

Use of Natural Deep Eutectic Solvents for Polymerization and Polymer Reactions

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Green chemistry is a key opportunity in chemistry and chemical engineering today because it can potentially preserve the environment and human health. It entails the choice of natural biodegradable raw materials and solvents, environmentally acceptable processes, and minimal use of non-hazardous chemicals. Previously, deep eutectic solvents (DES) have found many applications in organic, analytical, and polymer chemistry. The recent discovery of natural deep eutectic solvents (NADES), where many plant-abundant primary metabolites have been found to change their state from solid to liquid at certain temperatures when mixed in a proper ratio, should accelerate their use as replacements for common organic solvents that exhibit inherent toxicity and high volatility. In this work, we have reviewed the application of NADES as green, sustainable solvents in processes that involve polymerizations and polymer reactions. It is clear that many applications have already been explored. Undoubtedly more progress will be made in the future, and NADES will become more commonly used in polymer-related processes.

Keywords: natural deep eutectic solvents, polymer hydrolysis, polymer modifications, polymer reactions, polymerization

1. Introduction

Because of increasing environmental and safety concerns over the production and disposal of polymeric materials, there have been a lot of research and development (R&D) and commercial activities involving bio-based materials from agricultural feedstocks.^{1,2} Sustainable technologies are also needed to replace polymer products made from petroleum-based feedstock. In both R&D and production, the use of appropriate solvents is often critical. However, most chemical reactions cannot be conducted in water, and many organic solvents pose health and safety

hazards. The introduction of ionic liquids (ILs) as solvents was considered an improvement;³⁻⁵ yet many of them are expensive and are not really eco-friendly.⁶ A breakthrough has appeared in the form of deep eutectic solvents (DES).⁷⁻¹³ These constitute a new class of solvents obtained by mixing two or more substances, which form eutectic mixtures with melting points much lower than that of the individual components. Like ionic liquids, DES solvents have many attractive physicochemical properties, such as chemical and thermal stability, non-flammability, high electrical conductivity, and solubilization of a number of organic compounds. Thus, these materials have the potential of replacing conventional organic solvents for polymerization and polymer reactions. More recently, natural deep eutectic

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solvents (NADES), such as mixtures of choline chloride/urea, choline chloride/glycerol, and malic acid/glucose, have been found to be even more attractive because they comprise agro-based, natural, renewable components.¹⁴⁻²⁰

The use of DES and NADES in polymer science is fairly recent, but quite a few papers have already been published that relate to polymer chemistry. Previously, three review articles have appeared on the use of DES for selected polymerization reactions.^{12,13,21} Two related reviews deal with biocatalyses and biotransformations^{22,23} and one deals with biomass utilization²⁴ in the presence of DES. In this work, we have provided an updated review of polymerization and polymer reactions using NADES, with some related papers on DES included for convenience and future reference. It is the authors' hope that this work will stimulate further interest of this class of eco-friendly solvents among polymer scientists.

2. General Description of NADES

NADES constitute a new generation of deep eutectic solvents, introduced by Choi *et al.*¹⁴ A NADES solvent is defined as a combination of two or three natural, renewable, biodegradable and inexpensive natural substances which are capable of self-association, often through specific interactions, to form a eutectic mixture. These specific interactions are responsible for the decrease of the melting point of the mixture. The melting point of the eutectic mixture is generally lower than those of each individual component; in general, the NADES of interest are liquids from room temperature to 100 °C.

In past reviews, DES are sometimes considered to be mixtures of a salt and hydrogen-bond donor,^{9,10} or mixtures of hydrogen-bond acceptor (HBA), such as a quaternary salt, and a hydrogen-bond donor (HBD), such as an organic acid, carbohydrate, amine, or polyol.¹² When an HBD is used to form a eutectic mixture, charge delocalization is presumed to occur through hydrogen-bond formation between the HBA and the HBD molecules. As we surveyed the many NADES reported, it is clear that hydrogen bonding is not the only mechanism possible. We have grouped the common NADES into three types (Table 1) depending on the interactions between the components: (i) ionic, (ii) polar, and (iii) hydrogen bonding. The major difference between NADES and DES is the use of natural components in the former case, but the nature of the interactions is similar. Sometimes a clear distinction between NADES and DES cannot easily be made; for example, acetic acid, succinic acid, itaconic acid, levulinic acid, ethanol, ethylene glycol, 1,2-propanediol and others can be made from both petroleum and bio-based materials and processes. Note

also that the ionic interactions in DES are similar to the ionic interactions in ionic liquids, although the optimal molecules used for ILs and DES may be different. For convenience, some common NADES solvent systems are given in Table 2; their chemical structures are given in the Supplementary Information.

