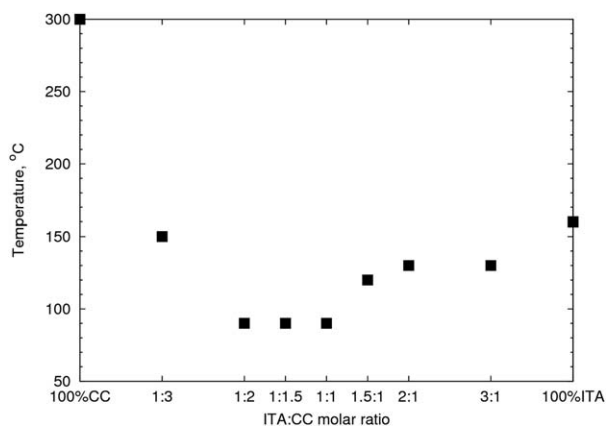


Figure 1. Phase diagram IA-CC mixtures. Points on graph indicate a melting temperature a mixture of IA with CC in appropriate molar ratio.

Up to now, there are only a few examples reported in the literature of free radical polymerization carried out in DES. It has been shown that radiation-initiated polymerization of methyl methacrylate in the mixtures of dimethylformamide or ethanol with ZnCl_2 -CC DES exhibits many unique features when compared with the polymerization in pure organic solvent.¹⁴ The addition of the DES results in higher monomer conversion, higher molecular weight, and multimodal molecular weight distribution of poly(methyl methacrylate). Recently, mixtures of acrylic monomers with CC or others ammonium salts have been reported as medium suitable for frontal polymerization.^{15–17} DESs demonstrated superior performance than regular organic solvent and even ionic liquids.

Itaconic acid is one of the twelve most important building block chemicals that can be produced from sugars via biological or chemical conversions.¹⁸ The acid and its derivatives are frequently used in production of various polymers, which are viable alternatives to acrylic and methacrylic acid based polymers. Recently, owing to the nontoxic nature of the acid and biocompatibility, IA-based copolymers have been synthesized in form of hydrogels for biomedical applications.¹⁹ IA is a well-known, unsaturated monomer that polymerizes via radical mechanism

with difficulties. Persulfates and water are used as a standard initiators and the most common solvent, respectively. However, the process takes quite a long time²⁰ and for that reason, persulfate activators such as amino alcohols (N,N-dimethylethanolamine)²¹ or sodium hypophosphite^{22,23} have been developed to increase the polymerization rate or decrease the process temperature. As stated earlier, polymerization IA is usually carried out in aqueous phase and to the best of our knowledge application of deep eutectic mixtures as a polymerization medium has not been previously reported.

In this study, a novel method for preparation of IA-based hydrogels by carrying out the polymerization-crosslinking of IA in DES was described. The catalytic effect of the ammonium salt to radical free polymerization was demonstrated.

MATERIALS

IA, CC, BAA, and ammonium persulfate (APS) were from Sigma-Aldrich. All the chemicals were analytical grade and used as received.

Preparation of Hydrogels in DES

The monomer and the cross-linking agent melt were formed by stirring of mixture of IA 5.20 g (40 mmol), CC 5.58 g (40 mmol), and BAA 3.1g (2 mmol) at 110°C for 1 h. Next, the liquid melt was cooled to room temperature and mixed with a solution of APS 0.456 g (2 mmol) in distilled water (0.7 mL). The total volume of the feed mixture was 9.7 mL. The polymerization was carried out for 2 h at 65°C in a heating block. The obtained glassy, solid composite (C-DES) was immersed in distilled water, which was changed every day, for 7–10 days, to remove CC, unreacted IA, and water-soluble polymeric fractions (detected by gel permeation chromatography). The purification of the polymers was monitored by AgNO_3 test and gravimetrically by weighting of the gel. Negative result of the chloride test and reaching of swelling equilibrium (constant weight of the gel) were assumed as end of the purification procedure. Finally, the hydrogel (H-DES) was lyophilized to obtain dry polymer (xerogel) sample (P-DES). Water insoluble gel fraction was calculated as ratio of weight of the dry gel to the weight of feed monomers.



