



Influence of counterion type on dielectric and electrorheological responses of poly(ionic liquid)s



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ABSTRACT

Different from classic water activated polyelectrolytes, poly(ionic liquid)s (PILs) bearing hydrophobic counterions show high electrorheological (ER) response in dry state. This offers opportunity for practical applications of polyelectrolyte-based ER materials in wide temperature region. For guiding the design of PIL-based ER materials with improved performance, understanding the structure-property relationship is very important. In this paper, a series of poly(*p*-vinylbenzyl trimethylammonium)-based PIL particles with different counteranions ([PVB₃TMA][X]) were synthesized with the goal of understanding the role of mobile counterions on ER response of PILs. To exclude particle shape effect, the PIL series were controlled to be monodisperse spheres with a similar diameter via microwave-assisted dispersion polymerization. Under electric fields, the ER response of PIL particles when dispersed in insulating oil was investigated by temperature-modulated rheological test. It showed that the ER response of PILs depends on the type of counteranions. The order of magnitude of ER response of PILs with different counteranion is trifluoromethanesulfonate (TfO⁻) > tetrafluoroborates (BF₄⁻) > bis-(trifluoromethanesulfonylimide) (TFSI⁻) > hexafluorophosphates (PF₆⁻). The mechanism behind the influence of counterion type on ER response was analysed by dielectric relaxation spectroscopy. It demonstrated that the influence of counteranion type on ER response may be related to the variation of size and plasticization effect of counteranions that has altered the transport dynamic of mobile counterions and ion motion-induced interfacial polarization.

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1. Introduction

Electrorheological (ER) fluids are a family of stimuli responsive smart material systems that are typically composed of polarizable particles dispersed in insulating carrier liquids. Under an external electric field stimulus, the dispersed particles are polarized and attracted each other by dipole–dipole interaction to form fibril-like structures along the direction of applied electrical field [1]. This structure construction can make ER fluids undergo a rapid phase transition from liquid-like state to solid-like state. As a result, the rheological properties (viscosity and viscoelastic) of ER fluids are quickly and controllably adjusted. This stimuli-responsive rheology has stimulated a lot of research interests in industrial application prospects involving automobile, mechanical polishing, tactile displays, food processing, crude oil production, and so on [2–5].

To promote practical applications, there has been extensive

research on the fabrication of electro-responsive ER particle materials in recent years. A variety of inorganic, organic, and composite particles have been proposed to be applicable in ER fluids [1,6–10]. Among these materials, polyelectrolytes are the promising candidates due to their low-cost and relatively high ER activity. Some classic polyelectrolyte particles, such as poly(lithium methacrylate), poly(sodium styrene sulfonate), and ion-exchange resins, have demonstrated to be high ER activity [11–13]. In dry state, however, the classic polyelectrolyte particles often lose their ER activity. This may be due to the weakness of ion motion-induced interfacial polarization because the counterions become immobile in dry polyelectrolytes. Therefore, the classic polyelectrolytes need to adsorb moisture to activate ER response. However, the adsorbed moisture inevitably causes thermal instability, chemical corrosion, and dielectric breakdown.

Very recently, a new kind of anhydrous polyelectrolyte ER system based on poly(ionic liquid)s (PILs) particles bearing fluorine counterions (e.g. bis(trifluoromethylsulfonyl)-imide ((CF₃SO₂)₂N⁻)) has been developed [14]. Due to the hydrophobic nature of

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fluorine-containing chemical structure and the large mobility of counterions in the absence of any external activators, the ER fluid with PIL particles as dispersed phase could exhibit strong ER response in dry state. This offers opportunity for practical applications of polyelectrolyte-based ER fluids in a wide temperature region. To guide the design of new PIL ER system with improved performance, it is worthy to deeply understand the mechanism behind ER response and the relationship between microscopic structure and macroscopic ER response on the molecular level. The preliminary dielectric spectra analysis has shown that the anhydrous ER response of PIL particles is associated with ion motion-induced interfacial polarization [14]. Thus, the microscopic molecular structure affecting ion transport and dielectric response should be very important. In the previous study, the size effect of side chains on ion transport and ER response has been specially studied by introducing different length of substituent alkyl chains onto the immobile ammonium charged site of PILs [15]. It has found that, in glassy state, the PIL particles with shorter substituent alkyl chains have the lower activation energy of ionic transport and faster relaxation time of ion motion-induced interfacial polarization and, as a result, they have stronger ER response. On the other hand, the influence of counterions themselves on ionic transport, dielectric response, and macroscopic ER response should be more direct [16–18]. However, many aspects addressing this are still incomplete. In particular, to explore the influence of counterions on ionic transport and thereby ER response in suspension systems remains challenge because it needs to eliminate the factor of the external particle morphology affecting ER response.

In this paper, we used a microwave-assisted dispersion polymerization technique to prepare monodisperse poly(*p*-vinylbenzyl trimethylammonium)-based PIL particles with different counteranions ([PVBtMA][X]) but similar diameters and extracted the role of mobile counterions on ionic transport, dielectric polarization and thereby macroscopic ER response in suspension system. By using a mixture of dimethylformamide (DMF) and ethanol as solvent, monodisperse PIL particles with not only polyatomic organic counteranions (e.g. trifluoromethanesulfonate (TfO⁻), bis(trifluoromethanesulfonylimide) (TFSI⁻)) but also polyatomic inorganic counteranions (e.g. tetrafluoroborate (BF₄⁻), hexafluorophosphate (PF₆⁻)) were well prepared. Scanning electron microscopy, ¹H nuclear magnetic resonance, Fourier transform infrared spectra, and differential scanning calorimeter were used to characterize the particle morphology, structure and thermal property. Under electric fields, temperature-modulated rheological tests were conducted to investigate the ER response of PIL particles when suspended in insulating carrier liquid. Dielectric relaxation spectroscopy was finally measured to analyze the mechanism behind the impact of counterion type on ER response. We demonstrated that the type of counterions has an important influence on the macroscopic ER response and this is related to the fact that the variation of size and plasticization of counteranions alters the transport dynamic of mobile counterions and ion motion-induced interfacial polarization.