Compared with IL, the process of making NADES is relatively simple, and the eutectic mixture can often be obtained in high purity and low cost. A typical preparative method consists of mixing components in a proper ratio under heating until a homogenous liquid is obtained. NADES generally exhibit properties such as low vapor pressure, low toxicity, water compatibility, biodegradability and non-flammability. All these properties make NADES viable alternatives to traditional organic solvents, which may have varying degrees of toxicity or volatility. Since NADES are easily prepared from relatively pure components, purification is usually not necessary, and often a 100% atom utilization rate is obtained.

NADES have been employed in a wide range of applications, including electrochemistry,²⁵⁻²⁸ bioenergy,²⁹⁻³² enzyme-catalyzed reactions,³³⁻³⁶ CO₂ adsorption,³⁷⁻³⁹ biomass processing,^{24,40,41} and separation and extraction of target compounds from natural products.⁴²⁻⁴⁸ In the next three sections, we shall provide a review of the application of NADES in processes that involve polymerizations and polymer reactions. As indicated above, sometimes the distinction between NADES and (non-natural) DES is not straightforward, and we have included some non-natural DES in the following review.

3. Polymerization

In polymer product development, polymerization is often needed to produce new or improved polymers. Whereas some polymers can be made neat or in water, the majority of polymers are made in organic solvents. Thus, eco-friendly solvents like NADES or DES can be useful here.

3.1. Addition polymers

In an approach used by Mukesh *et al.*,⁴⁹ a novel natural deep eutectic solvent was prepared by the endothermic complexation of choline chloride and orcinol at room temperature. Among *N*-isopropyl acrylamide (NIPAM), vinyl acetate (VA) and 2-hydroxyethyl methacrylate (HEMA), only HEMA was found to be self-polymerized in the above solvent at room temperature at optimized concentrations resulting in the formation of a highly stretchable gel.

Table 1. Types components, and examples of common natural deep eutectic solvents (NADES) and some non-NADES components

Interaction	NADES components	DES components	Examples
Ionic	(1) organic cations + carboxylic acids (2) amino acid + carboxylic acid (3) metal carboxylate salt + carboxylic acid	(4) organic cation + inorganic metal salts	organic cations: (i) choline chloride (ii) methyltriphenylphosphonium bromide, ethylammonium chloride, tributylammonium halide, <i>N,N</i> -diethylethanol ammonium chloride carboxylic acids: (i) lactic acid, maleic acid, acetic acid, oxalic acid, malonic acid, succinic acid, malic acid, citric acid, aconitic acid, tartaric acid, phytic acid, itaconic acid, caffeic acid, <i>p</i> -coumaric acid, cinnamic acid, gallic acid, suberic acid (ii) acrylic acid, methacrylic acid, <i>p</i> -toluenesulfonic acid, 2-hydroxybenzoic acid, phenylacetic acid
	(1) organic cation + sugar (2) organic cation + urea (3) amino acid + sugar (4) metal carboxylate salt + sugar	(1a) organic cation + hydroxy cpd (5) organic cation + amide (6) inorganic metal salt + sugars	acid salts: glutamic acid salt, sodium phytate sugars: erythritol, xylitol, adonitol, ribitol, sorbitol, xylose, rhamnose, glucose, fructose, sorbose, mannose, galactose, sucrose, trehalose, maltose, raffinose, inositol hydroxy compounds: glycerol, ethylene glycol, 1,2-propanediol, phenol, triethylene glycol, <i>o</i> -cresol, 2,3-xyleneol, isosorbide, 1,4-butanediol, resorcinol
Hydrogen bonding	(1) carboxylic acid + carboxylic acid (2) carboxylic acid + sugar (3) sugar + sugar (4) urea + sugar	(2a) carboxylic acid + hydroxy cpd (3a) polyol + hydroxy cpd (4a) urea + hydroxy cpd	amino acids: betaine, proline, alanine, serine ureas: urea, 1-methylurea, 1,3-dimethylurea, ethylene urea, thiourea, propylene urea amides: acrylamide, acetamide, trifluoroacetamide, benzamide inorganic metal salts: SnCl ₂ , ZnCl ₂ , CrCl ₃ , ZnClO ₄ , MgClO ₄

1a, 2a, 3a, 4a: similar to item 1, 2, 3 and 4, respectively, but not "natural".