Figure 2. Melts of IA-CC with various molar ratios after cooling to room temperature, from left to right: 1 : 3, 1 : 2, 1 : 1.5, 1 : 1, 1.5 : 1, 2 : 1, 3 : 1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

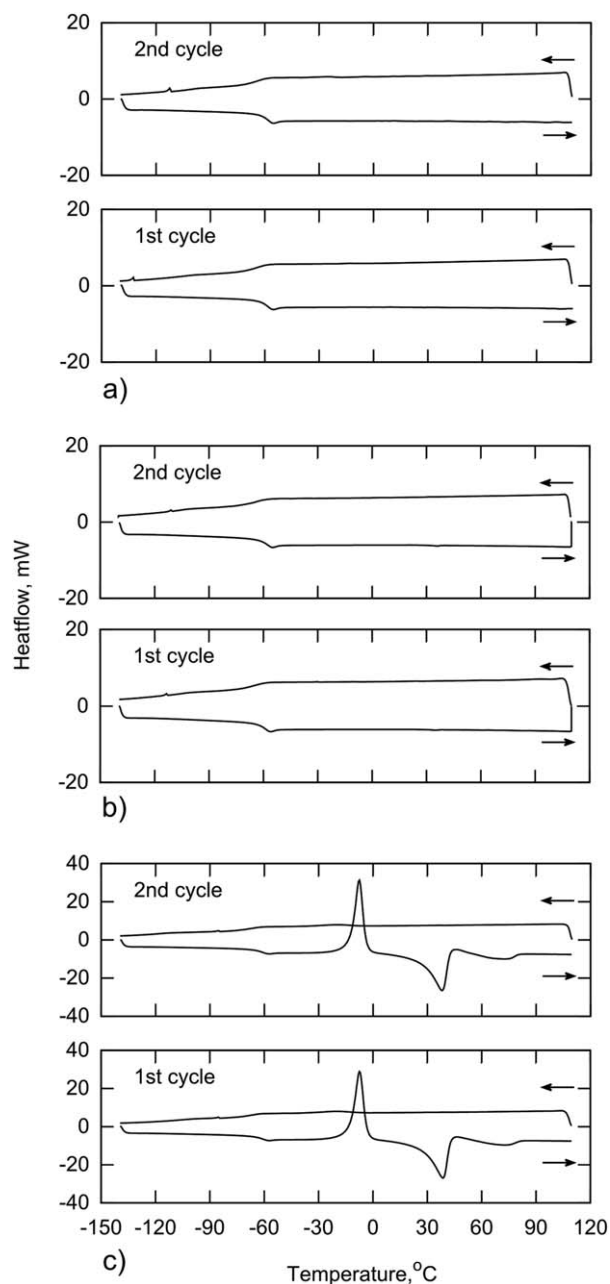


Figure 3. DSC curves of 1 : 1 (a), 1.5 : 1 (b) and 2 : 1 (c) IA-CC melts, showing two cooling and heating cycles in comparison.

Preparation of Hydrogels in Water

Mixture of 9 mL of freshly distilled water, 5.20 g of (40 mmol) IA, and 0.31 g of (2 mmol) BAA was heated with stirring at 65°C for 1 h. Next, a solution of APS 0.456 g (2 mmol) in distilled water (0.7 mL) was added. The polymerization was carried out for 2 h at 65°C in a heating block. The transparent, gel-like, crude product (C-WATER) was purified (H-WATER) and lyophilized (P-WATER) using the same protocol as for P-DES.

