ABSTRACT

It is a great challenge to reduce the amount of volatile organic compounds (VOCs) used in chemical and industrial processes. VOCs are the most frequently used solvents in solution polymerizations, owing to their compatibility with monomers and simplicity of separation. Due to the health and environmental concerns associated with VOCs, alternative solvents which are more environmentally benign are being investigated as potential replacements. Ionic liquids (ILs) show potentials as VOCs substitute and have received much attention for their environmentally non-hazardous conditions in recent times. They have become the focus of many trials because of their negligible vapour pressure, chemical stability, low flammability, high ionic conductivity, broad liquid temperature range and excellent ability to dissolve organic compounds. These new chemical materials can reduce the use of hazardous and polluting organic solvents due to their unique characteristics and participating in various new syntheses. Among these reactions, polymerization reactions in ILs have attracted much research interest due to their importance in science and technology. The demand for high-performance polymeric materials is growing steadily because of their superior performance characteristics which are expected from engineering polymers in areas such as aero-space, electronics, and automobile industries. With the aim of developing a green polymer chemistry approach, herein, the synthesis and properties of high-performance polymers, e.g., polyimides and polyesters are reviewed in the chemical point view of environmental friendly media using ILs.

Key Words: high-performance polymers; polyimides; polyesters; green chemistry; ionic liquids.

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INTRODUCTION

The "high performance" terminology refers to an exceptional stability upon exposure to some types of harsh environment and to properties that surpass those of traditional polymers. The development of high-performance polymers (HPPs) began in the late 1950s primarily to satisfy the needs of the aerospace and electronic industries [1]. The most prolific decade for HPPs was 1960s to 1970s where most thermally stable heterocyclic rings were incorporated into polymer structure. The 1970s saw the commercialization of several HPPs. Two of the more important contributions during this period were Kevlar by DuPont, a high modulus aromatic polyamide (PA)s fibre, and Ultem by General Electric, a thermoplastic polyetherimide [2,3]. As a mouldable polymer, Ultem offered a favourable combination of relatively low cost, excellent processability and moderate mechanical properties. Several other important scientific contributions were made during this period such as the emergence of high modulus and rigid rod polymers [4,5]. Among the many families of HPPs known, polyimides (PI)s and polyesters (PE)s as the most popular members are presented here to demonstrate the basic principles in polymer development.

POLYIMIDES

A class of high performance polymers and one of the most popular among them is polyimides (PI)s. These are highly versatile resins which can be adopted for various applications through their chemical intricacies, processing, molecular weight control, and reaction conditions [6,7]. More work has been done on PIs compared to all other HPP combined, owing to the accessibility of monomers, the ease of synthesis, and the overall consolidation of properties and cost. These polymers display outstanding thermal, mechanical, chemical and physical properties as well as low moisture absorption [8]. As the requirements for lighter weight, broader temperature performance, increased strength, durability and inertness continue to grow, PIs play central role in the drive for innovations of the future. Several books and review articles are available on PIs synthesis, properties and applications [9-11].

The first synthesis of an aromatic PI was reported in 1908 [12]. However, much of the credit for the development and commercialization of PIs products goes to DuPont, who benchmarked this endeavour in the 1960s with the release of Kapton H film, Vespel moulded parts and Pyre-ML wire varnish. This effort inspired other researchers in academic, industry, and governmental laboratories to pursue the chemistry, fabrication, and applications of PIs which had not been envisioned several decades ago [13,14].

Polyimides (PI)s are usually synthesized by the following methods: (i) reaction of an aromatic dianhydride and an aromatic diamine in a polar aprotic solvent like N-methylpyrrolidone (NMP), N,N'-dimethylacetamide (DMAc) as well as dimethylformamide (DMF) to form a polyamic acid (PAA) solution and subsequent cyclodehydration chemically or thermally to the PIs [15,16], (ii) melt polymerization of an aromatic dianhydride and an aromatic diamine [17], (iii) reaction of an aromatic dianhydride and an aromatic diisocyanate to form a seven membered ring that eliminates carbon dioxide to form the PIs [18,19], (iv) reactions of esters of aromatic tetracarboxylic acids with aromatic diamines in solution at high temperatures to form PIs [20], (v) reaction of an aromatic dianhydride or tetracarboxylic acid and an aromatic or aliphatic diamine in high boiling solvents (e.g., m-cresol) [21], (vi) use of monomers containing preformed imide rings through transimidization where a diimide enters reaction with a more basic diamine via a catalyst to induce an exchange reaction [22], (vii) nucleophilic displacement of activated nitro group in a compound with preformed imide rings with phenoxide anion [23,24], (viii) reaction of N-trialkylsilylated alicyclic diamines with alicyclic tetracarboxylic dianhydrides to form poly(amide acid trialkylsilyl esters) that are thermally converted to PIs [25], and (ix) reaction of an AB monomer containing an aromatic amine on one end and ortho carboxylic acid ester on the other end using a phosphorus catalyst to form a polyamide ester that is subsequently converted to PIs [26].

The reaction of an aromatic diamine and an aromatic tetracarboxylic dianhydride to form a
precursor PAA followed by chemical or thermal cyclodehydration to obtain PIs is the most popular synthetic route. High molecular weight PAA is formed readily when high purity monomers and dry polar aprotic solvents such as DMAc or NMP are used. Moisture should be excluded from both the reaction and the resulting PAA solution to prevent molecular weight reduction due to hydrolysis. Polyimides (PI)s are characterized by their strong resistance to degradation by thermo-oxidation reactions and their melting temperature is such that they can be used up to 300°C or more during hundreds of hours [27].

The annual world production of PI is a few thousands of tons. It is a relatively low volume compared to some other technical polymers, but, due to their high cost, PIs are intended for very high value added applications (depending on their structure, their cost can vary hundred-fold) and are thus important from the economic point of view. Their growth rate is high and estimated to reach as much as 20% in near future [27,28].

It is realized that although wholly aromatic PIs are materials that retain their properties almost unchanged for a long time at 250-300°C, but their applications as aromatic PIs and in general aromatic polyheterocycles are not possible from their melt and furthermore, their extreme structural rigidity and the high density of cohesive energy make them insoluble in many organic media [29,30]. Given the exceptional properties of the aromatic PIs, structural amendments were soon outlined in order to conquer these restrictions, and as a consequence of much research efforts made in this direction, the chemistry of PIs has greatly enriched, thanks to the many improvements achieved in these last thirty years [31-33].

