

Polymers from Biobased-Monomers: Macroporous Itaconic Xerogels Prepared in Deep Eutectic Solvents

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ABSTRACT: New methods of preparation of crosslinked polymers from itaconic acid as a renewable monomer have been explored. Synthesis of hydrogels and xerogels from the acid in deep eutectic solvents (DESs) are described and some basic properties of the materials are reported. Most importantly, a surfactant-free method of creation of macroporous poly(itaconic-co-bisacrylamide) by phase separation polymerization in binary mixture of the DES and poly(ethylene glycol) is demonstrated.

KEYWORDS: Choline chloride, free-radical polymerization-crosslinking, hydrogels, phase segregation, renewable monomers

1 INTRODUCTION

Itaconic acid (IA) is an unsaturated dicarboxylic acid produced by biochemical processes through fermentation of sugars [1]. According to reports by the U.S. Department of Energy [2] from 2004, IA is one of twelve biotechnological products with the greatest potential for industrial use (so-called platform chemicals). Due to its chemical structure, i.e., presence of double carbon-carbon bond and two carboxylic groups, IA is widely used as monomer and co-monomer in the manufacture of linear or three-dimensional crosslinked polymers. These crosslinked materials swell in water or biological fluids and form hydrogels. Hydrogels are receiving great interest due to their promising applications such as sensors, separation membranes, adsorbents, and materials in medicine and pharmacy as drug delivery systems [3]. Anionic hydrogels containing itaconic units could be used, for instance, for removal of heavy metals from wastewater [4] and for drug delivery applications [5, 6].

Because of its wide scope of applications, new methods of polymerization of the acid are still being researched. Most recently, we have demonstrated the use of deep eutectic solvents as neoteric media for IA polymerization [7, 8].

In 2001, the first paper dealing with polar solvents made by melting of quaternary ammonium salts

(QXs) and zinc or tin chlorides was published [9]. Because the melting point of the mixtures was much lower than the starting materials, the term deep eutectic solvents (DESs) was coined [10]. DESs can be prepared by the heating of ammonium salts—most often choline chloride (CC)—with, among others, hydrogen bond donors (HBD), for instance, amides, amines, alcohols, phenols or carboxylic acids. DESs seem to be a less expensive alternative to ionic liquids [11]; they can be prepared simply by heating (at ~100 °C) of readily available components, e.g., mass-produced choline chloride, renewable glycerol or natural polycarboxylic acids. DESs are interesting molecular complexes, on the one hand, and promising solvents for industrial application, on the other hand.

Recently, the use of DESs in the synthesis of polymers and related materials has been reviewed [11, 12] and many examples of DES-assisted fabrication of porous materials have been shown [13–16]. It has been emphasized that DESs can act as all-in-one solvent–template–reactant systems [11]. For instance, porosity in polymers was introduced by phase separation during polycondensation of formaldehyde with various phenolic DESs or by free-radical polymerization-crosslinking of high internal phase emulsions with DESs as the internal phase [17, 18].

In this work, we continue our study of DES-assisted preparation of itaconic-based hydrogels [8]. We have already demonstrated that it is possible to carry out free-radical polymerization-crosslinking of DES containing IA as HBD and CC as a QX. Additionally, we have found that because of activation of an initiator

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by CC both the polymerization rate and crosslinking degree is higher than in aqueous media [7, 8].

Herein we report our initial studies on the morphology of itaconic-based xerogels prepared in the DES. Moreover, some basic properties of the materials, like swelling ratio, metal ion affinities and BET surface area, were investigated. Finally, we successfully demonstrated that phase separation polymerization in a IA-CC-DES/poly(ethylene glycol) liquid-liquid dispersion results in creation of macroporous itaconic-based xerogels.

2 EXPERIMENTAL

2.1 Materials

IA, CC, N,N'-methylenebisacrylamide (MBA), ammonium persulfate (APS), poly(ethylene glycol)s with average molecular weight $M = 1500$ g/mol (PEG1500, mp 44–48 °C) and $M = 3000$ g/mol (PEG3000, mp 55–58 °C) were from Sigma-Aldrich. All the chemicals were analytical grade and used as received.

2.2 Methods

The morphologies of the polymer xerogels were examined using a Hitachi S-4700 scanning electron microscope. Prior to analysis, small samples (approximately 3 mm × 3 mm) of manually cleaved hydrogels in a full swollen state were dipped into liquid nitrogen. These vitrified specimens were immediately lyophilized. After freeze-drying, samples were mounted on a SEM stub using conductive double-sided tape and sputter-coated with graphite. Nitrogen adsorption/desorption isotherms were determined at 77 K with a Micromeritics ASAP 2010 instrument. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) equation from the adsorption isotherm over a pressure range of 0.06–0.3 p/p₀.