Swelling Measurements

The lyophilized gel (about 0.1 g, m_0) was immersed in distilled water for 48–72 h for equilibrate. After that, the hydrogel was taken out and weighted (m_1) after wiping off the excess water

from the surface with filtering paper. Swelling ratio (SR) was calculated as:

$$SR = (m_1 - m_0) / m_0.$$

Polymerization of IA Without the Cross-Linker

Mixture of 9.7 mL of freshly distilled water, 5.20 g (40 mmol) IA and 0.456 g (2 mmol) APS was heated for 2 h at 65°C. At appropriate time intervals a sample of the solution was withdrawn and diluted with water. Concentration of IA was determined using HPLC (Phenomenex Poly-Sep-P Linear column, 0.1 M NaNO₃ 1 mL/min, RI detector). For comparison polymerization of IA in DES was carried out at the same initial concentrations of the monomer and the initiator. Therefore, IA 5.20 g (40 mmol) and CC 5.58 g (40 mmol) was stirred at 110°C for 1 h. Next, the liquid melt was cooled to room temperature and mixed with a solution of 0.456 g (2 mmol) APS dissolved in distilled water (0.7 mL). The polymerization was carried out for 2 h at 65°C. At appropriate time intervals a sample of the mixture was withdrawn and diluted with water. Concentration of IA was determined using HPLC as described earlier.

General Methods

DESs were prepared by heating of mixture of IA and CC in the appropriate molar ratio (1 : 1, 1 : 1.5 or 1 : 2) at 110°C for 1 h. ¹H NMR spectra of DES (1:1 IA-CC) dissolved in D₂O (1% w/w) was recorded with a Varian Mercury VX-300 spectrometer. Differential scanning calorimetry (DSC) experiments were run on a DSC calorimeter DSC 822 Mettler Toledo. Between 20 and 25 mg of freshly prepared DESs (see above) were immediately placed inside alumina DSC crucibles. Nitrogen was used as a sweeping gas. First a sample was heated at 110°C for 15 min to eliminate their thermal history, next cooled from 110°C to -140°C, equilibrated for 15 min at this temperature, and finally heated from -140°C to 110°C. The sample was scanned two times. The rate of all scans was 10 K/min. The glass transition temperature (T_g) was determined from the midpoint of the heat capacity change during heating cycle. The thermogravimetric analysis (TGA) was conducted on a TGA 851e Mettler Toledo system. DESs samples were heated in alumina crucibles under air atmosphere with heating rate of 10 deg/min. The phase diagram of IA-CC mixtures was prepared as follows. Solid IA and CC was mixed with various molar ratios and placed into a capped vial. Next, vials were heated with mechanical stirring on a heating block at appropriate temperature for 30 min to ensure reaching the thermal equilibrium. DES formation temperature was taken as the temperature at which last crystals of the components disappeared. The samples were heated from 70°C to 150°C with 5°C ramps. FTIR spectra were obtained by a Biorad STS 165 spectrometer using KBr pellet technique. Elemental analyses (C, H, N, S, and Cl) were conducted with a Vario EL III analyzer (Elementar). Determination level of S and Cl was 0.5%.

RESULTS AND DISCUSSION

A series of IA-CC DESs were obtained by melting of the components with various ratios. It was found that mixtures ranged from 1 : 2 to 1 : 1 molar ratio of IA to CC can be prepared at lowest melting temperatures (Figure 1) and they remain liquid after cooling to room temperature (Figure 2).

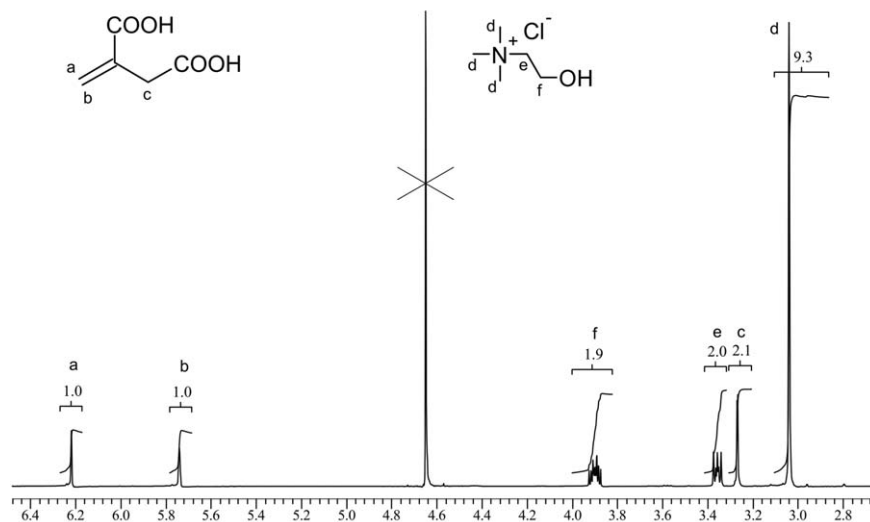


Figure 4. ^1H NMR spectra of 1% w/w 1 : 1 IA-CC DES solution in D_2O .