2. Experimental section

2.1. Chemicals

p-Vinylbenzyl trimethylammonium chloride ([VBTMA]Cl), 97%, lithium bis(trifluoromethane sulfonylimide) (Li[TFSI], 99%), lithium trifluoromethane sulfonamide (Li[TfO], 97%), sodium tetrafluoroborate (NaBF₄, 98%), potassium hexafluorophosphate (KPF₆, 99%), were purchased from Aldrich. Poly(vinylpyrrolidone) (PVP, K-30, weight-average molecular weight: 3.6×10^5 g/mol) was purchased from BASF. Dimethylformamide (DMF, 99.5%), 2,2'-

azobis(isobutyronitrile) (AIBN), was purchased from Sinopharm Chemical Reagent Co. Ltd. of China. These chemicals were used as received except that AIBN was purified by recrystallization in methanol.

2.2. Synthesis of IL monomers

All IL monomers were synthesized via one-step exchange reaction. Silver nitrate aqueous solution was used to test whether chloride ions were fully removed from IL monomers after water washing and ¹H NMR was used to confirm the component of IL monomers.

p-Vinylbenzyl trimethylammonium hexafluorophosphate ([VBTMA][PF₆]) was synthesized by mixing aqueous solutions of [VBTMA]Cl (6.0 g, 28.3 mmol) and KPF₆ (6.3 g, 34.2 mmol). After filtration, the precipitate was washed with DI water and ethanol. Silver nitrate aqueous solution was used to test whether chloride ions were fully removed in monomers. Finally, the powder was vacuum dried to obtain powder-like IL monomer [VBTMA][PF₆]. The yields were over 90%. ¹H NMR (DMSO-*d*₆, 400 MHz, ppm): 7.63 (d, 2H), 7.52 (d, 2H), 6.83 (m, 1H), 5.97 (d, 1H), 5.40 (d, 1H), 4.50 (s, 2H), 3.03 (m, 9H).

p-Vinylbenzyl trimethylammonium tetrafluoroborate ([VBTMA][BF₄]) was synthesized by mixing aqueous solutions of [VBTMA]Cl (6.0 g, 28.3 mmol) and NaBF₄ (3.8 g, 34.2 mmol). After filtration, the salt precipitate was washed with DI water and ethanol and then vacuum dried. The powder-like IL monomer [VBTMA][BF₄] was obtained. The yields were over 90%. ¹H NMR (DMSO-*d*₆, 400 MHz, ppm): 7.62 (d, 2H), 7.53 (d, 2H), 6.82 (m, 1H), 5.97 (d, 1H), 5.40 (d, 1H), 4.50 (s, 2H), 3.02 (m, 9H).

p-Vinylbenzyl trimethylammonium bis(trifluoromethane sulfonylimide) ([VBTMA][TFSI]) was synthesized by mixing aqueous solutions of [VBTMA]Cl (6.0 g, 28.3 mmol) and Li[TFSI] (9.8 g, 34.2 mmol). After phase separation, washing with DI water, and vacuum drying, the oily IL monomer [VBTMA][TFSI] was obtained. The yields were over 90%. ¹H NMR (DMSO-*d*₆, 400 MHz, ppm): 7.62 (d, 2H), 7.52 (d, 2H), 6.80 (m, 1H), 5.98 (d, 1H), 5.39 (d, 1H), 4.51 (s, 2H), 3.02 (m, 9H).

p-Vinylbenzyl trimethylammonium trifluoromethane sulfonamide ([VBTMA][TfO]) was synthesized by mixing aqueous solutions of [VBTMA]Cl (6.0 g, 28.3 mmol) and Li[TfO] (5.3 g, 34.2 mmol). After phase separation, washing with DI water, and vacuum drying, the oily IL monomer [VBTMA][TfO] was obtained. The yields were over 90%. ¹H NMR (DMSO-*d*₆, 400 MHz, ppm): 7.65 (d, 2H), 7.51 (d, 2H), 6.81 (m, 1H), 5.97 (d, 1H), 5.39 (d, 1H), 4.50 (s, 2H), 3.02 (m, 9H).

2.3. Synthesis of PIL particles

Scheme 1 shows the microwave-assisted dispersion polymerization of monodisperse poly[*p*-vinylbenzyl trimethylammonium]-based PIL particles with various counteranions, denoted as P [VBTMA][X] (where X are the counteranions including PF₆⁻, BF₄⁻, TFSI⁻, and TfO⁻). AIBN was used as initiator, PVP used as stabilizer, and a mixture of DMF and ethanol used as solvent.

Poly[*p*-vinylbenzyl trimethylammonium hexafluorophosphate] (P[VBTMA][PF₆]) particles was synthesized as follows: 1.10 g [VBTMA][PF₆] was dissolved in mixed solvent of 3 mL DMF and 12 mL ethanol. Then, 0.10 g PVP and 0.01 g AIBN were added in the solvent. After stirring at 25 °C for 30 min, the resulting solution was treated at 70 °C and stirring rate of 120 rpm under N₂ protection with a CEM Explorer microwave synthesis instrument. After reaction for 2 h, the precipitate was separated, washed with ethanol and vacuum dried to obtain the resulting monodisperse P[VBTMA][PF₆] particles. The yields were over 90%. ¹H NMR (DMSO-*d*₆,

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