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Rheological Behavior of Poly(m-phenyleneisophthalamide) in Ionic Liquid

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Summary

The rheological behavior of poly(m-phenyleneisophthalamide) (PMIA) in 1-n-butyl-3-methylimidazolium chloride ([Bmim]Cl, ionic liquid) has been investigated. The polymer in the concentration range of 2-20wt.% investigated exhibits very different behavior between [Bmim]Cl and DMAc/LiCl solvent. Unlike in DMAc/LiCl solvent, PMIA/[Bmim]Cl solution exhibits maxima in apparent viscosity-concentration plots in the range studied. The complex viscosity-frequency behavior of the PMIA/[Bmim]Cl solutions is similar to that of steady-state rheological behavior. The different rheological behavior shows the interaction between macromolecule and IL which is leading to the supermolecular aggregates in PMIA/[Bmim]Cl solution.

Introduction

Ionic liquids are salts that are usually liquids at room temperature. They are composed of a bulky organic cation such as imidazolium or pyridinium cation and a smaller inorganic ion such as Cl^-, PF_6^- or BF_4^-, they can be customized like organic solvents. However, ionic liquids are considered “green” because, unlike the volatile organic compounds(VOCs) they reply many of these compounds have negligible vapor pressure and can be recycled and reused repeatedly. Ionic liquids have emerged as unique solvents for a variety of applications, including liquid-liquid extraction, electrochemistry, ionic liquid crystals, and biphasic catalysis etc.[1-4] Recent researches have focused on ionic liquids which were used as solvent for polymers (such as cellulous)[5] and other investigators have reported some associated investigations on a series of polymer-ionic liquid composites.[6]

Owing to its good heat resistance including great electrical insulation properties at high temperature, PMIA has become technologically significant during the past decade. However, PMIA is difficult to process because of infusibility and poor solubility in organic solvents such as dimethylformamide(DMF) and dimethylacetamide (DMAc). lyophilic salts are used to increase the solvent power for these solvents which leads to interchain forces being stronger, inherent macromolecular rigidity or semicrystallinity. Papers about rheological behaviors of PMIA in the open literature appeared limited. Gan[7] and Klenin[8] discussed the solution properties of PMIA in DMAc. The latter authors[8] argued that there were association effects leading to supermolecular aggregates in these solutions. M.E.Hawley and B.C.Benicewicz studied the structure of various aromatic polyamide which dissolved in dimethylacetamide with different salt content. They concluded that the different salt content could change the degree of association between chains and, furthermore, the tendency of chains to form large bundles. Evidence was also found for coiling of multimolecular chains and a tendency to form large ordered multimacromolecular assemblies[9]. Daniel Harwood[10-11] and his co-workers described rheological properties of PMIA in dimethylacetamide(DMAc) /LiCl, where PMIA behaves as a flexible polymer molecule in DMAc/LiCl and PMIA was self-associated when dissolved in pure DMAc, however PMIA dissociated in DMAc/LiCl solvent system. The result of light scattering of PMIA in DMAc/LiCl solution shows distortion of the PMIA network, probably due to polymer-salt interaction. PMIA chains are prone to interchain aggregation with the tendency for association apparently increasing with the ionic strength of the solvent[12-13]. Therefore, we were interested in examining whether ionic liquids(IL) would dissolve PMIA and allow flexibility and control in the processing methodology with increased solution efficiency and reduction or elimination of undesirable solvents. The aim of the present paper is to choose a kind of IL, 1-n-butyl-3-methylimidazolium chloride ([Bmim]Cl) and to present a set of rheological data for the PMIA system. Particular attention is given to the concentrated solution properties of PMIA in [Bmim]Cl both in steady-state shear flow experiments and oscillatory shear flow experiments. The influence of the solvent on rheological behavior of PMIA solution is discussed, and possible polymer-IL interaction leading the supermolecular aggregates in PMIA/[Bmim]Cl solution is also considered.

Experimental

PMIA(Mw≈140,000g mol^{-1}), DMAc and LiCl were provided from DuPont China Holding Co.,Ltd, the Shanghai Chemical Company and J&K Chemical Ltd respectively. 1-n-butyl-3-methylimidazolium chloride [Bmim]Cl were synthesized and purified using the method by Elaiwi. et al [14]. The schematic representation of PMIA and [Bmim]Cl shown in Figure1. The dissolution experiments were carried out in a glass vial at 100-110°C without agitation. A series of PMIA/[Bmim]Cl solutions with polymer concentration from 2-20wt.% were prepared. Rheological behavior of PMIA/[Bmim]Cl solution were examined using the rotational controlled stress rheometer RS150L(Germany, HAAKE). Cone (25mm diameter and cone angle=1°) is