However, these melts show tendency to crystallize after some time (from minutes to days) depending on the IA-CC ratio. The most stable DESs were formed with low CC content, which is 1 : 1. The strong tendencies to supercooling of IA-CC DESs were proved by DSC (Figure 3). 1 : 1 and 1 : 1.5 mixtures have no melting or freezing points, but only glass transition temperatures at -60°C in both cases. This thermal behavior is typical for many ionic liquids, for example, some ethylammonium²⁴ and 1-*n*-butyl-3-methylimidazolium²⁵ ones and also resorcinol-3-hydroxypiridine-choline chloride DES.²⁶ In contrast, calorimetric data of the 1 : 2 IA : CC mixture show three phase transitions during a heating cycle: glass transition at -65°C , followed by a cold crystallization at -10°C and melting transition at 40°C . Similar thermal properties have been reported for ionic liquids, for example, ethylammonium formate,²⁴ 1-*n*-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide,²⁵ or 1-butylpyridinium tetrafluoroborate²⁷ and resorcinol based DESs^{10,26}.

Heating of mixture of the IA and CC may theoretically lead to formation of by-products: choline esters or carboxylate salts of choline and HCl. However, ^1H NMR spectra of D_2O solution of the DES (Figure 4.) show only signals of the components (i.e.)

IA and CC. Signals of the salt or the esters were not detected. These results prove that IA and CC do not undergo chemical transformations, (i.e.) esterification or dissociation during melting. Additionally, thermogravimetric measurements also indicate that the melts are stable in isothermal conditions at 110°C (the temperature of DES preparation) for at least 100 min (Supporting Information Figure S1, inset); however, heating above 180°C (Supporting Information Figure S1) led to thermal degradation of the material.

Taking into account the highest monomer concentration and relative weak tendency the melt to spontaneous solidification at room temperature, DES with 1 : 1 molar ratio of IA to CC was selected as the polymerization medium. The other prepared IA-CC mixtures, that is, 1 : 1.5 and 1 : 2 often crystallize just after cooling to room temperature and it makes polymerization experiments difficult to carry out. For comparison, we have studied properties of IA-based hydrogels prepared by two methods, that is, by polymerization in DES [Figure 5(a)] and in water [Figure 5(b)] under strictly the same conditions (temperature, time, initial concentrations of the monomer, the initiator and the cross-linking agent). It was found that BAA is soluble in the IA-CC DES. This is probably because formation of