Thus, the strategies to synthesize novel and processable aromatic PIs have focused on chemical modifications, mainly by preparing new monomers that provide less molecular order, torsional mobility and lower intermolecular bonding [34]. Some general approaches have been universally adopted, for examples: introduction of flexible linkages [35], introduction of side substituents [36], use of 1,3-substituted instead of 1,4-substituted monomers, and/or asymmetric monomers [37] and preparation of co-PIs from two or more dianhydrides or diamines [38]. In fact, most of the commercial, fully aromatic PIs contain ketone or ether linkages in their repeating units, and early works in the field soon demonstrated that dianhydrides having two phthalic anhydride moieties joined by bonding groups, gave more tractable PIs [39]. Many different linkages have been introduced to serve these purposes, with the most promising linkages being: -O-, CO, -S-, -SO2-, -C(CH3)2-, -CH2-, -CHOH-, -C(CF3)2- [38-40].

POLYESTERS

Polymers that contain at least one ester linking group per repeating unit are defined as polyesters (PE)s [41]. These polymers have entered our lives in a most ubiquitous manner as textiles, carpets, tyre cords, medical accessories, seat belts, automotive and electronic items, photographic film, magnetic tape for audio and video recording, packaging materials, bottles, etc. Their utility is illustrated by the vast range of their applications [42,43]. The synthesis and properties of PEs have been treated in numerous encyclopedia and general review articles [44-48]. The modern history of PEs began in the 1930s when Carothers proved the macromolecular theory of Staudinger from experimental studies on reactions between aliphatic dibasic acids and diols and established the relationships between degree of polymerization, conversion, functionality, and gel point which are the basics of step-growth polymerization [49,50].

In the 1990s, environmental concerns began to gain some grounds. The versatility of the ester linkage in undergoing hydrolysis, alcoholysis, and acidolysis in some conditions, makes PEs the polymers of choice to meet the increasing demand for recyclable and/or biodegradable polymers. This is the result of a renewed interest in aliphatic PEs, such as poly(lactones), poly(lactides) (PLLA), or copolyesters containing aliphatic moieties. Poly (ethylene terephthalate) (PET) production is also strongly driven by the demand of recyclable polymers [50].

Polyesters can be obtained by a wide range of reactions, notably polyesterifications between the dibasic acids and diols or their derivatives [41]. Many other reactions have been reported for the synthesis of
PEs e.g., reactions between dicarboxylic acid salts and dialkyl halides; reactions between chlorocar-bonyloxy-terminated monomers and diacids, or reactions between bis-ketenes and diols. These reactions, however, cannot be applied to the synthesis of high-molar-mass PEs under economically viable conditions and are limited to very specific laboratory-scale syntheses.

Two notable exceptions are the ring-opening polymerization (ROP) of lactones and lactides for the production of degradable PEs and the biosynthesis of aliphatic PEs by bacteria or genetically modified plants. Aliphatic-aromatic PEs such as PET and poly(butylene terephthalate) are processed into economically important fibres, films, and engineering thermoplastics. Wholly aromatic co-PES exhibit superior mechanical properties and heat resistance and have found a number of applications as high-performance thermoplastics [51].

Polyesters (PEs) are now one of the economically most important classes of polymers, with an overall world production between 35 and 40 million tons in 2007. This production is rapidly increasing and is expected to continue the same trend during the next decade, driven by packaging applications, due to a very favourable image of environmentally friendly and recyclable polymers in western countries, and by textile applications, due to a strong demand in the Far-East to satisfy the needs of an increasing population [41,51]. Although many monomers have been utilized, the typical commercial amorphous polyarylate is a PE containing bisphenol-A units and nearly equal proportions of isophthalate and terephthalate units [51].

Several approaches have been adopted for the synthesis of processable aromatic PE chains like: insertion of flexible aliphatic spacers between mesogenic units in polymer backbone [52-54], introduction of bulky lateral substituents on monomer units to increase interchain distance and prevent close packing in polymer crystal [55-59], introduction of non-mesogenic units in polymer chains and copolymerization of two or more mesogenic monomers yielding copolymers with random distribution of repeating units [41,60,61]. The popularity of this very versatile and diverse group of materials can easily be explained by the favourable properties brought by the ester functionality, flexibility and biodegradability.

IONIC LIQUIDS

In most of the above methods for the synthesis of PIs and PEs, the use of highly polar conventional solvents is indispensable. These solvents are hazardous, toxic, flammable, and harmful and often with various ecological shortcomings. For this reason, there is a great need for the development of new methods through environmentally friendly media which could change the traditional solvents for polymerization process.

Volatile organic solvents are common reaction media for commercial production of different chemicals [62]. It is a huge challenge to reduce the amount of these solvents in chemical and industrial processes because they are one of the major contributors to air pollution [63,64]. Research on chemical manufacturing has focused on testing different approaches to cut down the emission of VOCs [65].

Among many solvents, ionic liquid (ILs) have been rather sanguinely viewed as environmentally friendly or "green" solvents. Because of interesting chemical physics problems and the multiplicity of their uses, attention in ILs suddenly increased [66]. They are substances that are completely composed of ions and in liquid state at or close to room temperature [67,68].

In our recent review paper [69] we have demonstrated that ILs can be used in many different processes, e.g., synthesis of polyamides. Jain et al. [70] and Greaves et al. [71] have shown that ILs act as good solvents for a wide variety of chemical processes. Their good miscibility with other organic solvents or monomers are the major topics of the work of Parvulescu et al. [72], and their long-term thermal stability was discussed by Martins et al. [73]. Liao et al. [74] showed that their highly ionic character enhances the reaction rates to a great extent in many reactions. Controllable physicochemical properties through judicious selection of the cations and anions [75,76] and their negligible volatility [77-80] were also introduced.

Ionic liquids (ILs) are progressively used by
polymer chemists as solvents and catalyst. There are several outstanding review articles in recent years, about the use of ILs in polymerization processes, e.g., Kubisa discussed the application of ILs as solvents for polymerization processes [81] and in the synthesis and modification of polymers [82], Ueki et al. showed advances, challenges, and opportunities of producing macromolecules in ILs [83], Lu et al. have reviewed the advanced applications of ILs in polymer science [84], Kubisa showed the polymerization processes-progress and challenges of ILs as solvents [85], Gibson presented the ILs and their derivatives in polymer science and engineering [86] and Xie et al. discussed the promotion of atom transfer radical polymerization and ring-opening metathesis polymerization in ILs [87].

According to the above review articles, the employment of ILs as solvent for polymerization have some obvious benefits, e.g., increased MW and narrower polydispersity in comparison to organic solvents. Herein, we are going to review the recent developments in the application of ILs in the production of HPPs such as PIs and PEs.

