Journal of Colloid and Interface Science 485 (2017) 183–191

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

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

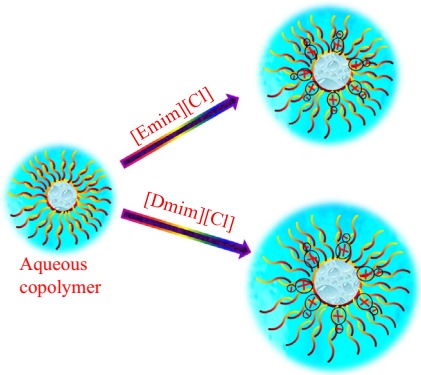
Regular Article

Thermo-responsive triblock copolymer phase transition behaviour in imidazolium-based ionic liquids: Role of the effect of alkyl chain length of cations

Reddicherla Umapathi, Pannuru Venkatesu *

Department of Chemistry, University of Delhi, Delhi 110007, India

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 14 July 2016
Revised 14 September 2016
Accepted 14 September 2016
Available online 15 September 2016

Keywords:
Triblock copolymer
Ionic liquids
Critical micellization temperature
Aggregation studies
Morphological changes

ABSTRACT

Different biophysical techniques such as fluorescence spectroscopy, dynamic light scattering (DLS), viscosity (η) and Fourier transform infrared (FTIR) spectroscopy have been carried out to characterize the effect of imidazolium-based ionic liquids (ILs) on the thermo-responsive triblock copolymer, poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly-(ethylene glycol) (PEG-PPG-PEG). In addition, to demonstrate the distinct morphological changes of various self-assembled morphologies, we further employed field emission scanning electron microscope (FESEM). To investigate the effect of alkyl chain length of the cation, concentration of the ILs and the related Hofmeister series on the phase behaviour of PEG-PPG-PEG, we used a series of ILs possessing same Cl^- anion and a set of cation $[C_nmim]^+$ with increasing alkyl chain length of cation such as 1-ethyl-3-methylimidazolium chloride ([Emim][Cl]), 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]), 1-hexyl-3-methylimidazolium chloride ([Hmim][Cl]) and 1-decyl-3-methylimidazolium chloride ([Dmim][Cl]). The critical micellization temperature (CMT) of the copolymer in the presence of well hydrated cations is directly correlated to their hydration. The overall specific ranking of ILs in decreasing the CMT of PEG-PPG-PEG in aqueous solution was [Emim][Cl] > [Bmim][Cl] > [Hmim][Cl] > [Dmim][Cl]. The trend of these ILs followed the well-known Hofmeister series of cations of ILs. The present study provides important information about the solution properties that can be helpful to tune the IL or temperature-sensitive copolymer CMT and micelle shapes which are crucial for understanding the drug delivery mechanisms.

Abbreviations: ILs, ionic liquids; CMT, critical micellization temperature; LCST, lower critical solution temperature; PEG-PPG-PEG, poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly-(ethylene glycol).

* Corresponding author.
E-mail addresses: venkatesup@hotmail.com, pvenkatesu@chemistry.du.ac.in (P. Venkatesu).

http://dx.doi.org/10.1016/j.jcis.2016.09.034
0021-9797/

1. Introduction

Poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly-(ethylene glycol) (PEG-PPG-PEG) block copolymers with their rich structural polymorphism are interesting type of amphiphilic block copolymers commonly known as Pluronics (BASF) or Polaxamers [1–5]. These interesting types of amphiphilic block copolymers are commercially available in a variety of molecular weights and PEG/PPG ratios and are used extensively in aggregation behaviour [6], nano particle synthesis [7], drug delivery [8], gene delivery [9], as polymer gel electrolytes [10,11], as template for synthesizing mesoporous carbon materials [12], biomolecular separation [13], soil remediation [14] and other scientific fields [15–23]. Nowadays, the systematic studies on interactions of nano particle dispersions under various conditions are progressively increasing [24–26]. Furthermore, the copolymer-nanoparticle composite materials have been a topic of extensive interest in the field of smart materials due to their synergistic hybrid properties and particularly a promising synthetic tool to produce multifunctional nanoparticles with various ordered structures [24,27–33]. The majority of these applications are associated with the formation of micelles or thermodynamics of temperature-induced micellization in aqueous solution. Therefore, micellization behaviour of block copolymers has attracted great attention from the scientific world over the decades.

Among various triblock copolymers, PEG-PPG-PEG type copolymers with hydrophilic PEG block and hydrophobic PPG block are considered as the most prominent copolymers because of their high surface active nature and their ability to form micelles above their critical micelle concentration (CMC) or critical micelle temperature (CMT). Above their CMT, the copolymer chain aggregates into micelles with hydrophobic PPG blocks as the core and hydrophilic PEG blocks as the corona [1–5]. The chemical structure of PEG-PPG-PEG is presented in Fig. 1.