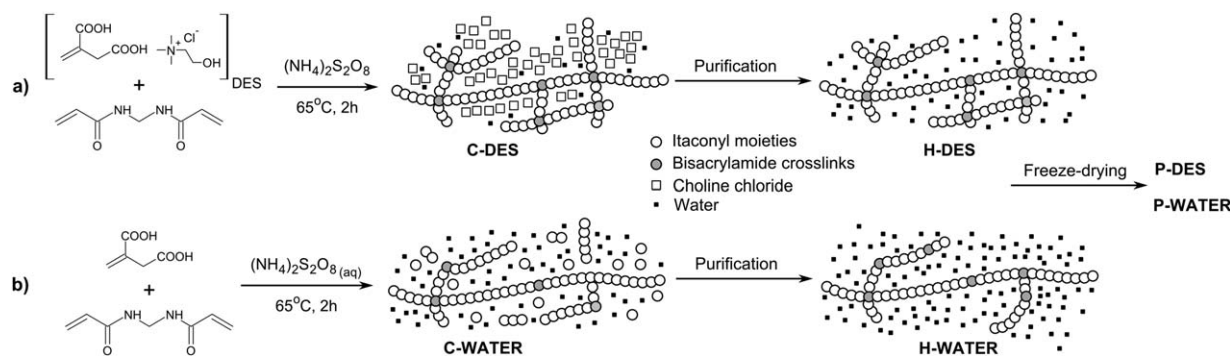


Figure 5. Preparation of poly(itaconic acid) crosslinked by BAA by: (a) polymerization in DES (P-DES) and (b) polymerization in water (P-WATER), and tentative structures of resulting composites (C-DES and C-WATER) and hydrogels (H-DES and H-WATER).

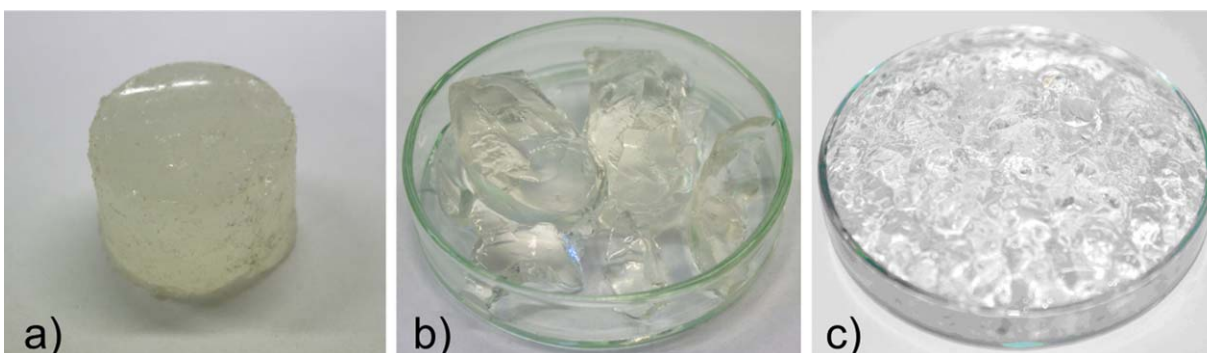


Figure 6. Forms of obtained materials: (a) solid product of in situ copolymerization-crosslinking of IA in DES before purification by water (C-DES); (b) hydrogel prepared in DES (H-DES); (c) hydrogel prepared in water (H-WATER). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

hydrogen bonds between the amide (acted as HBD) and chloride anion of the choline salt.²⁸ In opposition, the persulfate initiator is insoluble in DES. To avoid dilution of the reaction mixture, the minimum amount of water needed to dissolve APS was used. Therefore, the initiator was added to the reaction mixture as a saturated aqueous solution. Total content of water in the feed mixture was c.a. 5.6% w/w, what corresponds to 1 : 1 : 1 molar ratio of IA, CC, and water, respectively.

In the case of polymerization in DES, an increase of the reaction mixture viscosity was observed shortly after the polymerization initiation and a complete solidification occurred after about 30 min. The process was continued for total time of 2 h to give a crude, solid material (C-DES) [Figure 6(a)]. However, polymerization in water led to formation of gummy, transparent product (C-WATER). In both cases, polymeric composites were leached out by copious of water and after purification transparent gels were obtained (H-DES and H-WATER) [Figure 6(b,c)]. Control experiments have shown that polymerization of IA both in water and in DES without addition of cross-linking agent yield very viscous, completely water-soluble liquid, what might suggest that copolymerization between IA and BAA is responsible for formation of solid-like products such as C-DES and C-WATER.