Bednarz *et al.*⁵⁰ devised new methods of preparation of hydrogels and xerogels from itaconic acid in DES involving choline chloride. Moreover, a surfactant-free method of creating macroporous poly(itaconic-*co*-bisacrylamide) by phase separation polymerization in binary mixture of the DES and poly(ethylene glycol) was shown.

In several papers, Mota-Morales *et al.*⁵¹⁻⁵³ carried out frontal polymerization using DES. In the first paper,⁵¹ they demonstrated superior performance for the frontal polymerizations using mixtures of acrylic acid or methacrylic acid and choline chloride, relative to regular organic solvents

and even ionic liquids. They also showed full recovery of choline chloride after polymerization. In a second paper,⁵² they extended their work to acrylic acid and acrylamide and also incorporated an active filler into the polymeric matrix. In yet another paper,⁵³ they synthesized macroporous poly(acrylic acid)-carbon nanotube composites by frontal polymerization in DES. They have recently written a review article on this topic,²¹ where more detailed information on this and related work can be found.

Wang *et al.*⁵⁴ used several DES for atom transfer radical polymerization (ATRP) of methyl methacrylate with FeBr₂

Table 2. Commonly used combinations of natural deep eutectic solvents

NADES components	Molar ratio
Choline chloride:urea	1:2
Choline chloride:oxalic acid	1:1
Choline chloride:malonic acid	1:1
Choline chloride:succinic acid	1:1
Choline chloride:citric acid	2:1, 1:1, 1:2, 1:3
Choline chloride:lactic acid	1:1
Choline chloride:malic acid	1:1, 1:2, 1:3
Choline chloride:malic acid:water	1:1:2
Choline chloride:glycerol	1:1, 1:2, 1:3, 1:4
Choline chloride:glycerol:water	1:2:1
Choline chloride:glucose	1:1
Choline chloride:glucose:water	1:1:1, 5:2:5
Choline chloride:xylitol	1:1
Choline chloride:xylitol:water	1:1:2, 1:2:3
Betaine:sucrose	1:1, 2:1, 4:1
Betaine:citric acid	1:1
Betaine:citric acid:water	1:1:5
Citric acid:proline	1:1, 2:1, 3:1
Citric acid: β -alanine:water	1:1:3
Citric acid:glucose	2:1, 1:1
Citric acid:glucose:water	1:1:5
Lactic acid:glucose	5:1
Lactic acid:glucose:water	5:1:3
Lactic acid: β -alanine	1:1
Lactic acid: β -alanine:water	1:1:3
Lactic acid:proline	1:1
Malic acid:glucose	1:1, 1:2
Malic acid:proline	1:1
Malic acid:sorbitol	1:1
Malic acid:sorbitol:water	1:1:3
Glucose:fructose	1:1
Glucose:sucrose	1:1

in the absence of any additional ligands. They classified DES in three types: amide compounds (type I), inorganic salts (type II) and quaternary ammonium salts (type III). Owing to the nature of DES, the system developed was much more environmentally benign and relatively cheap in comparison with most conventional iron-catalyzed ATRP systems reported. Moreover, the DES-tuned ATRP could be a great opportunity to utilize environmental friendly media and could drastically reduce the high costs caused by common ligands. In a related work, ATRP of methyl methacrylate in the presence of glycerol/1,3-dimethyl-2-imidazolinone was reported by Tian *et al.*⁵⁵

In another paper, Mendonça *et al.*⁵⁶ used $\text{Na}_2\text{S}_2\text{O}_4$ and choline chloride/urea as supplemental activator and reducing agent ATRP for several hydrophilic monomers. The resulting polymers exhibited low polydispersity. Block copolymers were also prepared.

A different study⁵⁷ entailed the enzyme-mediated free radical polymerization of acrylamide in choline chloride/urea and choline chloride/glycerol. There was a decrease in the activity of the enzyme (horseradish peroxidase), but acrylamide could be fully converted to polymer with similar molecular weight as aqueous polymerization. An advantage of NADES was the low temperature (4 °C) that could be used for polymerization, whereas no polymer was found for the polymerization in water.

