



# Free-radical polymerizations of and in deep eutectic solvents: Green synthesis of functional materials



Josué D. Mota-Morales<sup>a,\*</sup>, Regina J. Sánchez-Leija<sup>b</sup>, Arturo Carranza<sup>c</sup>, John A. Pojman<sup>c</sup>, Francisco del Monte<sup>d</sup>, Gabriel Luna-Bárceñas<sup>b</sup>

<sup>a</sup> Centro de Física Aplicada y Tecnología Avanzada, Universidad Nacional Autónoma de México, Querétaro, Querétaro, 76230, Mexico

<sup>b</sup> Centro de Investigación y de Estudios Avanzados, Unidad Querétaro, Querétaro, 76230, Mexico

<sup>c</sup> Department of Chemistry, Louisiana State University, Baton Rouge, LA, 70803, United States

<sup>d</sup> Materials Science Factory, Instituto de Ciencia de Materiales de Madrid-ICMM, Consejo Superior de Investigaciones Científicas-CSIC, Campus de Cantoblanco, Madrid, 28049, Spain

## ARTICLE INFO

### Article history:

Received 7 April 2017

Received in revised form 15 August 2017

Accepted 28 September 2017

Available online 5 October 2017

### Keywords:

Free-radical polymerization

Deep eutectic solvent

Green chemistry

Polymer

Nonaqueous

## ABSTRACT

The increasing environmental awareness has led to the search for alternative reaction media to reduce or eliminate the use of organic solvents in polymer science. Deep eutectic solvents (DESs), a subclass of ionic liquids, have emerged as sustainable solvents for a plethora of chemical reactions. In this Trend Article, DES utilization in free-radical polymerizations will be discussed. Two main fields of application are reported. In the first section, monomers able to undergo free-radical polymerization while taking part in a DES, as hydrogen bond donor or ammonium salt, so called DES monomers, are presented. In the second section, the role of DESs as solvents, where the polymerization takes place, either in the same phase or in an emulsion, is described. Finally, the properties of the polymers resulting from these particular methods of synthesis are discussed with emphasis on their green aspects.

© 2017 Elsevier B.V. All rights reserved.

## Contents

1. Introduction .....	139
2. Free-radical polymerization of DESs: deep eutectic monomers .....	142
2.1. Free-radical polymerization of DES containing monomers as HBD .....	142
2.2. Free-radical polymerization of DES containing cationic monomers .....	143
3. Free-radical polymerization in DES .....	143
3.1. Homogenous free-radical polymerizations in DES .....	143
3.1.1. Atom transfer radical polymerization assisted by DES .....	146
3.1.2. Free-radical polymerization in DES mediated by the enzyme horseradish peroxidase .....	146
3.1.3. Self-polymerization of a monomer in a DES .....	149
3.2. Heterogeneous free-radical polymerization of HIPE containing DES .....	149
3.2.1. Nanocomposites from free-radical polymerization of HIPEs stabilized by surfactants/nanoparticles .....	150
4. Future directions .....	150
Acknowledgements .....	150
References .....	150

## 1. Introduction

Deep eutectic solvents (DESs) were first described in 2003 when Abbott and colleagues coined the term to refer to binary mixtures of ammonium salts (acting as hydrogen-bond acceptors, HBAs) and non-ionic hydrogen-bond donors (HDBs) with a composition

\* Corresponding author.

E-mail addresses: [mota.josue@hotmail.com](mailto:mota.josue@hotmail.com), [jmota@fata.unam.mx](mailto:jmota@fata.unam.mx) (J.D. Mota-Morales).

corresponding to a eutectic point [1]. DESs are considered as a subclass of ionic liquids, *i.e.*, they contain ions (coming from the ammonium salt) associated with a second component, so that the resulting mixture is in liquid phase at temperatures below 100 °C. Several physicochemical techniques have been applied to demonstrate their analogy to the properties already known for traditional room temperature ionic liquids (ILs), for example negligible vapor pressure, high thermal and chemical stability, ionic conductivity, electrochemical window, high viscosity, dissolution capability toward both ionic and non-ionic compounds, etc. [2]. These particular DESs are of type III following the classification proposed by Abbott et al., [3], *i.e.*, see Fig. 1.

It is, however, the great plasticity of DESs in terms of composition that has positioned them in the spotlight of materials science [3]. Contrary to their IL parents for which electro-neutral cation/anion ratio has to be preserved, DESs can be tailored by either changing the nature of their counterparts (ammonium salt or HBA, and HDB) or by fine-tuning their molar ratio close to the eutectic point [4]. Moreover, the range of interactions in the case of a DES is broader than in an IL, encompassing both ionic and hydrogen bonding between their constituents [5–8]. This ability has been pointed out by referring to DESs as “designer solvents” or “advanced ionic liquids” [9].