Synthesis of High Performance PIs in ILs

It is clear that ILs are promising reaction media for the formulation of different HPPs. In order to investigate the efficiency of an IL as a specific catalytic and reaction medium in PIs synthesis, Vygodskii et al. have studied the polycyclization reaction of 1,4, 5,8-naphthalene tetracarboxylic acid dianhydride (DA NTCA) [88] and 3,3-bis(4'-aminophenyl) phthalide (APH) [89] using ILs in the absence of any additional catalyst and reported as the first works on the use of ILs as a solvents and activated agent for polycondensation reaction. They obtained high-molecular-weight PIs with inherent viscosities of 0.52 to 1.09 dL.g⁻¹ (Scheme I). Preceding findings for the reactions performed in organic solvents such as DMF, DMac, NMP, nitrobenzene and m-cresol in the absence of any catalyst even at temperatures as high as 200°C had shown that the reaction of such monomers has to be carried out at 180-220°C and in the presence of carboxylic acid as a catalyst [88].

The influences of various reaction parameters on this polycyclization reaction in 1,3-dibutylimidazolium bromide ([Bu₂Im]Br) as the reaction medium were examined to determine optimum monomer concentrations and reaction temperatures and duration. Vygodskii et al. [89] also examined the influence of IL structure on the inherent viscosity of the PI and found that the best results are obtained in ILs with symmetrical structure. They also investigated the IL alkyl chain length on the polycondensation using ILs with alkyl chains of n carbon atoms where n = 2-6 and 12. The results of their study showed that polycyclization occurs in homogeneous solutions of ILs with n ≤ 4, whereas quick precipitation of the PIs was observed in ILs with n > 4. Vygodskii et al. found that the use of hydrophobic ILs, e.g., 1,3-dibutylimidazolium tetrafluoroborate ([Bu₂Im]BF₄), 1-butyl-3-methylimidazolium tetrafluoroborate ([BuMIm]BF₄),

Scheme I. Synthesis of high performance PIs in imidazolium types ILs [88,89].
1,3-dibutylimidazolium hexafluorophosphate ([Bu₂Im] PF₆) and 1-ethyl-3-methylimidazolium bis(triflyl)amide ([EMIm](CF₃SO₂)₂N in the synthesis of PIs did not result in the formation of high MW polymers.

In another study by Vygodskii et al. [90], various high molecular weight PIs such as, polynaphthyleneimides and poly[naphthylene-bis-(benzimidazole)]s including functional (sulphonated) types have been obtained in IL with quantitative yields at the room temperature (RTIL) in the absence of catalyst of any kind (Scheme II). The influence of various reaction parameters including ILs of cationic and anionic types, monomer structure and concentration, reaction temperature, upon MW of PI ($\eta_{inh}$) was investigated. PI inherent viscosity ($\eta_{inh}$) depends greatly on IL nature as well and the results indicated that the best outcome is obtained in ILs of symmetrical cation. The dominant IL alkyl chain length on the polycondensation was also estimated. The poly-cyclization which occurred as a homogeneous process in ILs had Et, Pr, and Bu groups whereas rapid

Scheme II. Preparation of different PIs in ILs [90].
precipitation of this polymer took place in ILs having groups with longer alkyl chains. High molecular weight PI ($\eta_{inh} = 2.10 \text{ dL.g}^{-1}$) was obtained by the interaction of APh and 3,3',4,4'-biphenyltetracarboxylic dianhydride (BDA) after 3 h heating at 180°C.

Sulphonated diamine monomers, such as 2,2'-benzidine disulphonic acid and $p$-phenylenediamine-sulphonic acid have been employed. High molecular weight sulphonated PIs are formed in bromide IL for shorter times (9-11 h) without any further activator. The influence of various reaction parameters on such polycyclization reaction in [Bu$_2$Im]Br as the reaction medium was studied enabling the optimum reaction parameters estimation (monomer concentration $c$, reaction temperature $T$, and time $t$). Concentration dependence monotonically reached a plateau level at $c = 0.6 \text{ mol.L}^{-1}$, whereas this dependence showed a maximum at $c = 0.4 \text{ mol.L}^{-1}$ upon using nitrobenzene as reaction medium. The resulted polymers have found wide applications in many high technologies due to their excellent thermally stability, high mechanical strength, superior chemical resistance, electrical and other properties.

Tamada et al. [91] used imidazolium type IL for the polycondensation reaction 4,4'-oxydianiline and pyromellitic dianhydride. At first, the solubility of the starting materials in ILs was evaluated and the results indicated that these starting materials were hardly soluble in 1-benzyl-3-methylimidazolium bis(triflyl) amide ([BzMIm](CF$_3$SO$_2$)$_2$N) addition of imidazolium type zwitterion, 1-(1-butyl-3-imidazolio)butane-4-sulphonate (ZI) certainly improved their solubility. When [BzMIm](CF$_3$SO$_2$)$_2$N containing 40 mol% ZI was used, phase separation did not happen in this mixed solution containing both starting materials after being cooled to room temperature. After preparing prepolymer in [BzMIm](CF$_3$SO$_2$)$_2$N containing 40 mol% of ZI at room temperature, polycondensation was carried out in the same solution at 100°C, 200°C, and then 300°C for every 1 h to obtain PI. An inherent viscosity of the obtained PI (0.05 g in 10 mL concentrated sulphuric acid) was 1.3 dL.g$^{-1}$, higher than that prepared in only [BzMIm] (CF$_3$SO$_2$)$_2$N (0.9 dL.g$^{-1}$). The higher average molecular weight of the PI was attributed to the improved solubility of the starting materials by the addition of ZI that enabled the preparation of the PAA prepolymer without heating before imidation.

Alici et al. [92] reported the polymerization of 1,4-bis(3-aminopropyl) piperazine in NMP catalyzed by an IL. The IL used was only 5 wt% of the organic solvent. The polymerization by the IL catalyst was well-controlled, producing polymers with controlled molecular weights and low polydispersity. After the polymerization, the IL catalyst settled on the bottom of the reactor where it was easily separated from the polymer solution. To determine the efficiency of an IL as a catalytic medium in PI synthesis, a piperazine based monomer was chosen as a model compound. Because piperazine-based monomers exhibit low reactivity towards dianhydrides and do not form high MW PIs via common 2-stage polycondensation procedure in organic solvents (e.g., NMP and m-cresol) in the absence of a catalyst. The results demonstrate that high molecular weight PIs are formed in such a novel reaction medium with ILs acting as a catalyst. Properties of PIs greatly depend on the nature of the ILs as well as $pK_a$ values of the monomer. The PI samples obtained by polymerization in various ILs were analyzed by size exclusion chromatography. Comparing with the polymer synthesized in NMP, the samples synthesized in ILs show higher molar masses, polydispersities and higher solubilities in dipolar aprotic media. The use of ILs results in higher molar masses of the polymers which can exceed even the molar masses obtained from bulk polymerization. Consequently, the $T_g$ of the polymers is increased and their thermal degradation is reduced in comparison with the polymer produced via solution polymerization in NMP.