2.2.1 Preparation of Hydrogels

A series of hydrogels in DES was prepared. A mixture of IA 5.20 g (40 mmol) and CC 5.58 g (40 mmol) was heated while stirring at 110 °C in a beaker placed on a magnetic stirrer for 1 h until a clear viscous liquid was formed. In the obtained DES, an appropriate amount of MBA was dissolved. After dissolution of the crosslinking agent, the mixture was cooled to rt and APS 0.456 g (2 mmol) as a saturated aqueous solution (0.7 mL) was added. The polymerization was conducted at 60 °C for 2 h. After that, crude product was immersed in distilled water, which was changed every day, for 7–10 days, to remove CC, unreacted IA

and water-soluble polymeric fractions. The purification of the polymers was monitored by AgNO₃ test and gravimetrically—by weighting of the hydrogel. A negative result of the chloride test and reaching of swelling equilibrium (constant weight of the hydrogel, m_H) were assumed as the end of the purification procedure. Finally, a hydrogel was lyophilized and the obtained xerogel weighted (m_X).

Yield of the water-insoluble gel fraction (Y) was determined by gravimetric method and calculated using equation:

$$Y = \frac{m_X}{(m_{IA} + m_{MBA})} \cdot 100\% \quad (1)$$

where m_X is a weight of the xerogel, m_{IA} and m_{MBA} are weights of starting monomers.

Swelling ratio (SR) was calculated as:

$$SR = \frac{m_H - m_X}{m_X}, \text{ gH}_2\text{O/g xerogel} \quad (2)$$

where m_H is a weight of swollen hydrogel in equilibrium state.

Macroporous hydrogels were prepared in a similar way, but after dissolution of the crosslinking agent; additionally, 1.1 g of poly(ethylene glycol) was added at 60 °C. The mixture was stirred for a few minutes until white dispersion formed. The polymerization process was carried out in the absence of any surfactant.

The reference hydrogel was prepared in nearly saturated aqueous solution of IA (5.2 g IA per 12 ml of water) at 60 °C and the purification procedure of the crude hydrogel was the same as described above.

The hydrogels were labeled according to a medium (A – aqueous, D – DES), the % molar ratio of crosslinking agent and molecular weight of PEG used (if applicable).

2.2.2 Cu²⁺ Uptake

A sample of 50 mg of a xerogel was immersed in 30 mL of 6 mM Cu(NH₃)₄²⁺ in 1 M ammonia at rt. The concentration of the copper complex was determined directly by spectrophotometric method. The absorbance of the solution was measured at 608 nm at 30 min time intervals until constant value was obtained, i.e., sorption equilibrium was reached (usually 2–3 h). Concentration of the complex was determined from a calibration curve, and the Cu²⁺ uptake was calculated as:

$$\text{Uptake} = \frac{(C_0 - C_{eq}) \cdot V \cdot M_{\text{Complex}} \cdot 1000}{m_X}, \text{ mg Cu}^{2+}/\text{g} \quad (3)$$

where C_0 and C_{eq} are initial and equilibrium concentrations of copper complex (mol/dm³), V is solution volume = 30 mL and m_X is a xerogel sample weight (g).

3 RESULTS AND DISCUSSION

The chemical crosslinked hydrogels were prepared via free-radical polymerization of IA and MBA as shown in Figure 1. Feed ratios of the monomer, the crosslinking agent and the initiator are listed in Table 1.

It is well known that macroporous polymeric materials can be formed, for instance, as a result of the phase separation during the free-radical crosslinking copolymerization of vinyl and divinyl monomers in the presence of an inert diluent [19]. In the case of polymerization in DES, where HBD is a vinyl (e.g., IA) or a divinyl monomer (e.g., MBA), the secondary component of the DES, i.e., quaternary ammonium salt (e.g., CC) acts as the diluent. Here, we studied polymerization in two systems: IA-CC-MBA and IA-CC-PEG-MBA, where PEG was used as an additional second inert diluent.