Ionic liquids (ILs) have been widely prompted as designer solvents, due to their tunable and unique properties [34,35]. They have attracted considerable attention over the recent years in diverse scientific fields [34–42]. The appropriate modification of cation and anion can tune their hydrophobicity/hydrophilicity, thus making it possible to be used according to the need and demand of the reaction conditions. Nevertheless, the growing importance of these designer solvents (ILs) in biophysical chemistry renders the challenges of characterization and understanding of the Hofmeister series effects generated by the more complex ions of ILs [43–45]. Moreover, the phase transition behaviour of polymers in ILs remains poorly understood because of the difficulties in obtaining the structural information of polymers in the presence of the ions of ILs.

In 2013, Lutter et al. [43] carried out cation effects involving ionic salts on triblock copolymer aggregation, which showed a key role of the hydration of cations in determining the interactions between the ionic salts and the polymer. Studies related to the effect of cation of ionic salts are progressively explored, nevertheless, they are comparatively less explored, particularly taking into account of ILs. In general, anion variation is thought to have greater significance on systems than the cation [2]. As a result, studies of the effects of cations are complicated than similar studies of anions in several ways. Although, as mentioned above, there are numerous approaches dedicated to investigate the effect of Hofmeister series of ions based on experimental as well as molecular dynamic simulation to elucidate the phase transition behaviour of polymer solutions, yet such studies of polymer-IL interactions mainly focusing on cation variation are still lacking in the literature. Moreover, no conclusive experimental results have explored the influence of imidazolium-based ILs on the CMT of PEG-PPG-PEG.

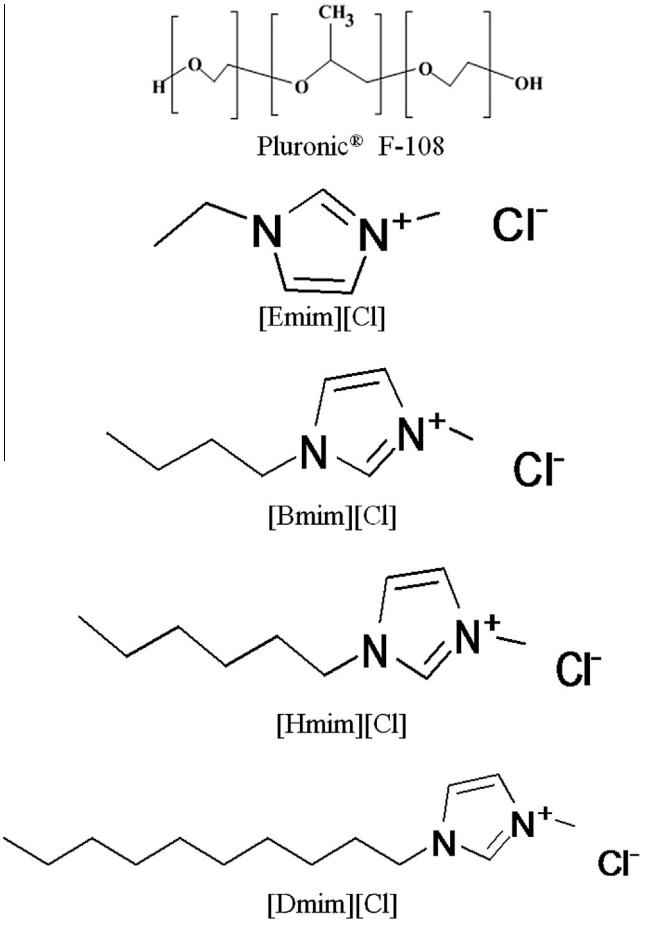


Fig. 1. The chemical structures of PEG-PPG-PEG (Pluronic® F-108), [Emim][Cl], [Bmim][Cl], [Hmim][Cl] and [Dmim][Cl].

Recent studies [44,46,47] on the self-assembly and the aggregation characteristic behaviour of the common anionic, cationic, and non-ionic block copolymers in ILs show a strong dependence on temperature in aqueous medium mainly due to the temperature-dependent solubilities of their constituent blocks in aqueous solution. Since self-assembly of PEG-PPG copolymers in ILs can be regulated flexibly. These block copolymers are soluble in water at low temperature as a result, these molecules remain in their aqueous solutions as unimers. Considerable efforts have been forwarded by the researchers to control the self-assembly of amphiphilic block copolymers. Several reports have revealed that chemical structure of amphiphilic copolymers as well as the environmental conditions such as pH [48–50], temperature [51–54] and ion concentrations [55,56], play a crucial role to accomplish manipulation of the self-assembly behaviour of amphiphilic copolymers. Despite numerous studies with different types of co-solvents on the solution properties of triblock copolymers, influence of ILs as co-solvents on micellization behaviour is still not explored properly. The origin of their varying solution properties through unfavourable/favourable interactions between polymer blocks and ions of ILs remains a matter of debate.

Previously [2], we investigated the specific anion effects on the CMT of PEG-PPG-PEG and proposed the underlying molecular mechanism of the IL effect on copolymer aqueous solution. Pursuant to our continued research work, herein, we report the