Liquid mixtures between HBDs and HBAs have also received different names depending on some features of either of the original compounds forming the mixture or the mixture itself. For example, Choi et al. [10] prepared DESs composed of naturally occurring molecules in 2011 and called them “natural deep eutectic solvents” (NADESs). Ruß and König [11] reported the formation of the closely related low-melting mixtures (LMMs) based on bulk carbohydrates, sugar, alcohols or citric acid combined with different urea and inorganic salts. More recently, Kroon and co-workers mixed organic acids (as HBDs) with natural amino acids and/or essential nutrients (as HBAs) to obtain a set of mixtures exhibiting glass transitions but not melting points, so named for this reason as low-transition temperature mixtures (LTTMs) instead of DESs [12]. An additional sort of diversity is the use of the term DES to refer to near-to-eutectic mixtures or aqueous dilutions of DES because of their neoteric-solvent features [13–15]. Because of the diversity of names used to describe mixtures formed between HBDs and HBAs, the scientific community needs to establish a standard nomenclature. Recent works have aimed to correct some widespread misconceptions and to establish a correct definition of what a DES is [16–18]. In this work, we will use DES as the acronym to refer to the low melting mixtures described below while the scientific community finds a more accurate description that encompasses all the above-mentioned mixtures.

As for greenness, DESs are often described as sustainable solvents. Indeed, many of the first DESs reported by mixing choline chloride (ChCl) with bio-based HBDs (urea, glycerol, ethylene glycol, citric acid, etc.) are biodegradable, highly biocompatible and inexpensive [19]. The simple preparation of a DES in its pure state by just mixing the two components is an outstanding green feature as it involves syntheses with 100% atom economy [20]. The low volatility of DESs provides an advantage over volatile organic solvents in a range of organic reactions [11], which has increased over the last decade and keeps growing [21,22]. Finally the possibility of recovering the DESs when they do not take part of the reaction adds sustainability to their use as solvents [23,24]. Altogether, these advantages put DESs in the forefront of ionic liquids' applicability and scalability within a sustainable framework.

Although DESs are generally stable, there are some rare reports of side-reactions occurring during DES formation. For example, ammonia can form in the archetype ChCl/urea DES at high temperatures due to urea degradation [25], or there are reactions between the DES constituents when prepared by heating, as with ester for-

mation between ChCl and some carboxylic acids [26]. Another important issue is that due to the hydrogen-bonded nature of DESs, most are water-miscible and hygroscopic, and it is uncertain whether water (even at low concentrations) affects the DES structure to the benefit or detriment of certain applications.

Both ILs and DESs have been used widely in polymer science. Poly(ionic liquids) (Poly(ILs)) are synthesized by polymerization of existing IL monomers or by chemical modification of polymers to introduce cation/anion functionalities in their structure. ILs have been used in free-radical polymerization processes as green media, co-catalysts/initiators, specialty polymer additives, and in the development of functional polymers and derivatization of biopolymers. The electrolyte properties of ILs integrated to a polymer backbone, have expanded the traditional design of solid polyelectrolytes into more complex and versatile forms (hydrogels, nanoparticles, films, hyperbranched, etc.) and hence into new applications. Applications of Poly(ILs) include thermoresponsive materials, carbon materials, catalysis, porous polymers, separation and absorption materials, energy harvesting/generation and a multitude of other biological applications [27]. Poly(ILs) are generally synthesized by free-radical polymerization of the IL monomers among which, vinylimidazolium-based ILs are the most studied. These results have been summarized in excellent reviews covering both Poly(ILs) [27–32] and DESs [23,33]. However, apart from the very specific examples, Kubisa stated that it is not always clear how useful it is to replace typical organic solvents by ILs in polymer synthesis, as the former are still needed to either separate the polymer from the IL media or to purify the resulting Poly(ILs) [28].

Because of the almost countless combinations of HBDs and salts to form DESs (even without a general rule to predict their formation [34]), their role as solvents is just one aspect of their possible function in materials sciences. If one of the DES counterparts is reactive (*i.e.*, undergoes chemical transformation upon the appropriate triggering), then the DES becomes the medium in which the reaction takes place and is also the reactant. It can be considered that the reactive component of DES evolves/decomposes, leaving behind the inert component embedded in the product resulting from the transformation [35]. Thus the spatial composition of the final material results from the time scale matching between the reaction rate and the rate of phase separation of the polymer from the DES [36–38], where the viscosity, driven by intermolecular interactions, plays a prominent role.

Thus, DESs have been used in polycondensations, where one of the components was also a reactant, thus called all-in-one systems [33]. Electrochemical polymerization of conductive monomers has also been explored taking advantage of the ionic conductivity of DESs [39–43], including the FeCl<sub>3</sub>-catalyzed oxidative polymerization of 3-octylthiophene [42]. DESs playing the role of curing agents in epoxy resins [44], monomer [45,46] and initiator [13] in ring-opening polymerization were recently reported.

Moreover and in contrast to polymerizable ILs by free radicals, DESs containing monomers circumvent their potential uncontrolled polymerization during their derivatization as anions or cations. Two main ways to introduce monomers into a DES have been described. The first approach involves the use of neutral monomers (typically available as commodities, such as acrylic acid, methacrylic acid and acrylamide) as the HBD, the simply mixing of which with the appropriate salt yields a homogenous liquid.

The resulting DES containing a monomer and an inert ammonium salt is a liquid phase in which the monomer retains its chemical functionality so that, after free-radical polymerization, the resulting polymer composite exhibits a homogeneous composition despite the absence of any solvent during polymerization [47]. In the second approach, the formation of DES by polymerizable ammonium salts (*e.g.* cholinium bromide-derived acrylates)

Download English Version:

<https://daneshyari.com/en/article/7825904>

Download Persian Version:

<https://daneshyari.com/article/7825904>

[Daneshyari.com](https://daneshyari.com)