All hydrogels were synthesized at 60 °C for 2 h and the ratio of initiator to the monomer was kept

constant. The referenced hydrogel PA-5 was prepared in a saturated aqueous solution of IA. Hydrogels PD-2, PD-5, PD-10 and PD-15 were synthesized in DES using different amounts of crosslinking agent ranging from 2 mol% to 15 mol% with respect to the monomer. In other words, the reaction medium consisted of MBA dissolved in molten CC-IA mixture (DES). Additionally, hydrogels PD-5-1500 and PD-5-3000 were prepared with the same crosslinker amount as for polymer PD-5, but as an additional inert diluent, 9 wt% of PEG1500 or PEG3000 was added to the feed. Chemical structures of obtained poly(itaconic-co-bisacrylamide) hydrogels were confirmed by elemental analysis and FTIR spectroscopy as described before [8].

It was observed that in the case of DES-mediated reactions, after 20–30 min of polymerization the reaction mixture solidifies (transforms into semitransparent rubbery and then glassy monolith [8]). Thus, in fact, DES is a liquid reaction medium only at the initial stage of the polymerization. The same effect was

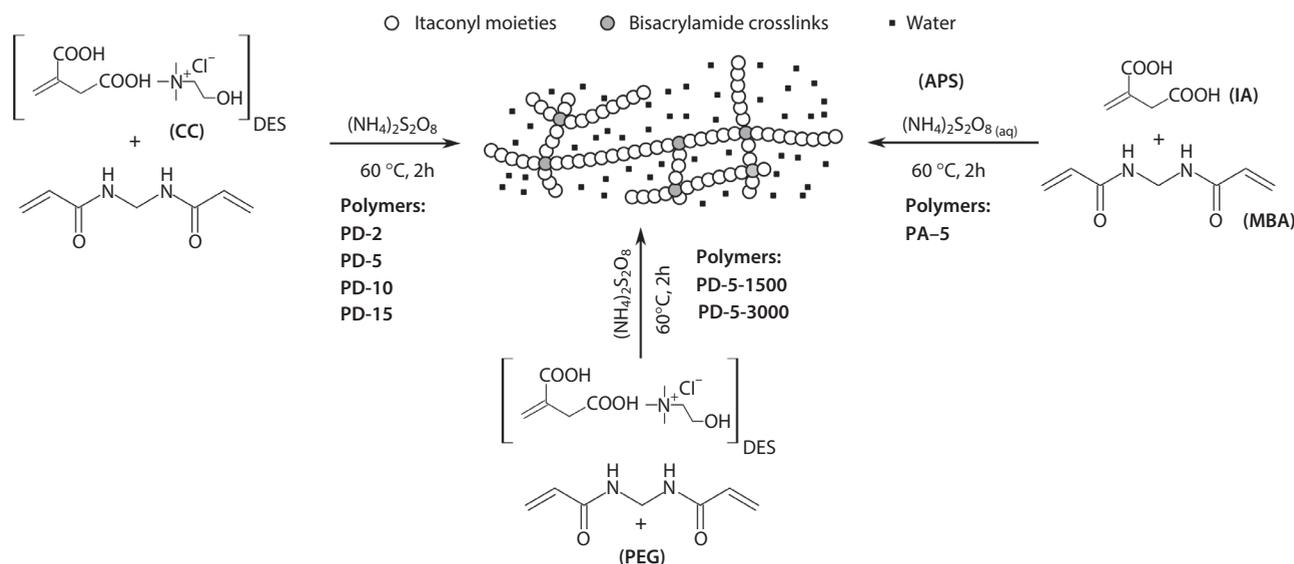


Figure 1 Synthesis of hydrogels.

Table 1 Preparation conditions of hydrogels (60 °C, 2 h), yield of the gel fraction (Y, %), swelling ratio (SR, gH₂O/g xerogel) and equilibrium Cu(NH₃)₄²⁺ uptake (mgCu²⁺/g xerogel).

Hydrogel	Molar ratio			Diluent, 9% w/w	Medium	Yield of the gel fraction (Y), %	SR	Cu ²⁺ Uptake
	IA	MBA	APS					
PA-5	1	0.05	0.05	-	Aqueous	57	72.0	73
PD-2	1	0.02	0.05	-	DES	29	223.0	83
PD-5	1	0.05	0.05	-	DES	98	7.5	31
PD-10	1	0.10	0.05	-	DES	100	3.0	24
PD-15	1	0.15	0.05	-	DES	100	2.6	18
PD-5-1500	1	0.05	0.05	PEG1500	DES	64	7.5	26
PD-5-3000	1	0.05	0.05	PEG3000	DES	74	6.0	27

noticed in the other systems, where a monomer was both a DES component, and a polymerization substrate [12].

