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Linear viscoelasticity of poly(acrylonitrile-co-itaconic acid)/1-butyl-3-methylimidazolium chloride extended from dilute to concentrated solutions

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ABSTRACT

The solution rheology of poly(acrylonitrile-co-itaconic acid) (poly(AN-co-IA)) in 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) spanning dilute, semidilute unentangled and entangled regimes were investigated. The exponents in the specific viscosity $\eta_{sp} \sim$ overlap parameter $c[\eta]$ power law were 1, 2 and 4.7 for dilute, semidilute unentangled and entangled regimes, respectively, which were found to be consistent with the scaling prediction for neutral linear polymers in θ-solvent. For dilute solutions (lower than 0.9 wt.%), the linear viscoelastic responses were observed to be in good agreement with the Zimm model (Flory exponent $\nu = 0.5$). While for semidilute unentangled solutions (between 0.9 and 8 wt.%), results obtained had been found to be consistent with Rouse model. Considering Flory exponent $\nu = 0.5$ and the concentration dependences of the specific viscosity and relaxation time, it had been evaluated that poly(AN-co-IA) in [BMIM]Cl behaves as a neutral polymer in θ-solvent. It had also been suggested that according to the unusual deviation of Cox-Merz rule, poly(AN-co-IA)/[BMIM]Cl solutions are typical neutral polymeric liquids for the concentrated solutions but have shown a more complicated behavior at high deformation rates.

1. Introduction

Diverse applications of polyacrylonitrile (PAN) homopolymer and copolymers in apparel end products, home furnishings and industrial products, particularly in high performance PAN precursor for carbon fibers are quite evident [1,2]. However, interactions between the dipolar nitrile groups of PAN limit its solubility in some specific polar solvents, such as dimethylformamide (DMF), dimethylacetamide (DMAc) and dimethyl sulfoxide (DMSO) [3]. From 2004, Cheng et al. [4] found that PAN could be polymerized in ionic liquids (ILs). Meanwhile, it is interesting to find that both homo- and co-polyacrylonitrile could be dissolved in ionic liquid without degradation [5,6] other than the natural polymers [7,8].

Recent advancements in ILs have widened the scope of their application in preparation of good quality PAN fibers [6,9,10]. PAN solutions have a vital effect in solution processing like wet spinning, dry-jet wet spinning [6] and electrospinning [10]. As a result, rheological properties of PAN/ILs concentrated solutions have received considerable attention. The rheology of poly(acrylonitrile-co-methyl acrylate) and poly(acrylonitrile-co-methyl methacrylate) in [BMIM]Cl [5,6,11] and PAN homopolymer in ionic liquid such as 1-butyl-3-methylimidazolium bromide ([BMIM]Br) [10,12,13] had been studied. As the rheological behaviors of most polymers in ILs [14–21], such as cellulose, cellulose derivatives, amylose, agarose, polyarylsulfone, poly(*m*-phenyleneisophthalamide) and poly(vinyl alcohol), PAN/IL solutions with higher concentrations typically exhibit shear

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thinning behavior, and the viscosity increases significantly with the increasing PAN concentration, molecular weight and inverse temperature [5,6,10–13]. Upon dissolution of copolymer in polar solvents (DMSO and DMF), the ionogenic groups were found to dissociate from polar comonomers in the acrylonitrile copolymer chains; which was suggested to be responsible for polyelectrolyte effect of poly(AN-co-IA) solutions in respective polar solvents [22,23]. Up till now, however, the studies have not been reported whether poly(AN-co-IA) behaves as polyelectrolyte in ILs or not. From the studies of Liu's, it is found that poly(styrenesulfonate) in IL solutions had the same scaling relation between concentration and specific viscosity as the neutral polymer in dilute solutions [24] although poly(styrenesulfonate) is a typical polyelectrolyte.

The rheology of PAN/IL solutions has not been sufficiently studied. Such important rheological properties as the entanglement concentration c_e and relaxation time (τ), which are vital for fiber spinning also have not been reported. For dilute and semidilute unentangled PAN/IL solutions, there are not enough rheological studies on intrinsic viscosity ($[\eta]$) and the linear viscoelastic response, which can be used to describe the dynamics of PAN in ILs. The scope of this paper accounts for the systematic study of the rheology of poly(AN-co-IA) in [BMIM]Cl to illustrate the linear viscoelastic response in different concentration regions. Emphasis was also laid on the spanning of these polymeric solutions from dilute, semidilute unentangled to entangled regimes. The concentration dependences of specific viscosity, relaxation time were studied and compared with the scaling prediction.