Such effects are prevalent for ILs having different cation and anion structures. Nevertheless, significant differences in the molar mass and the polydispersity were found between the polymers synthesized in various ILs, hence the optimization of polymerization requires a careful selection of IL. Imidazolium based ILs are preferable over $n$-alkyl-4-methylpyridinium and aliphatic ammonium salts since they exert a more favourable effect on polymerization. High molar masses of polymers are favoured by high viscosities of the imidazolium salts or by conducting polymerizations close to the melting temperature of the ILs. One may speculate that this behaviour is due to
locally ordered structures that favour the polymerization reaction under these conditions. Above all, efficient recycling of the ILs after polymerization, as needed for practical applications, is feasible by simple decantation and extraction procedures.

Recently, PI nanoparticles were obtained by the heterogeneous polycondensation of different aromatic tetracarboxylic acids and diamines in imidazolium-based IL as continuous phase by Frank et al. [93]. Because of the amphiphilic character of the IL, no additional surfactant is required for the stabilization of the employed dispersions. The low vapour pressure and high thermal stability of the reaction medium allow the use of high temperatures needed for the condensation reaction. The reaction takes place without commonly added extra components like LiCl or Py.

The obtained PI was characterized by IR spectroscopy and gel permeation chromatography. Electron microscopy (TEM and SEM) shows a homogeneous morphology of the nanoparticles. These results show that PI nanoparticles in the range of 100 nm can be prepared by heterogeneous polycondensation in [EMIm](CF3SO2)2N as IL without the addition of any further activating or stabilizing agents. The PIs which are insoluble in IL could be easily separated by precipitation with a bad solvent and centrifugation. SEM images show that the surface of the particles is structured and has some small dimples. All particles show a high thermal stability by thermogravimetric analysis (TGA) and a decomposition temperature at around 520°C.

Synthesis of High Performance Copolymer of PIs in IL
Mallakpour et al. [94] reported the polycondensation of N,N'-[(4,4'-oxydiphthaloyl)-bisphenylalanine diacid with various aromatic diamines in different media by both direct and indirect polymerization methods (Scheme III). Poly(amide imide)s (PAI)s were synthesized by the direct step-growth polymerization reactions of an equimolar mixture of chiral diacid with several different aromatic diamines in an IL medium which acted as both a solvent and a catalyst in conjunction with triphenylphosphite (TPP). In this reaction, use of NMP/LiCl/Py or NMP/CaCl2/Py systems is not necessary. This reaction is safe and green in addition to saving time, energy and cost. Step-growth polymerization reaction was carried out by the variation of the IL, reaction time, reaction temperature, and amount of TPP. It was shown that all these parameters had a critical effect on the polymer chain growth. The best temperature for PAI synthesis was 100°C for 2.5 h, where high MW poly(amide imide)s (PAI)s were obtained at this temperature. To compare the efficiency of this novel method of polymerization (method A) with classical methods, three other different methods were used for the preparation of PAs from related monomers. These methods are termed as the direct step-growth polymerization in a tosyl chloride (TsCl)/Py/DMF system (method B), the solution polymerization reaction in a cold NMP solution (-5°C) in the presence of a small amount of TsCl (method C), and the polycondensation reaction of mentioned monomer at the reflux temperature of DMAc in 1 min (method D) [94].

In method A, the synthesis and separation of diacid chloride was not necessary, and the reaction proceeded as a one-pot reaction, starting from free dicarboxylic acid and IL was just used as a solvent and catalyst. The possibility of the recovery and reuse of an IL/catalyst system and the ability to dissolve monomers are further advantages of using IL systems in method A. The yields, inherent viscosities, and optical activities of the polymers prepared via method A were higher. This information shows that the IL/TPP method is not only a safe and green route but it is more efficient at the same time [94].

High MW optically active PAIs have been synthesized in IL media and their properties such as optical activity, solubility and thermal stability were studied by Mallakpour et al. [95]. At first, ILs bearing different alkyl groups and different anions were synthesized and their applications as efficient solvents and as catalysts were examined for the direct polymerization. For these studies, two different counter-ions such as Br- and Cl- were chosen. After optimizing all conditions, several PAIs were synthesized by direct polycondensation reactions of an equimolar mixtures of N,N'-(4,4'-hexafluoroisopropylidenediphthaloyl)-bis-L-methionine diacid monomer and several different aromatic diamines in an IL media which acting both as a solvent and as a catalyst in conjunction with TPP under microwave irradiation.
Polycondensation was carried out at different types and amounts of ILs and duration of irradiation of microwave and power level of its instrument. All these parameters showed critical effects on the polymer chain growth. When the amount of IL was high the resulting starting materials turned dark and subsequently burned. When the power level was lowered, no polymeric materials were obtained and at higher power level, the mixture was again burned. Therefore, the shorter period and lower microwave power level were quite necessary, otherwise too vigorous reaction would occur leading to the degradation of the reaction mixture. The inherent viscosities of the resulting polymers were in the range of 0.66-0.94 dL·g⁻¹ and the yields were 92-96%.

Mallakpour et al. [96] also reported for the first time the application of RTILs and tetrabutylammonium bromide (TBAB) as catalyst as well as reaction medium for the synthesis of heterocyclic poly(amide-ester)s (PAE)s having naphthalene and urazole moieties. They found that 4-(3-hydroxynaphthalene)-1,2,4-triazolidine-3,5-dione does not form high MW PAEs by common procedures in NMP in the absence of catalyst of any kind. Thus, the reaction of such monomer is commonly carried out in the presence of triethylamine (TEA) or Py as a catalyst. The results showed that, ILs allow obtaining moderate-molecular weight PAEs in the absence of any additional catalyst.

Scheme III. Synthesis of PAs from optically active isosorbide-derived diamine and various diacyl chlorides and diacids [92].
The polycondensation reactions lead to the formation of polymers having inherent viscosity of 0.18-0.34 dL.g⁻¹ and good relative thermal stability. They found that a combination of IL and catalyst do not lead to significant changes at properties of polymers, therefore, it seems that ILs act as solvent and catalyst both [96].

Aromatic copoly(ester-amide)s co-(PEA)s, containing a 9,10-anthraquinone moiety in the main chain were synthesized from the polycondensation reaction of terephthaloyl chloride and various ratios of p-phenylenediamine and 1,4-dihydroxyanthraquinone in different imidazolium type ILs as novel solvents [97]. In a study by Yavari et al., different ILs having various anions and cations with different alkyl chain lengths were synthesized and then were used as solvents for polymerization reaction [97].