The effect of a reaction medium, crosslinking agent amount and the diluent on polymerization yield, swelling ratio, sorption properties and morphology of xerogels were investigated. The process of free-radical polymerization of IA is faster in DES than in water (most common solvent for IA polymerization). This is probably because of activation of the persulfate initiator by CC [7, 8]. The higher polymerization rate causes formation of more crosslinked hydrogels, with a lower swelling ratio [8]. The phenomenon explains differences in *SR* of hydrogel PA-5 and PD-5. As expected, addition of increasing amounts of MBA results in formation of hydrogels with a higher crosslink degree, manifested by a smaller swelling ratio (hydrogels PD-2, PD-5, PD-10 and PD-15). Additionally, it can be seen that *SR* is correlated with sorption properties of investigated hydrogels. Copper ions uptake increases when *SR* increases. It means that accessibility of carboxylic groups of poly(itaconic-co-bisacrylamide), which are responsible for the metal ions binding, is better for hydrogels with a lower crosslink degree. This effect has been observed many times before for other poly-electrolyte hydrogels, e.g., for poly(acrylic acid-co-acrylamide) [20].

Polymers PD-5-1500 and PD-5-3000 have been prepared in the presence of PEG, and they have similar properties as PD-5 synthesized in the absence of PEG. The addition of PEG results in a decrease in yield of

crosslinked fraction and a decrease in affinity of PD-5-1500 and PD-5-3000 xerogels to copper ions.

Hydrogel pore structure can be assessed by mercury intrusion porosimetry, thermoporometry, and nitrogen adsorption, or by visual methods like scanning electron microscopy (SEM) [21]. As can be seen in Figures 2 and 3, structure of the materials is very different. The xerogels PA-5 and PD-2 show similar flake-like spongy morphology typical of highly swelled hydrogels. The shape of pores results from ice-templating [22], so, in fact, in these cases water plays the porogen role. In contrast, the xerogel PD-5 prepared by freeze-drying of hydrogel synthesized in DES with the same crosslinking agent amount as PA-5 has a compact structure and macropores are not present. It seems that contrary to other studies [13–16], in IA-CC DES, the ammonium salt does not segregate during the polymerization. CC molecules may form strong associations with carboxylic groups of poly(itaconic-co-bisacrylamide), which probably prevent formation of CC-rich domains with micrometric size, thus creating macropores in the xerogel. For that reason, an additional inert diluent was introduced into the polymerization mixture to develop macroporous poly(itaconic-co-bisacrylamide) in the DES.

As expected, use of poly(ethylene glycol) results in the creation of a well-defined highly porous network (PD-5-1500 and PD-5-3000). The shapes of the structures and the voids indicate that a phase separation had taken place. The diameter of the pores ranged from 1 to 2 μm or from 2 to 4 μm for PD-5-1500 or PD-5-3000 xerogels, respectively (Figure 3).

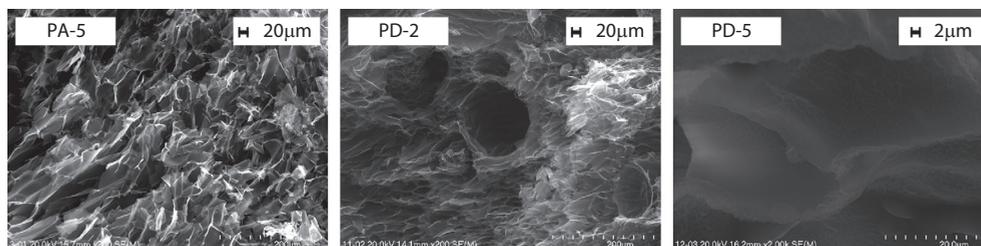


Figure 2 SEM micrographs of xerogels prepared in the absence of PEG.

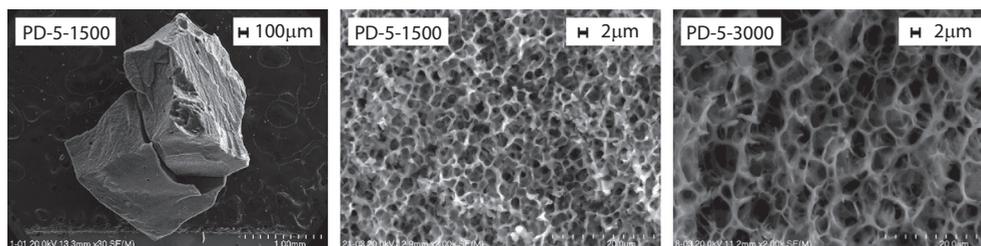


Figure 3 SEM micrographs of xerogels prepared in DES in the presence of PEG.