2. Experimental

2.1. Materials

PAN copolymer poly(AN-co-IA) (Acrylonitrile: Itaconic acid = 96:4) was provided by Sinopec Shanghai Petrochemical Co., Ltd. (Shanghai, China) with a weight-average molecular weight of 8.6×10^4 g/mol and polydispersity index 1.79, determined by gel permeation chromatography (GPC, Calibration was performed with narrow polydispersity polystyrene). The ionic liquid [BMIM]Cl used was synthesised and purified according to the procedures described in the literature [25]. The density values of poly(AN-co-IA) and [BMIM]Cl are 1.17 and 1.07 g/cm^3, respectively. The water content of [BMIM]Cl measured by the Karl Fischer titration (ZSD-2 with a precision of 0.05%, Shanghai Anting Electric Instruments Co. Ltd., China) is less than 0.1 wt.%.

2.2. Solution preparation

The poly(AN-co-IA) powder was dried in a vacuum oven at 60 °C for 10 h. Afterwards, the dried poly(AN-co-IA) powder was quickly dispersed in [BMIM]Cl. The resulting slurry was heated in a vacuum oven at 90 °C for 10 h to produce a viscous solution. A series of such solutions with concentrations varying from 0.1 wt.% to 18 wt.% were prepared. The solutions were found to be clear and appeared to be homogenous at 80 °C. All the samples were sealed and stored in desiccators for further testing.

2.3. Rheological measurements

The rheological measurements were carried out on a rotational rheometer (Physica MCR 301, Anton Paar). The concentric parallel plate geometry (diameter: 25 mm) was utilized for highly concentrated solutions with viscosity above 100 Pa s and another concentric parallel plate geometry (diameter: 80 mm) for solutions with viscosity from 0.1 to 100 Pa s. The chosen gap was 1 mm for all measurements. Steady shear profiles were examined at the temperature of 80 °C covering a shear rate range from 0.1 to 1000 s^{-1}. For oscillatory shear tests, the linear viscoelastic (LVE) region was firstly determined by performing a dynamic strain sweep for each solution with a fixed angular frequency of 6.3 rad/s, and then the dynamic frequency sweep measurements were tested within LVE region from 628 rad/s to 0.1 rad/s. The temperature control was done by Peltier effect within ± 0.01 °C of the preset value.

3. Results and discussion

3.1. Viscoelasticity of poly(AN-co-IA)/[BMIM]Cl solutions at steady shearing mode

The steady shear profiles of poly(AN-co-IA)/[BMIM]Cl solutions were examined at 80 °C. As shown in Fig. 1. At lower concentrations (c < 0.5 wt.%), the apparent viscosity of the solutions kept constant extending nearly all the

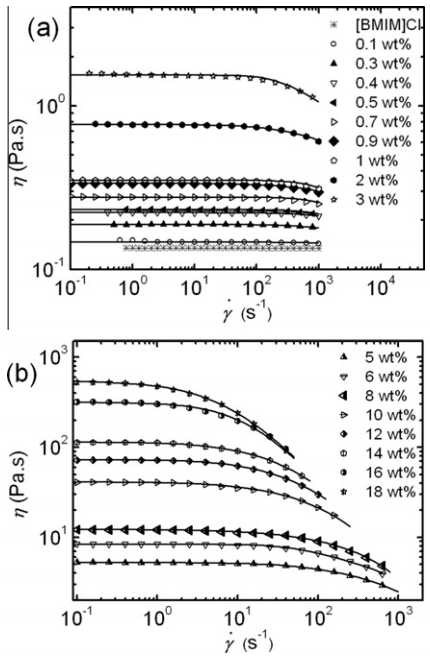

Fig. 1. The steady shear profiles of poly(AN-co-IA)/[BMIM]Cl solutions at 80 °C, (a) 0.1–3 wt.%, (b) 5–18 wt.%. Solid lines are the fitting results according to the Carreau model.