The formations of poly(itaconic acid) crosslinked by BAA as the reactions product (P-DES, P-WATER) were proved by elemental analysis and IR spectroscopy. The results of elemental analysis of polymers (P-DES, P-WATER) are listed in Table I. The samples (Table I, entry 1 and 2) have similar elemental composition

except of small difference of carbon content. The obtained results differ from the calculated for hypothetical anhydrous polymer structure (Table I, entry 3). However, taking into account hydration of the polymers—approximately by one water molecule per one IA unit typical for poly(itaconic acid)²⁹ the copolymer composition was recalculated (Table I, entry 4). Finally, molecular formulas of the copolymers were corrected by changing of cross-linker and hydrated water amounts (Table I, entry 5 and 6) to fit most accurately to the experimental data (Table I, entry 1 and 2). Obtained results, especially analysis of nitrogen content, proved formation of copolymers of IA and BAA. Additionally, both polymers contain similar amounts of BAA (~7.5% mol) independently from the preparation method used. Moreover, very low Cl content (<0.5%) as a CC residue, demonstrated that the ammonium salt could be easily removed from crude polymer in opposition to polymers prepared *in situ* in ionic liquids.³⁰ Results of sulfur analysis indicate that both polymers have traces of this element. Unfortunately, limited detection limit of sulfur by elemental analysis prevent quantitative studies of sulfate end-groups in the polymers.

The polymers (P-DES and P-WATER) were also characterized by IR spectroscopy (Figure 7). Both spectra are comparable, indicating that the chemical structure of obtained polymers is almost identical. The spectra show characteristic bands for poly(itaconic acid)^{29,31–33}: 1725 cm^{-1} (C=O stretching), 1430 cm^{-1} (CH_2 bending), 1400 cm^{-1} (O-H bending), and 1200 cm^{-1} (C-O stretching). It should be noted that the carbonyl stretching vibration bands appearing for the polymers

Table I. Comparison of Elemental Analyses of Poly(itaconic-co-bisacrylamide) Polymers

Entry	Polymer	C (%)	H (%)	N (%)	S (%)	Cl (%)
1	P-DES	41.25	5.45	1.42	<0.5	<0.5
2	P-WATER	39.60	5.25	1.37	0.6	<0.5
3	Calculated for $(\text{C}_5\text{H}_6\text{O}_4)_n(\text{C}_7\text{H}_{10}\text{O}_2\text{N}_2)_{0.05n}$	46.62	4.72	1.02	0	0
4	Calculated for $(\text{C}_5\text{H}_6\text{O}_4 \cdot \text{H}_2\text{O})_n(\text{C}_7\text{H}_{10}\text{O}_2\text{N}_2)_{0.05n}$	41.23	5.46	0.90	0	0
5	Calculated for $(\text{C}_5\text{H}_6\text{O}_4 \cdot \text{H}_2\text{O})_n(\text{C}_7\text{H}_{10}\text{O}_2\text{N}_2)_{0.08n}$	41.64	5.49	1.42	0	0
6	Calculated for $(\text{C}_5\text{H}_6\text{O}_4 \cdot 1.5\text{H}_2\text{O})_n(\text{C}_7\text{H}_{10}\text{O}_2\text{N}_2)_{0.08n}$	39.45	5.79	1.37	0	0

Reaction conditions: 65°C, 2 h, [IA]0 = 4.1 mol/L, [BAA]0 = 0.2 mol/L, [APS] = 0.2 mol/L (molar ratio of [BAA]:[IA] = 0.05).

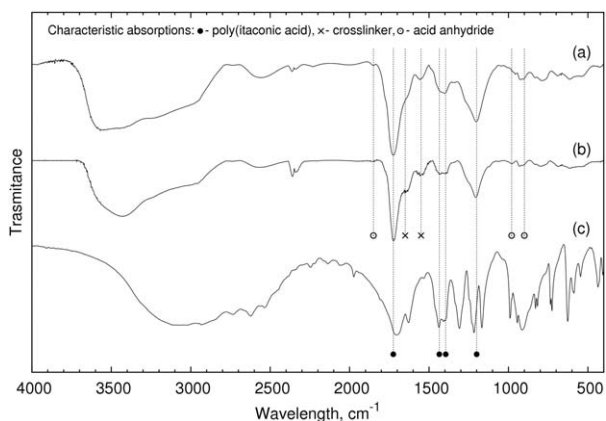


Figure 7. FTIR spectra of polymers (a) P-DES, (b) P-WATER, (c) IA.