The result showed that for ILs having the same alkyl substituents, there is a strong dependency between alkyl chain length and PAE viscosity. By increasing the alkyl chain length of the ILs, the viscosity of PAEs is decreased. ILs containing n-butyl chains seemes to be the best solvents for copolymer synthesis and as far as the anions are concerned, the best results were obtained in ILs with Br⁻ ions. The resulted copolymers exhibit colour characteristics and thermal stability. The presence of the amide groups in the backbone of these polymers enhances their thermal stabilities. Inherent viscosities of the polymers obtained in 1,3-dialkylimidazolium bromide were between 0.28 to 0.42 dL.g⁻¹. The polymers had λ_max values of 300-593 nm. The presence of the amide groups in the backbone of these polymers enhances their thermal stabilities.

**Synthesis of High Performance PEs in ILs**

In order to develop green polymer chemistry, enzymatic PEs synthesis in ILs has already been carried out by some researchers. Biocatalytic reactions in ILs have also shown higher selectivity, faster rates and greater enzyme stability. However, these solvents present other challenges, among them difficulties in purifying ILs and controlling water activity and pH, higher viscosity and problems with product isolation [98]. Given the recent interest in the use of enzyme catalysis in ILs, it is likely that this area of research will become increasingly important.

Nara et al. [99] investigated the lipase-catalyzed polycondensation of diethylene octane-1,8-dicarboxylate and 1,4-butanediol (BD) as the substrates by employing *Pseudomonas cepacia* lipase supported on Celite, PS-C, as the biocatalyst in [BuMIm]PF₆ as the reaction medium. To establish the initial rate of the enzyme catalyzed transesterification in [BuMIm]PF₆, different experiments were designed. The decay of diethyl octane-1,8-dicarboxylate was monitored on GC as a function of time. The results revealed a high initial rate of transesterification as indicated from the rapid consumption of the monomer. This signified the rapid assembly of low molecular weight oligomers by

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Scheme IV. Polycondensation reaction of 4-(3-hydroxynaphthalene)-1,2,4-triazolidine-3,5-dione with several aliphatic diacidchloride in TBAB and [Isopr₂Im]Br [94].
sequential condensation of monomers on to the developing chains. The molecular weight of the PE obtained was monitored at different intervals of time during the course of polymerization at room temperature. After 1 day, the reaction furnished a polymer (obtained on precipitation using methanol) possessing an average molecular weight of 2230 (g.mol⁻¹) as determined by gel permeation chromatography (GPC) analysis. The authors claim that no substantial improvement in the molecular weight of the polymer was seen with time, thereafter. However, after 7 days there was a marginal decrease in the average molecular weight of the polymer isolated and also the GPC profiles exhibited a gradual increase in low molecular weight oligomers. Thus, it appears that the PE undergoes lipase-catalyzed disproportionation. At ambient temperature low MW oligomers were obtained after 7 days, and the molecular weight increased to 4500 g.mol⁻¹ at 60°C. This is understood from the reactions that were studied for very long periods of time (12-15 days) which gave fewer polymers of high molecular weights after precipitation by methanol. The low polydispersity of 1.03-1.26 reported was attributed to the insolubility of the polymer in the IL once it exceeds a certain molecular weight.

The ROP of ε-caprolactone (CL) was first carried out using lipase CA as catalyst in [BuMIm]BF₄ and [BuMIm]PF₆ by Uyama et al. [100]. This group investigated both lipase-catalyzed ROP of CL and the polycondensation of diethyl adipate and diethyl sebacate, respectively with 1,4-butandiol. The ROP in [BuMIm]PF₆ resulted in oligomers (Mₙ < 850 g.mol⁻¹) over 3 days, whilst Mₙ of 4200 g.mol⁻¹ was obtained after 7 days. The molecular weights of the polycyondensates were less than 1500 g.mol⁻¹ in both [BuMIm]PF₆ and [BuMIm]BF₄.

Heise et al. [101] have reported the enzymatic synthesis of PEs in 1-butyl-3-methylimidazolium bis(triflyl)amide ([BuMIm][CF₃SO₂]₂N), [BuMIm] PF₆ and [BuMIm]BF₄ RTILs by ROP and polycondensation (Scheme V). Enzymatic ROP of CL or enzymatic polycondensation of dimethyl adipate as well as dimethyl sebacate with BD in three RTILs were performed by this group. For CL, they found that [BuMIm]PF₆ and [BuMIm]BF₄ resulted in an inhomogeneous reaction mixture upon polymerization, leading to polymerization characteristics similar to bulk polymerization. In contrast, for [BuEIm][CF₃SO₂]₂N characteristics similar to polymerization in toluene were observed. Molecular weights of 7000-9500 g.mol⁻¹ were obtained. For the polycondensation of dimethyl adipate and dimethyl sebacate with 1,4-butanol the low volatility of the ILs allowed the reactions to proceed in an open vessel at temperatures close to the boiling point of the condensation byproduct and molecular weight up to 5400 g.mol⁻¹ was obtained. This aspect, in combination with the tunable solvent hydrophilicity of ILs could offer an advantage in the polymerization of highly polar monomers with low solubility in...
organic solvents. The authors concluded that the tunable solvent hydrophilicity of ILs might offer an advantage in the polymerization of highly polar monomers with low solubility in organic solvents such as sorbitol. The molecular weights of poly(ε-caprolactone) (PCL) did not exceed 10000 g.mol$^{-1}$. But the highest molecular weight of the PEs synthesized from ester-exchange polymerization only reached 5400 g.mol$^{-1}$. The authors suggested that low molecular weights were due to the immiscibility of the PEs with the ILs when their MW reached a certain limit.

ε-Caprolactone has also been polymerized by microwave-assisted ROP in the presence of [BuMim]BF$_4$ using zinc oxide as a catalyst [102]. The temperatures of the mixtures of CL and [BuMim]BF$_4$ have been measured and found to increase with both an increasing power level and an IL concentration. By adding 30 wt% IL, PCL with a weight-average molar mass of 28500 g.mol$^{-1}$ was obtained at 85 W for 30 min. The results indicate that the polymerization could be efficiently enhanced in the presence of ILs under microwave irradiation because ILs can effectively absorb microwave energy.