Tentative experiments indicate that both PEG1500 and PEG3000 are not soluble in the IA-CC mixture. At the polymerization temperature (60 °C) both PEG1500 and PEG3000 are liquids. Liquid-liquid dispersion of the PEG in the DES (Figure 4) is stable at 60 °C for at least 15 min, but after that time, PEG microdroplets undergo coalescence and separation into two phases occurs. However, as the polymerization-crosslinking proceeds, viscosity of the system increases rapidly, which could prevent the complete separation, and in this way polymerization-induced phase segregation could occur. Gelation undergoes in monomer-rich phase deposited in the interstices between interconnected PEG microdroplets.

To study the effect of the PEG on micro- and mesoporosity (pores with diameters between 0.2 and 50 nm) of the xerogels, BET surface area analysis was carried out (Table 2). Specific surface area of the xerogel PD-5-1500 is reduced 8 times and total micro- and mesopores volume is decreased 21 times with respect to the properties of PD-5 xerogel, thus added PEG results in a decrease of micro- and mesoporosity of the xerogel. It is obvious that the surface area characterized by BET analysis is limited to mesopores with a diameter up to 50 nm. For that reason macropores created in PD-5-1500 xerogel and visible on SEM micrographs (Figure 3) were not detected by this method. Full characterization of macroporosity of the xerogels by mercury porosimetry is planned in further, systematic studies.

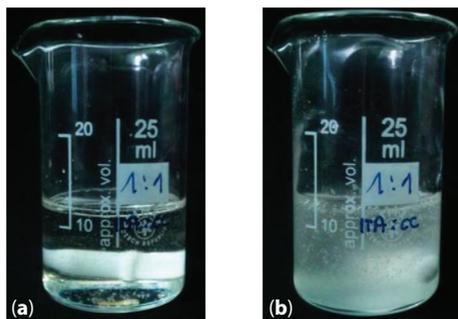


Figure 4 DES formed by heating of choline chloride with itaconic acid in 1:1 molar ratio before (a) and after (b) addition of PEG1500 at 110 °C (9 wt%) – mixture cooled to rt.

Table 2 Influence of PEG additive on micro- and mesoporosity of xerogels: specific surface area (S_{BET}), total pores volume (V_{total}), micropores volume (V_{mi}), mesopores volume (V_{me}).

Sample	S_{BET} m ² /g	V_{total} cm ³ /g	V_{mi} cm ³ /g	V_{me} cm ³ /g
PD-5	50.1	0.30	0.01	0.29
PD-5-1500	5.9	0.14	0.002	0.012

Taking into account the similar swelling ratio and Cu²⁺ uptake of PD-5 and PD-5-1500, it is difficult to explain such strong differences in the xerogels' texture caused by the presence of PEG during the polymerization process. A decrease of the gel content of 64% for PD-5-1500 and 74% for PD-5-3000 in comparison to 98% for PD-5 might suggest the influence of PEG on the polymerization-crosslinking course. Another hypothesis could be that PEG-induced lateral aggregation of poly(itaconic-co-bisacrylamide) might occur as supposed for poly(acrylamide) gels [23].

4 CONCLUSION

This initial study has shown that it is possible to fabricate porous itaconic xerogels in DES. Depending on the crosslinking amount and synthesis protocol used, it is possible to prepare materials with different availability of carboxylic groups, morphologies and specific surface area. It should be stressed that phase separation polymerization in a binary DES-PEG system in the absence of any surfactant resulted in creation of macroporous xerogels.

The materials have many possible applications. The copper uptake achieved suggests the potential use of the xerogels to remove heavy metals from wastewater. Additionally, due to the nontoxic nature of reagents used (IA, CC, PEG), the hydrogels/xerogels prepared in the DES could be considered as solid supports for immobilization of microbial cells and/or enzymes. Moreover, because of the loss of micro- and mesoporosity and reduced availability of carboxylic groups, macroporous poly(itaconic-co-bisacrylamide) hydrogels prepared by phase separation polymerization seem to be promising materials for use as stationary phases in chromatography of biomolecules [24] or as scaffolds for cell proliferation [25, 26].

Further detailed works are currently being undertaken to study the mechanisms and factors that influence the microphase separation in DES-PEG systems during polymerization.

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