In a paper by Fernandes *et al.*,⁵⁸ biodegradable deep-eutectic mixtures were used as electrolytes for the electromechanical synthesis of conducting polymers. The NADES consisted of a 1:2 mixture of choline chloride and ethylene glycol. The polymer used as a model was polyaniline. Cyclic voltammetry was employed for polymerization and for the characterization of the growth of the polymer. The polyanilines thus prepared exhibited nanoparticulated morphology and high reversibility to doping/dedoping, which evidenced fast charge transport across the films. Excellent conductivities higher than 50 S cm^{-1} were found using this approach.

Park and Lee⁵⁹ employed DES as an alternative reaction media in FeCl_3 -catalyzed oxidative polymerization of 3-octylthiophene (3-OT). The synthesis of poly(3-OT) using choline chloride:urea (ChCl:U) or choline chloride:urea:thiourea (ChCl:U:TU) reached a yield of 100% within 2 and 3 h at 50 °C, respectively. In the case of ChCl:U, the yield became higher than that of conventional polymerization in chloroform after 4 h. These authors found that the DES also had the potential of replacing ILs and conventional volatile organic solvents for the development of environmentally benign industrial processes with respect to organic light-emitting diodes (OLEDs), optical sensors, and luminescent devices.

Hosu *et al.*⁶⁰ utilized electropolymerization in DES to prepare poly(methylene blue) (PMB) polymers with different nanostructured morphologies. PMB films were synthesized on glassy carbon electrodes (GCE) by potential cycling from a mixture of 90% ethaline (choline chloride:ethylene glycol) and 10% aqueous solution with different ionic composition, i.e., Na^+ , SO_4^{2-} , ClO_4^- , NO_3^- , Cl^- . PMB polymer films with unique nanostructures have been successfully synthesized in ethaline plus 10% v/v aqueous solution of 0.1 M NaOH and 0.1 M HClO_4 in the final DES optimized mixture. All PMB films obtained from DES (PMB_{DES}) exhibited higher redox currents and a significantly lower charge transfer

resistance than PMB obtained in aqueous media (PMB_{aq}). Moreover, GCE modified with PMB_{DES} obtained at different scan rates, from 100 to 500 mV s^{-1} , revealed their superior sensing performance compared to $\text{GCE}/\text{PMB}_{\text{aq}}$, and that PMB_{DES} obtained at 150 mV s^{-1} scan rate is the most suitable for this purpose.

3.2. Condensation polymers

García-Argüelles *et al.*⁶¹ showed that DES could serve not only as an efficient solvent for polymerization but also as an efficient carrier of active principal ingredients. Thus, they successfully prepared biodegradable poly(octanediol-co-citrate) polyesters using a DES solvent including quaternary ammonium or phosphonium salts and octanediol. In the resulting polymers, the presence of quaternary ions (i.e., choline chloride, tetraethylammonium bromide, hexadecyltrimethylammonium bromide, and methyltriphenylphosphonium bromide) inhibited bacterial growth in the early post-implantation steps, as tested in cultures of *Escherichia coli* on solid agar plates. Some of these antibacterial, biocompatible, and biodegradable polyesters might be potential candidates for the preparation of antimicrobial wound dressings. In a similar approach, Serrano *et al.*⁶² synthesized novel poly(octanediol-co-citrate) elastomers containing high loading of lidocaine at temperatures below 100 °C by means of deep eutectic mixtures of 1,8-octanediol and lidocaine. The preservation of lidocaine integrity resulted in high-capacity drug-eluting elastomers.

Gómez-Patiño *et al.*⁶³ carried out the polymerization of 10,16-dihydroxyhexadecanoic acid (main monomer of the tomato cuticle obtained from agro-residual wastes) using choline chloride + ZnCl_2 as catalyst at three different temperatures (80, 90, and 100 °C). The resulting polyesters obtained under these conditions were insoluble in most of the organic solvents and showed different physicochemical properties. At 80 °C, the products were obtained as powders, but at higher temperature, they were found as viscous liquids.