Lipase-catalyzed polymerizations of L-lactide (LA) were carried out in four kinds of ILs in order to investigate the effect of ILs on the conversion, molecular weight, and yield of the obtained PLLA by Yoshizawa-Fujita et al. [103] which demonstrated lipase-catalyzed ROP of LA in different ILs. The anion species of ILs showed significant effects on the conversion, molecular weight, and yield. The results suggested that the anion of ILs has a molecular interaction during the polymerization. The monomer conversions and molecular weights for [BuMim]BF$_4$ and [BuElm](CF$_3$SO$_2$)$_2$N were higher than those of conventional bulk and solution methods, whereas the polymer yields were relatively lower than those of bulk polymerization. The low yield for the ILs method was probably due to the solubility of PLLAs in ILs. Although the obtained PLLAs were isolated from the reaction solutions by several consecutive extractions with toluene, it was difficult to fully extract PLLAs from ILs. Therefore, better solubility of PLLAs in ILs induced lower polymer yields.

Further technical improvements are needed to achieve high polymer yields. The optimization of ionic components of ILs may also contribute to better yields. The $M_n$ values of PLLAs in the ILs were clearly higher than those of PLLAs obtained in bulk and in toluene (<44000 g.mol$^{-1}$). The effect of lipase content on the $M_n$ of PLLA was also investigated. When [BuMim]BF$_4$ was used as solvent, the highest $M_n$ was obtained at a lipase content of 10 wt%. In the case of [BuElm](CF$_3$SO$_2$)$_2$N, the most suitable lipase content depended on the polymerization temperature. [BuMim]BF$_4$ was suitable to obtain higher molecular weight PLLA and higher polymer yield at lower lipase contents.

PLLA is usually produced using metallic catalysts such as SnOct$_2$ in ROP and Tin(II) chloride dihydrate/p-toluene sulphonic acid (SnCl$_2$.2H$_2$O/TSA) in melt polycondensation. Nevertheless, metal-free catalysts are becoming more desirable since they may make the product safer and more biocompatible. PLLA with molar mass of about 20000 g.mol$^{-1}$ was synthesized at high yield (over 70%) in the presence of various 1,3-dialkylimidazolium salts by Wang et al. [104] for the first time. The product exhibits satisfactory colour (white to slightly yellow), optical purity (89-95%) and crystallinity (40-55%). As compared with the well-known binary catalyst system (SnCl$_2$.2H$_2$O/TSA), the catalysts used by this group are better in terms of higher PLLA yield and discoloration prevention, although being comparable in terms of racemization.

Fu et al. [105] synthesized high MW aliphatic PEs for the first time, in 1-alkyl-3-methylimidazolium ILs via two-step polycondensation using a simple catalyst, SnCl$_2$.2H$_2$O. Oligomers, other than diacids and diols, were used as the starting materials to eliminate the large amount of water generated in the initial stage of the oligomer formation. Moreover, the molecular weight of the resulting PEs was found to depend on the activity of the catalyst in the ILs and the miscibility of aliphatic PE/IL. The former factor was dominated by the anion of the ILs. The latter factor could readily be tuned by varying the anion and/or the cation of the ILs.

A clear correlation was found between the miscibility of aliphatic PE/IL and the extent to which their solubility parameters match. Keeping the diol/diacid ratio of the oligoesters higher than unity...
was found to be essential to the growth of the molecular weight. The activity of catalyst in ILs and the miscibility of aliphatic PE/IL were proved to be two key factors controlling the molecular weight of the PEs. The Sn\textsuperscript{2+} catalyst remained active in CF\textsubscript{3}SO\textsubscript{2})\textsubscript{2}N ILs, and was substantially suppressed in PF\textsubscript{6}\textsuperscript{-} ones. The miscibility was found to be the function of both the anion and the cation of the ILs. Hildebrand solubility parameter was identified as a semi-quantitative criterion in choosing ILs for the PEs with a given chemical composition [106]. Using a multiple-parameter approach may provide more details of individual interactions between IL and PE.

Fradet and coworkers reported the synthesis of poly(glycolic acid) (PGA) in imidazolium-based ILs either directly from glycolic acid or from preformed oligomer [107]. Low PGA yields were obtained by direct method because of the severe evaporation of the monomer at high reaction temperature. The PGA with the highest degree of polymerization up to 45 was obtained by the post-polymerization of the pre-formed oligomer in [BuEIm](CF\textsubscript{3}SO\textsubscript{2})\textsubscript{2}N. The author claimed that the precipitation of PGA in reaction medium and the low efficiency of metal catalysts in the ILs limited the achievable MW. The activity of common esterification catalysts, such as Zn(OAc)\textsubscript{2}, was low which may be due to preferential interactions between the catalyst and IL anions, instead of interactions between catalyst and carboxylic acid end groups. Therefore, the miscibility of PE/IL and the activity of catalysts in ILs are the two essentials factors for these types of polymerization.

ROP of five lactones catalyzed by Candida antarctica lipase B in ILs yielded poly(hydroxyalkanoates) of moderate MW up to 13000 g.mol\textsuperscript{-1}. In [BuEIm](CF\textsubscript{3}SO\textsubscript{2})\textsubscript{2}N and with a low weight ratio of enzyme to lactone (1/100), polymers from β-propiolactone, δ-valerolactone, and CL with degrees of polymerization as high as 170, 25, and 85 were obtained in the order given. Oligomers from β-butyrolactone and γ-butyrolactone with degrees of polymerization of 5 and a copolymer of β-propiolactone and γ-butyrolactone with a degree of polymerization of 180 were also obtained.

Water-immiscible ILs are superior to water-miscible ILs. Reducing the water content of the enzyme, they improved the degree of polymerization by as much as 50% for β-propiolactone and CL [108]. Yarrowia lipolytica lipase (YLL), Candida rugosa lipase (CRL), and porcine pancreatic lipase (PPL) were employed successfully as catalysts in the enzymatic ROP of CL in the presence of [EMIm]BF\textsubscript{4}, [BuMIm]PF\textsubscript{6}, 1-butylpyridinium tetrafluoroborate ([BuPy][BF\textsubscript{4}]), 1-butylpyridinium trifluoroacetate ([BuPy][CF\textsubscript{3}COO]), and 1-ethyl-3-methylimidazolium nitrate ([EMIm][NO\textsubscript{3}]), respectively [109]. PCLs with MW within the range of 300-9000 g.mol\textsuperscript{-1} were obtained. \textsuperscript{1}H and \textsuperscript{13}C NMR analyses on PCLs formed by YLL, CRL, and PPL as catalysts showed asymmetric telechelic α-hydroxy-ω-carboxylic acid end groups.

