Progress in Polymer Science 36 (2011) 1754–1765

Contents lists available at ScienceDirect

Progress in Polymer Science

journal homepage: www.elsevier.com/locate/ppolysci

New developments in polymer science and technology using combination of ionic liquids and microwave irradiation

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ARTICLE INFO

Article history:
Received 18 June 2010
Received in revised form 12 January 2011
Accepted 15 February 2011
Available online 11 March 2011

Keywords:
Green chemistry
Microwave energy
Ionic liquid
Polymerization

ABSTRACT

The purpose of this review is to provide appropriate details concerning the application of ionic liquids (IL)s associated with microwave-assisted polymer chemistry. From the viewpoint of microwave chemistry, one of the key significant advantages of ILs is their high polarity, which is variable, depending on the cation and anion and therefore can effectively be tuned to a particular application. Hence, these liquids offer a great potential for the innovative application of microwaves for organic synthesis as well as for polymer science. ILs efficiently absorb microwave energy through an ionic conduction mechanism, and thus are employed as solvents and co-solvents, leading to a very high heating rate and a significantly shortened reaction time. Since an IL-based and microwave-accelerated procedure is efficient and environmentally benign, we believe that this method may have some potential applications in the synthesis of a wide variety of vinyl and non-vinyl polymers. This review describes application of combination of ILs with microwave irradiation as a modern tool for the addition and step-growth polymerization as well as modification of polymers and it was compared with ILs alone and conventional polymerization method.

Contents

Abbreviations: $[(CF_3SO_2)_2N]$, bistrifluoromethanesulfonate; $[BF_4]$, tetrafluoroborate; $[BMIM][BF_4]$, 1-butyl-3-methylimidazolium tetrafluoroborate; [BMIM][Cl], 1-butyl-3-methylimidazolium chloride; $[BMIM][PF_6]$, 1-butyl-3-methylimidazolium hexafluorophosphate; $[CF_3SO_3]$, trifluoromethanesulfonate; [EMIM][OAc], 1-ethyl-3-methylimidazolium acetate; $[EMIM][EtSO_4]$, 1-ethyl-3-methylimidazolium ethylsulfate; $[PF_6]$, hexafluorophosphate; $[(i\text{-}P)_2IM][Br]$, 1,3-diisopropylimidazolium bromide; $[P_2IM][Br]$, 1,3-dipropylimidazolium bromide; AN, acrylonitrile; DMF, *N*,*N*-dimethylformamide; HMF, 5-hydroxymethylfurfural; ILs, ionic liquids; k_p, propagation rate constant; k_t, termination rate constant; MMA, methyl methacrylate; M_n, number-average molar mass; MROP, microwave-assisted ring opening polymerization; NPI, *N*-phenyl maleimide; Poly(IL), poly(ionic liquid); PA, polyamide; Poly(NIPAAm), poly(*N*-isopropylacrylamide); Poly(TMC), poly(trimethylene carbonate); r_p, polymerization rate; S, styrene; TBAB, tetrabutylammonium bromide; TMC, trimethylene carbonate; TPP, triphenyl phosphite; ε-CL, ε-caprolactone.

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doi:10.1016/j.progpolymsci.2011.03.001

1. Introduction

With the increasing awareness of the environmental, one of the primary driving forces in chemical industries as well as research laboratories is the requirement to develop replacements for the traditional toxic and volatile organic solvents in commercial chemical processes. In a search for more efficient, and at the same time more environmentally green processes, chemists have lately turned their attention to the new class of potential solvents, namely ionic liquids (IL)s, which have become a part of the so-called green chemistry [1–7]. ILs have fascinating properties, such as extremely low volatility, non-flammability, wide liquid temperature range, good thermal stability, recyclability, good dissolving ability, excellent microwave absorbance, designable structures, high ionic conductivity, and a wide electrochemical window. The nonvolatile nature of ILs is useful in minimizing solvent consumption. Recently, these liquids have attracted attention due to their significant role in controlling the reaction as a catalyst in a variety of green chemistry processes [8–10], and for use in polymer synthesis [2,11–13].

As an alternative to conventional heating techniques and as an environmentally benign process, microwave irradiation is a rapid volumetric heating, efficient, selective, and energy saving synthetic method to heat molecules directly through the interaction between microwave energy and molecular dipole moments of the starting materials [14–16]. Lately, there has been increasing interest in microwave irradiation for polymerization reactions [17–20].

ILs interact very efficiently with microwaves through the ionic conduction mechanism, and are quickly heated without any considerable pressure increase [16]. The temperature profiles and the thermal stability of ILs under microwave irradiation conditions were reported by Leadbeater and Torenius [21]. Their results demonstrated that the addition of a small amount of IL (0.1 mmol mL^{-1}) to a non-polar solvent (e.g., toluene and hexane) can induce dramatic changes in the heating characteristics of the solvent under microwave irradiation that can result from the change in the overall dielectric properties of the reaction medium. Wasserscheid and co-workers [22] have also studied heating behavior of ILs under multimode microwave conditions. To combine the benefits of microwave technique and ILs (environmentally friendlier and energy saving) several organic reactions have been carried out in IL under microwave irradiation. Two reviews on the use of microwave irradiation and ILs in organic synthesis were published by Martínez-Palou [23,24]. The application of microwave irradiation for enzymatic reactions in ILs has also been investigated [25,26], and the combination of microwave-assisted reactions with IL has been applied for the synthesis of various nanomaterials [27,28]. This method, which is a fast and environmentally friendly route for the preparation of nanostructured materials has also been employed in the preparation of zeolites [29]. In contrast to their utilization in organic chemistry, the application of microwave activation in conjunction with ILs in macromolecules synthesis has scarcely been exploited.

1.1. Microwaves

Microwaves are electromagnetic irradiation in the frequency range 0.3–300 GHz (wavelengths of 1 mm to 1 m), between infrared radiation and radio frequencies. Microwave radiation was discovered as a heating method in 1946, with the first commercial domestic microwaves being introduced in the 1950s. The first commercial microwave for laboratory utilization was recognized in 1978. Over the last decade, microwave dielectric heating as an environmentally benign process has developed into a highly valuable technique, offering an efficient alternative energy source for numerous chemical reactions and processes. It has many advantages compared to conventional oil-bath heating, such as non-contact heating, energy transfer instead of heat transfer, higher heating rate, rapid start-up and stopping of the heating, uniform heating with minimal thermal gradients, selective heating properties, reverse thermal effects (heating starting from the interior of the material body), energy savings and higher yields in shorter reaction time.

Microwave heating is based dielectric heating, the ability of some polar liquids and solids to absorb and convert microwave energy into heat. In this context, a significant property is the mobility of the dipoles by either ionic conduction or dipolar polarization and the ability to orient them according to the direction of the electric field. The orientation of the dipoles changes with the magnitude and the direction of the electric field. Molecules that have a permanent dipole moment are able to align themselves through rotation, completely or at least partly, with the direction of the field. Therefore, energy is lost in the form of heat through molecular friction and dielectric loss. The amount of heat produced by this process is directly related to the capability of the matrix to align itself with the frequency of the applied electric field. If the dipole does not have enough time to realign, or reorients too rapidly with the applied field, no heating occurs. The allocated frequency of 2.45 GHz employed in all commercial systems is