Two papers^{64,65} dealt with the curing process of epoxy resin with DES serving as solvents and catalysts. The eutectic mixture of choline chloride and urea was shown to initiate the polymerization of diglycidyl ether of bisphenol A (DGEBA) to a low molecular weight resin in the absence of a hardener.⁶⁴ Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC) were used to study the reaction kinetics. In a different approach, a mixture composed of choline chloride and ZnCl_2 or SnCl_2 was studied as a cationic catalyst for epoxy curing, using rheometry, DSC, and FTIR techniques.⁶⁵ A curing mechanism was reported, together with the solvent effect and various polymer properties.

A series of papers by Gutiérrez and co-workers⁶⁶⁻⁶⁸ were published on resorcinol-formaldehyde (RF) resins made in the presence of DES. In the first paper,⁶⁶ they polymerized RF resins in choline chloride-ethylene glycol. Carbonization of the resulting RF gels resulted in the formation of monolithic carbons with good conversion rates. Incorporation of carbon nanotubes (CNTs) was possible by adding CNTs in the DES during the preparation of the RF gels. In the second paper,⁶⁷ they made DES with choline chloride, resorcinol (and urea) and prepared RF resin directly in this DES. In the third paper,⁶⁸ they used a DES with resorcinol, choline chloride (0.928 g), and glycerol (0.612 g), added phosphoric acid, and formaldehyde. The resulting resin was carbonized to form phosphate-functionalized carbon monoliths.

In a related paper, Chen *et al.*⁶⁹ used choline chloride and urea to produce phenol-formaldehyde resin in a two-stage synthesis. The product was subjected to ambient drying and thermal treatment at 800 °C in nitrogen to generate carbon xerogels that exhibited a hierarchical porous structure. The xerogel contained nitrogen (from urea) at about 5-9%, which might be desirable for CO_2 capture.

4. Polymer Reactions

4.1. Modifications of synthetic polymers

Two papers were reported on polymer reactions involving DES and poly(ethylene terephthalate) (PET). In one report,⁷⁰ rapid hydrophilic modification of poly(ethylene terephthalate) (PET) fabric was carried out by deep eutectic ethylene glycol-choline chloride mixture under microwave irradiation. Alkali concentration and microwave irradiation time were found to be critical factors in determining surface characteristics of PET. The addition of merely 0.5% sodium hydroxide to the treatment drastically changed the fiber surface from hydrophobic to highly hydrophilic.

Another report⁷¹ used urea and ZnCl_2 together with ethylene glycol to degrade PET. With the DES, the degradation time was much shortened with a minimum number of degradation products. The reaction conditions were mild, and the reaction time minimized through optimization of reaction parameters. The high catalytic activity of DES was attributed to the synergetic catalysis of hydrogen bonds and coordination bonds formed between DES catalyst and ethylene glycol.

4.2. Modifications involving polysaccharides and biomass

Three papers dealt with reactions of polysaccharides.⁷²⁻⁷⁴ In a promising study,⁷² two types of NADES involving

urea and glycine were screened as media for facilitating methylation of chitosan. The results indicated that NADES did mediate selective *N*-methylation in the absence of NaOH, with no polymer scission, when compared with conventional synthesis of *N*-methylated chitosan. ¹H nuclear magnetic resonance (NMR) spectra confirmed selective *N*-methylation in case of products obtained using urea, while that obtained using glycine demonstrated some *O*-methylation. Another green method employed lipase to methylate chitosan; the reaction was successful with the lipase from *Burkholderia* species, but unsuccessful with *Candida antarctica* lipase. The paper also reported the use of dimethyl carbonate as a benign methylating agent.

A green, new, and relatively cheap approach was shown to be suitable for synthesizing a cellulose-based macro-initiator.⁷⁴ When the amounts of cellulose and zinc-based ionic liquid were fixed at 0.5 g and 18 mL, respectively, the degree of substitution of the cellulose-based macro-initiator obtained was increased from 11.0 to 17.4% as the reaction temperature was increased from room temperature to 40 °C. When the amount of cellulose was cut in half, a degree of substitution of 27.5% was achieved due to lower viscosity and better homogeneity of the reaction medium.

In a different reaction,⁷³ choline chloride coated on silica-supported AlCl₃ permitted the dehydration of carbohydrates in low boiling point organic solvents. The concept was based on the *in situ* formation of a deep eutectic liquid phase on the catalyst surface, thus facilitating the interaction between the solid catalyst and insoluble carbohydrate.