The hydrolysis of PET was studied using [BuMIm]Cl as solvent and acid-functionalized 1-methyl-3-(3-sulphopropyl)-imidazolium hydrogen sulphate ([MHSO\textsubscript{3}Im][HSO\textsubscript{4}]) as catalyst. The effects of temperature, time, and dosages of solvent and catalyst on hydrolysis results were examined. Under the optimum conditions of m(PET)/m(H\textsubscript{2}O)/m[BuMIm]Cl/m[MHSO\textsubscript{3}Im][HSO\textsubscript{4}]: 3/4/6/0.6, reaction temperature 170°C and time 4.5 h, the conversion of PET and the yield of terephthalic acid (TPA) were almost 100% and ≥ 88%, respectively. After easy separation from the product, the ILs could be reused eight times without noticeable reduction in the conversion of PET and yield of TPA. Hence, an environmental friendly strategy for chemical recycling of PET was developed [110].

Because PAs such as nylon are one of the most common polymers used in daily life and are produced in vast amounts each year, introduction of an effective and green method for depolymerization of this material is necessary. Several successful depolymerization reactions of PAs have been reported by different authors [111-113]. Recently, Kamimura et al. [114,115] provided a new usage of ILs that would serve as a key material for realizing zero-emission chemical recycling process of plastics (Scheme VI). Treatment of a PAs such as nylon-6 in ILs at 300°C resulted in the effective depolymerization to monomeric amides, which were readily isolated through direct distillation from the reaction pot. The ILs were recycled and they still worked as good reaction media after being used five times. This group also reported the syntheses
of novel functionalized ammonium salts that effectively catalyze depolymerization of nylon-6 in ILs [116]. Their result showed that depolymerization of nylon-6 in ILs giving monomeric caprolactam in high yield through direct distillation [116].

Lipase activity and stability was investigated in dialkylimidazolium and pyrrolidinium-based ILs with a variety of anions including PF_{6}, acetate, nitrate, methane sulphonate, trifluoroacetate, and trifluoromethylsulphonate by Russell et al. [117]. The initial rate of lipase-catalyzed transesterification of methyl methacrylate in these ILs and several organic solvents was examined as well as the polytransesterification of divinyl adipate and 1,4-butanediol. Free lipase CRL catalyzed the transesterification of methyl methacrylate in [BuMIm]PF_{6} at a rate 1.5 times greater than in hexane. However, no detectable activity was observed in all the "hydrophilic" ILs studied. Polytransesterifications performed in [BuMIm]PF_{6} using Novozym 435 produced PEs with weight average MW limited to 2900 g.mol^{-1} due to precipitation of the polymer.

Solvatochromic studies and partition coefficient measurements suggest that ILs are more polar and hydrophilic than organic solvents such as hexane, acetonitrile, and tetrahydrofuran. Stability studies indicate that lipases exhibit greater stability in ILs than in organic solvents including hexane.

*Candida antarctica* lipase B has been successfully used as catalyst for the copolymerization of dialkyl diester with diol and lactone to form aliphatic PEs [118]. The polymerization reactions were performed using a two stage process: first stage oligomerization under low vacuum followed by second stage polymerization under high vacuum.

Use of the two-stage process is required to obtain products with high MW at high yields for the following reasons: (i) the first stage reaction ensures that the monomer loss via evaporation is minimized to maintain 1/1 diester to diol stoichiometric ratio, and the monomers are converted to non-volatile oligomers; (ii) use of high vacuum during the second stage accelerates equilibrium transesterification reactions to transform the oligomers to high molecular weight polymers. Thus, terpolymers of ω-pentadecalactone (PDL), diethyl succinate (DES), and BD with a MW of whole product (non-fractionated) up to 77000 g.mol^{-1} and M_w/M_n between 1.7 and 4.0 were synthesized in high yields (e.g., 95% isolated yield). A desirable reaction temperature for the copolymerizations was found to be around 95°C.

At 1/1/1: PDL/DES/BD monomer molar ratio, the resultant terpolymers contained equal moles of PDL, succinate, and butylene repeat units in the polymer chains. \(^1\)H and \(^13\)C NMR analyses were used to determine the PE microstructures. The synthesized PDL-DES-BD terpolymers possessed near random structures with all possible combinations of PDL, succinate, and butylene units via ester linkages in the polymer backbone. Furthermore, thermal stability and crystallinity of a pure PDL-DES-BD terpolymer with 1/1/1 PDL of succinate to butylene unit ratio and MW of 85400 g.mol^{-1} were studied by TGA and differential scanning calorimetery (DSC). The copolyester was found to be a semi-crystalline material with a T_g of -34°C and a T_m of 64°C, which degrades in a single weight loss step centered at T_{max} of 408°C.

Hyperbranched copolymers were prepared by the heat transesterification of 4-hydroxycinnamic acid (4HCA) and 3,4-dihydroxycinnamic acid (DHCA) with a high 4HCA composition dissolved in TFA. The nanoparticles were formed after two homo-
geneous copolymer solutions were mixed in DMF and TFA, both being good solvents for the copolymer P(4HCA-co-DHCA). We confirmed that the driving force for particulation was solvent interactions that produce ion pairs which elevate the polarity of the solvent to such a degree to dissolve the copolymers [119].

Zhang et al. [120] presented an effective and convenient method for grafting LA from unmodified cellulose by ROP in homogeneous mild conditions. By using 4-dimethylaminopyridine (DMAP) as an organic catalyst, cellulose-graft-PLLA (cellulose-g-PLLA) copolymers with a molar substitution (MSPLLA) of PLLA in a range of 0.99-12.28 were successfully synthesized in IL, 1-allyl-3-methylimidazolium chloride [AllMIm]Cl, at 80°C. The amount and length of grafted PLLA in cellulose-g-PLLA copolymers were controlled by adjusting the molar ratios of LA monomer to cellulose. The structure and thermal properties of cellulose-g-PLLA copolymers were characterized by 1H NMR, 13C NMR, DSC, TGA and optical microscopy. The DSC results revealed that the copolymers exhibited a single glass transition temperature, Tg, which sharply decreased with the increase of MSPLLA up to MSPLLA 8.28 (DSPATHLA 2.19) and increased slightly with a further increase in lactyl content. When MSPLLA was above 4.40, the graft copolymers exhibited thermoplastic behaviour, indicating the intermolecular and intramolecular hydrogen bonds in cellulose molecules had been effectively destroyed. By using a conventional thermal processing method, fibres and disks of cellulose-g-PLLA copolymers were obtained.

CONCLUSION

Because of the superior performance characteristics for HPPs such as PIs and PEs, the demand for these types of polymeric materials is growing steadily. Traditional methods for the preparation of these materials use a large number of polar high-boiling-point organic solvents which generally create several ecological problems apart from the over cost of the synthetic methods. The minimization of industrial pollution of these materials is one of the society's biggest challenges in coming years.