shift to higher wave number region with comparison to the frequencies observed for the monomer [Figure 7(c)] because of disappearance of conjugation $C=C-C=O$ caused by polymerization. Moreover, infrared spectra of P-DES and P-WATER show small signals at 1850 cm^{-1} , 980 cm^{-1} , and 900 cm^{-1} that could be assigned to cyclic acid anhydride absorption, indicating some dehydration of the polymers during drying.²⁹ Additionally, bands at 1650 cm^{-1} ($C=O$ stretching) and 1550 cm^{-1} ($N-H$ bending) confirm presence of BAA moieties in the polymers.³⁴

The results of elemental and IR analysis indicate formation of poly(itaconic acid-co-bisacrylamide) and also point out that the polymers have rather similar chemical structures and elemental compositions. In contrast, examination of yield of the gel fraction and affinity of water for obtained polymers shows a strong effect of a polymerization method used on these properties (Table II). Yield of the gel fraction in polymerization-crosslinking of IA in CC melt is much higher than in water solution, what could indicate relevant catalytic effect of CC. Additionally, swelling ratio of the gel obtained in the melt is six times lower when compared with synthesized by the standard method. This finding suggests that the polymer obtained in water contains less crosslinks than prepared in the melt. Taking into account comparable amount of the cross-linker in P-DES and in P-WATER (estimated based on nitrogen content), significant differences in water swelling for the polymers could be explained by higher crosslink density of the polymer obtained in DES (Figure 5).

To elucidate a reason of the difference between cross-links density of P-DES and P-WATER, rate of IA polymerization was roughly estimated and compared. Conversion of IA as function of polymerization time was determined both in DES and in aqueous medium for the same initial concentrations of the monomer and the initiator (Figure 8). The polymerization went to $>90\%$ conversion of IA in 2 h in DES, whereas only 50% in water solution. It is clearly evidenced that the presence of CC significant increase of the polymerization rate. Higher polymerization rate indicates higher concentration of growing macroradicals what increase probability of formation of crosslinks between the crosslinker and the monomer. The acceleration effect of DESs on free-radical polymerization have been already reported,^{14,15} but the details have not been investigated yet.

Table II. Yield of the Gel Fraction and Affinity of Water for Obtained Polymers

Polymer	Water insoluble gel fraction (%)	Water swelling, g H ₂ O/g
P-DES	91	11
P-WATER	33	66

The values represent mean of duplicate in an experiment. Reaction conditions: 65°C , 2h, $[IA]_0 = 4.1\text{ mol/L}$, $[BAA]_0 = 0.2\text{ mol/L}$, $[APS] = 0.2\text{ mol/L}$.

The lack of explanation results probably from complexity of the process mechanism, due to strong interactions between DES's components. These interactions may lead to formation of supramolecular structures, where the monomer forms favorable ordered aggregates facilitating polymerization.^{35,36} Quaternary ammonium salts are able to associate with protic compounds (e.g., carboxylic acids) *via* hydrogen bonding,^{37–39} thus one can speculate that by analogy to some metal salts (e.g., $ZnCl_2$) or ionic liquids,^{40,41} both the carboxylic monomer complexes or growing macroradical complexes formed in DESs could be more reactive than nonassociated species. Moreover, DES might lower rate constant of a polymerization termination related to the high viscosity of a solution, similar to effects observed for some ionic liquid-mediated radical free polymerization.⁴¹ Additionally, ammonium salts are known to catalyze decomposition of persulfates^{42–44} and also the rate of the decomposition depend on the pH and the presence of IA.^{45,46} From that reasons, DESs can directly influence on the rate constant of an initiator decomposition, thus increase overall polymerization rate. In other words, CC might activate decomposition of APS to radicals and thus increases initiation rate of polymerization. Furthermore, CC as a quaternary ammonium salt could be applied as a phase transfer catalyst (PTC)⁴⁷ though that choline cation is relative hydrophilic, what results poor solubility of CC in common organic solvents and causes only rare use of this salt as PTC agent.^{48,49} PTC free-radical polymerization of vinyl monomers with water-soluble peroxydisulfates as initiators and crown ethers or quaternary ammonium salts as phase-transfer