Biomass obtained from brown seaweed, *Sargassum tenerrimum*, was complexed with the deep-eutectic choline chloride and FeCl₃ mixture and converted to graphene nanosheets through pyrolysis at 700–900 °C under 95% N₂ and 5% H₂ atmosphere.⁷⁵ The nanosheets thus synthesized were tested for their electrocatalytic activity in the oxygen reduction reaction (ORR) in alkaline fuel cells. The results suggested that the functionalized graphene sheets could be a sustainable replacement for existing precious metal-based ORR catalysts.

A review²⁴ was published on lignocellulosic biomass utilization and conversion, including extraction of phenolic compounds, delignification, conversion to furanic derivatives, and processing of biodiesel and other fuels.

4.3. Hydrolysis of polymeric materials

DES and NADES have been found to be particularly useful for the hydrolysis of agro-based polymeric materials. Thus, in one report,⁷⁶ NADES were formed at elevated temperatures (60–100 °C) by combining choline chloride

with carboxylic acids (anhydrous oxalic acid, oxalic acid dihydrate, *p*-toluenesulfonic acid monohydrate, and levulinic acid) and then used to hydrolyze less ordered amorphous regions of cellulose. All the NADES treatments resulted in degradation of wood fibers into micro-sized fibers, and after mechanical disintegration, carbon nanocrystals (CNCs) were successfully obtained from choline chloride/oxalic acid dihydrate-treated fibers. No CNCs was observed with the combination of NADES with other organic acids. This acidic NADES method was more advantageous over previously reported CNC productions, because of milder processing conditions and easily obtainable and relatively inexpensive biodegradable solvents with low toxicity, relative to ionic liquids.

In another study,⁷⁷ corncob residues were pretreated with three different DES systems: choline chloride/glycerol, choline chloride/imidazole, and choline chloride/urea. The pretreated biomass was subsequently subjected to enzymatic saccharification and found to have enhanced sugar levels. Choline chloride/imidazole was the most effective solvent tested and could be applied at a lower temperature (80 °C) than that required to achieve similar results with choline chloride/glycerol (150 °C).

Xu *et al.*⁷⁸ developed an effective corn stover (CS) pretreatment method for biobutanol fermentation. Seven DES were synthesized and evaluated in the pretreatment of CS (choline chloride/urea, choline chloride/glycerol, choline chloride/formic acid, choline chloride/acetic acid, choline chloride/oxalic acid, choline chloride/malonic acid, choline chloride/citric acid). In particular, choline chloride/formic acid displayed excellent performance in the pretreatment of corn stover by removal of hemicellulose and lignin as confirmed by scanning electron microscopy (SEM), FTIR and X-ray diffraction (XRD) analysis. After optimization, glucose released from pretreated CS reached 17.0 g L⁻¹ and yield of 99%. The CS hydrolysate was successfully utilized in butanol fermentation by *Clostridium saccharobutylicum* DSM 13864, achieving butanol titer of 5.63 g L⁻¹ with a yield of 0.17 g g⁻¹ total sugar and productivity of 0.12 g L⁻¹ h⁻¹. The authors concluded that DES could be used as a promising and biocompatible pretreatment method for the conversion of lignocellulosic biomass into biofuel.

Gunny *et al.*⁷⁹ studied the applicability of DES-cellulase system for lignocellulose hydrolysis from rice husk. The DES consisted of choline chloride and a hydrogen-bond donor molecule (glycerol, ethylene glycol, or malonic acid). Cellulase showed higher activity and stability where more than 90% of its original activity was retained in the presence of DES based on glycerol or ethylene glycol. In view of the higher glucose production and lower energy consumption as compared to the diluted alkali pretreatment method,

the authors proposed that those DES could be regarded as potential solvents for lignocelluloses pretreatment.

Kumar *et al.*⁸⁰ used NADES for the pretreatment of lignocellulosic biomass rice straw and the separation of high-quality lignin and holocellulose in a single step. Two types of NADES reagents were prepared using lactic acid/betaine (LA-BE) and lactic acid/choline chloride (LACC) in several molar ratios. They found that LACC at molar ratio of 5:1 extracted the maximum amount of lignin ($68 \pm 4 \text{ mg g}^{-1}$) from the rice straw biomass, and subsequent enzymatic hydrolysis of the residual holocellulose enriched biomass showed maximum reducing sugars of $333 \pm 11 \text{ mg g}^{-1}$ with a saccharification efficiency of $36.0 \pm 3.2\%$ in 24 h at 10% solids loading.