These days there is a great demand for the development of new methodologies for polymerization process using environmentally benign media which could replace the common solvents and give adequate solubility to polymerization. ILs have great potential as a non-volatile organic medium for polymerization and polymer processing due to the near-zero vapour pressures, inexpensive, non-flammable, excellent microwave absorbing ability and easy to make. The use of ILs as industrial solvents can result in economical, social, and ecological impacts because of their effects on human health and environment. Additionally, polymerization reaction in ILs may also improve the chemistry of synthesis and the quality of the resulting polymers, such as higher reaction rate, higher molecular weight and easier recycling.

ILs can also be suitable for many forms of direct polycondensation due to the high temperatures often employed in this type of polymerization reaction. Non-volatile nature and stability at high temperature make the ILs excellent candidates as reaction media as well as catalysts for the preparation of these types of polymers. Therefore, with the purpose of developing green polymer chemistry, the synthesis and properties of HPPs such as PIs and PEs in ILs media is reviewed.

Although there are many advantages to use ILs for the polymerization reactions still there are some disadvantages which need to be challenged including cost of ILs, effective recycling limitation and its environmental pollution if it comes into contact with nature. This part of the limitation concerned needs more research works in order to overcome the problems. One of the suggestions would be fabrication and application of ILs which are readily biodegradable. At the end, it is predicted that this new technology will soon be a popular method for the laboratory scale as well as industrial scale synthesis of HPPs.

ACKNOWLEDGEMENT

We wish to express our gratitude to the Research Affairs Division of Isfahan University of Technology.
(IUT), for financial support. Further financial support from National Elite Foundation (NEF) and Center of Excellency in Sensors and Green Research (IUT) are also gratefully acknowledged.

ABBREVIATIONS

\[ \text{[AllMIm]Cl} : 1\text{-Allyl-3-methylimidazolium chloride} \]
\[ \text{[BzMIm](CF}_3\text{SO}_2\text{)N} : 1\text{-Benzy1-3-methylimidazolium bis(triflyl)amide} \]
\[ \text{APh} : 3,3\text{-Bis(4’-aminophenyl)phthalide} \]
\[ \text{BDA} : 3,3’,4,4’\text{-Biphenyltetracarboxylic dianhydride} \]
\[ \text{BD} : 1,4\text{-Butanediol} \]
\[ \text{[BuMIm]Cl} : 1\text{-Butyl-3-methylimidazolium chloride} \]
\[ \text{[BuMIm]PF}_6 : 1\text{-Butyl-3-methylimidazolium hexafluorophosphate} \]
\[ \text{[BuMIm]BF}_4 : 1\text{-Butyl-3-methylimidazolium tetrafluoroborate} \]
\[ \text{[BuMIm](CF}_3\text{SO}_2\text{)N} : 1\text{-Butyl-3-methylimidazolium bis(triflyl)amide} \]
\[ \text{[BPy]BF}_4 : 1\text{-Butylpyridinium tetrafluoroborate} \]
\[ \text{ZI} : 1-(1\text{-Butyl-3-imidazolio)butane-4-sulphonate} \]
\[ \text{CRL} : \text{Candida rugosa lipase} \]
\[ \text{CL} : \text{e-Caprolactone} \]
\[ \text{DES} : \text{Diethyl succinate} \]
\[ \text{[Bz2Im]Br} : 1,3\text{-Dibenzylimidazolium bromide} \]
\[ \text{[Bu2Im]Br} : 1,3\text{-Dibutylimidazolium bromide} \]
\[ \text{[Bu2Im]PF}_6 : 1,3\text{-Dibutylimidazolium hexafluorophosphate} \]
\[ \text{[Bu2Im]BF}_4 : 1,3\text{-Dibutylimidazolium tetrafluoroborate} \]
\[ \text{DSC} : \text{Differentials scanning calorimetry} \]
\[ \text{DMF} : N,N\text{-Dimethylformamide} \]
\[ \text{DMAc} : N,N\text{-Dimethylacetamide} \]
\[ \text{DMSO} : \text{Dimethylsulphoxide} \]
\[ \text{[EMIm](CF}_3\text{SO}_2\text{)N} : 1\text{-Ethyl-3-methylimidazolium bis(triflyl)amide} \]
\[ \text{[EMIm]NO}_3 : 1\text{-Ethyl-3-methylimidazolium nitrate} \]
\[ \text{ILs} : \text{Ionic liquids} \]
\[ \text{GPC} : \text{Gel permeation chromatography} \]
\[ \text{T}_g : \text{Glass-transition temperatures} \]
\[ \text{HPPs} : \text{High performance polymers} \]
\[ \text{LA} : \text{l-Lactide} \]
\[ \text{[M-3-HSO}_3\text{Im][HSO}_4\text{]} : 1\text{-Methyl-3-(3-sulphopropyl)imidazolium hydrogen sulphate} \]
\[ \text{NMP} : \text{N-Methylpyrrolidone} \]
\[ \text{MW} : \text{Molecular weights} \]
\[ \text{PDL} : \text{ω-Pentadecalactone} \]
\[ \text{PAA} : \text{Polyamic acid} \]
\[ \text{PAs} : \text{Polyamide} \]
\[ \text{PAEs} : \text{Poly(amide-ester)s} \]
\[ \text{PAIs} : \text{Poly(amide-imide)s} \]
\[ \text{PCL} : \text{Poly(ε-caprolactone)} \]
\[ \text{PEs} : \text{Polyesters} \]
\[ \text{PET} : \text{Poly(ethylene terephthalate)} \]
\[ \text{PIs} : \text{Polymides} \]
\[ \text{PGA} : \text{Poly(glycolic acid)} \]
\[ \text{PLL} : \text{Poly(lactide)} \]
\[ \text{PPL} : \text{Porcine pancreatic lipase} \]
\[ \text{Py} : \text{Pyridine} \]
\[ \text{ROP} : \text{Ring-opening polymerization} \]
\[ \text{RTIL} : \text{Room temperature ionic liquids} \]
\[ \text{SEM} : \text{Scanning electron microscopy} \]
\[ \text{TBA} : \text{Tetrabutylammonium bromide} \]
\[ \text{TPA} : \text{Terephthalic acid} \]
\[ \text{TGA} : \text{Thermalgravimetric analysis} \]
\[ \text{TEA} : \text{Triethylamine} \]
\[ \text{TPP} : \text{Triphenylphosphite} \]
\[ \text{TPA} : \text{Terephthalic acid} \]
\[ \text{TsCl} : \text{Tosyl chloride} \]
\[ \text{TEM} : \text{Transmission electron microscopy} \]
\[ \text{VOCs} : \text{Volatile organic compounds} \]
\[ \text{YLL} : \text{Yarrowia lipolytica lipase} \]
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