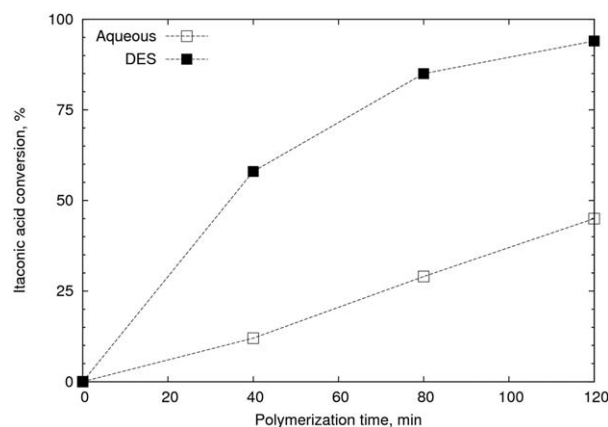


Figure 8. Time-conversion curves in the polymerization of IA in aqueous ($[CC]_0 = 0$) and DES medium ($[CC]_0 = 3.6\text{ mol/L}$). In both cases $[IA]_0 = 3.6\text{ mol/L}$, $[APS]_0 = 0.2\text{ mol/L}$ and polymerizations were carried out at 65°C without addition of cross-linker ($[BAA]_0 = 0$).

agents has been subject of many studies in recent years.^{50–55} Mechanism of free-radical polymerization under PTC conditions is complex and depends on the type of the monomer, organic solvent and the PTC-agent used. Generally, it involves the transfer of peroxydisulfate anion from the aqueous phase to the monomer-containing organic phase by phase-transfer catalyst where the ion pair initiates polymerization following its decomposition to the sulfate anion^{50,52} with rates greater than those of conventional peroxodisulfate salts (e.g., NH_4^+ , K^+) in aqueous solutions. However, some studies suggest that a significant part of the initiation could be effected also by phase-transferred sulfate radical generated in the aqueous phase.^{51,54} The effect of water on the polymerization rate seems to depend on the nature of phase-transfer catalyst – persulfate complex and monomer types, for example, the polymerization of methyl methacrylate initiated by potassium peroxodisulfate/18-crown-6 system occurs in the absence of water.⁵⁶ In opposition, no polymerization of this monomer took place using the system ammonium peroxodisulfate/hexadecyl pyridinium chloride in ethyl acetate/water⁵¹. Polymerization of IA in DES requires small amounts of water in the feed (to dissolve the persulfate initiator). From that reason, formation of choline persulfate intermediate could not be excluded and PTC-like mechanism of the polyreaction might be also considered as one of hypothesis in future investigations of free-radical polymerization in DES. However, detailed studies of mechanism of polymerization of IA in DES, including kinetics measurement and estimation of molecular weight of poly(itaconic acid) are needed to explain the phenomena. The studies are in progress and will be reported separately.

CONCLUSIONS

In summary, the synthesis of itaconic acid–choline chloride DESs in various molar ratios have been described and some selected properties of these melts were studied. It was found that the DESs are metastable at room temperature, except the equimolar mixture which was found suitable as a polymerization medium. This study has demonstrated that copolymerization-crosslinking of itaconic acid with *N,N'*-methylenebisacrylamide in the DES is a useful method for preparation of hydrogels. Comparative studies indicate that IA undergoes faster copolymerization in DES than in water, and probably for that reason the obtained product has higher cross-link density. It seems to be possible acceleration effect of choline chloride in the free-radical copolymerization reaction, but the mechanism of the phenomena remains unclear.

Our preliminary work (results not presented here) have shown that the hydrogels are useful as metal cations (Cu^{2+} , Co^{2+} , Ni^{2+}) absorbents. Moreover, due to biocompatibility of IA and nontoxic solvent used (CC) presented method of the polymers synthesis could be especially useful to hydrogels for biomedical and biotechnological applications. Future work on the mechanism and kinetics of free-radical polymerization and copolymerization of IA in DES are in progress.

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