5. Assessments

As documented in the rapidly growing literature, NADES possess many advantages. They are eco-friendly, biodegradable, non-toxic, and sustainable. They are easy to prepare, low in volatility and flammability, and chemically and thermally stable. The components of NADES are readily available, relatively inexpensive, and can be recycled if needed. Although most NADES can be made without water, water can be added in many cases to provide a wider range of applications.

For the situation of polymerization and polymer reactions, NADES have some specific advantages over organic solvents. First, most NADES consist of a combination of a cationic species and an anionic species; thus, the solvent has a higher electrical conductivity than most organic solvents. The high conductivity has been helpful in electrochemical synthesis of conducting polymers,⁵⁸ oxidative polymerization of 3-octylthiophene,⁵⁹ and electropolymerization of poly(methylene blue).⁶⁰ The high conductivity may also be conducive to microwave-assisted reactions and processes, although the current applications are relatively scarce.^{70,81} Secondly, the quaternary ammonium salts used in some NADES have been shown to impart antimicrobial properties to the resulting polyesters.⁶¹ Thirdly, the deep eutectic solvents can serve as catalysts in some cases, e.g., polymerization of DGEBA,⁶⁴ epoxy curing,⁶⁵ degradation of poly(ethylene terephthalate),⁷¹ methylation of chitosan,⁷² and degradation of carbohydrates.⁷³ Fourthly, NADES appear to be good solvents for reactions involving biomass. Thus, they have been used for the hydrolysis of the amorphous region in cellulose,⁷⁶ and pre-treatment of corn stover,⁷⁸ rice straw,⁸⁰ and rice husk⁷⁹ for biomass conversion.

Despite the promise, the use of NADES has its limitations. First, there is only a limited understanding of

the solubility mechanism so that one cannot predict the solubility of a given material (e.g., a monomer or a polymer) in a NADES solvent. Thus, a prospective user needs to try different NADES solvents to see if they can be beneficial for a polymer reaction. Secondly, many NADES solvents are viscous and difficult to handle; in some cases, this viscosity can be remedied by the addition of water. Thirdly, some of the components of NADES (e.g., in Table 2) are not chemically inert; therefore, care is needed to select the components not likely to participate in (or interfere with) the intended reaction. Finally, since NADES components have low volatility, it may be difficult sometimes to recover the solute from the NADES.

6. Conclusions

Polymers constitute a major category of industrial products with significant economic impact. The syntheses and production of polymers typically involve polymerization and polymer reactions. These processes are often carried out in organic solvents, which may incur some health or safety hazards. The discovery of deep eutectic solvents (DESs) has stirred up a lot of research interest in the chemistry community; this interest has been augmented by the recent addition of natural deep eutectic solvents (NADES), where many bio-based substances were found to change their state from solid to liquid at certain temperatures when mixed in a proper ratio. Because of their newness, these new solvents have not been extensively used in polymer science thus far, although quite a few papers have appeared.

In this review, the current use of NADES for polymerization and polymer reactions is reviewed. Although no specific emphasis has been placed on biomacromolecules, there have been several references to the use of NADES with respect to reactions of biomacromolecules (particularly hydrolysis), e.g., cellulose,^{74,76} chitosan,⁷² other polysaccharides,^{73,77} biomass and lignocelluloses,^{24,40,41,78-80} and lipid-related materials.²⁹⁻³¹ This is probably a promising area for future research. In view of NADES as agro-based and environmentally friendly reaction media, we believe they have great promise as green solvents for polymer science. We hope this review may be informative to polymer scientists and help to accelerate the adoption of these solvents as replacements for organic solvents that may exhibit inherent toxicity, volatility, and/or flammability.

Supplementary Information

Mention of trade names or commercial products in this publication is solely for the purpose of providing

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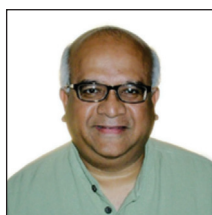
Supplementary data are available free of charge at <http://jbcs.sbg.org.br> as PDF file.

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