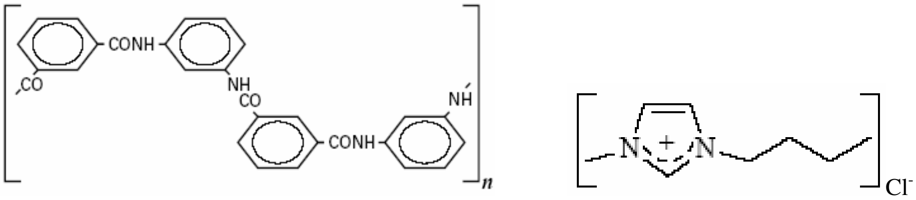

Figure 1. Schematic representation of Poly(m-phenyleneisophthalamide) (PMIA) and 1-n-butyl-3-methylimidazolium chloride [Bmim]Cl

used and dynamic frequency scanning was performed from 0.1 to 250 radian/s and the measurements were carried out at 50°C-120°C.

Results and discussion

Figure 2 shows the rheological behavior of PMIA in DMAc/LiCl. In the shear rate range PMIA/DMAc/LiCl solution exhibits shear thinning fluid behavior, which is well-known for aramide solutions. And Figure 3 shows the apparent viscosity of a series of concentration of PMIA at different shear rate. As shown in Figure 3, apparent viscosity generally increases with increasing PMIA concentration and is independent of shear rate over a wide range of shear rates. The apparent viscosity-concentration behavior of PMIA in DMAc/LiCl solutions is similar to that reported by earlier investigators[10,11], while the rheological behaviors of PMIA in [BmimCl] is different from that in DMAc/LiCl. The rheological properties of PMIA in [Bmim]Cl is presented in Figure 4. In the concentration range less than 12wt.% the rheological behavior of PMIA solution is close to Newtonian flow, apparent viscosity increases with the increase in concentration of PMIA, when it comes to an critical concentration(14wt.%), the solution exhibits shear thinning fluid behavior. Apparent viscosity drops quickly with increasing shear rate, and the trend becomes distinct with the increasing concentration. During the low shear rate, the apparent viscosity of the solutions increases with increasing concentration. In the range of high shear rate, apparent viscosity of the concentrated solutions drop greatly, some concentrated curves(>14wt.%) fall below the apparent viscosity of the low concentration solution(<12wt.%). The most obvious curve is the apparent viscosity of 20wt.% PMIA solution which fall even below the apparent viscosity of the 2wt.% PMIA solution (shear rate>473.8 s^{-1}). The relationship between PMIA concentration and apparent

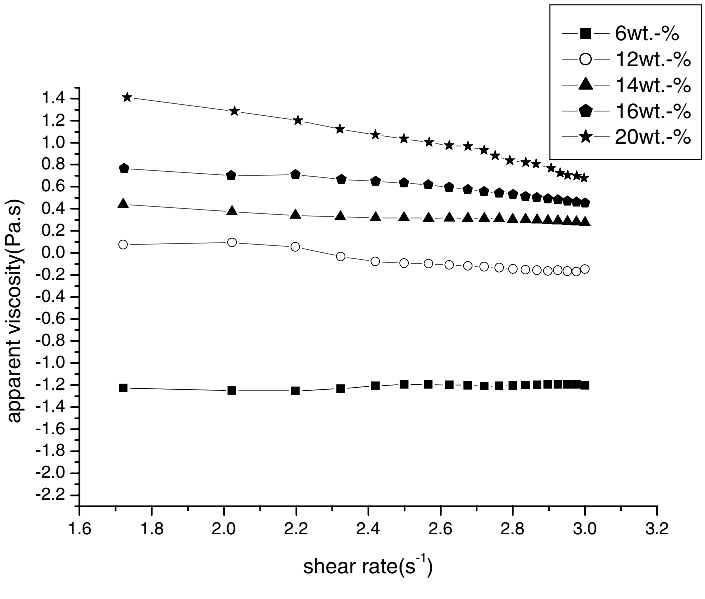

Figure 2. Relationship between apparent viscosity and shear rate for PMIA in DMAc/LiCl with various PMIA concentrations (80°C)

viscosity in [Bmim]Cl is presented in Figure5. As shown in Figure5, at low shear rate (about 52.7s^{-1}), apparent viscosity increases with the increasing concentration of PMIA. However, when the shear rate comes to 263.2s^{-1}, the apparent viscosity meets a peak value, after that apparent viscosity decreases with the increasing concentration. With the increasing of shear rate, the trend becomes distinct.

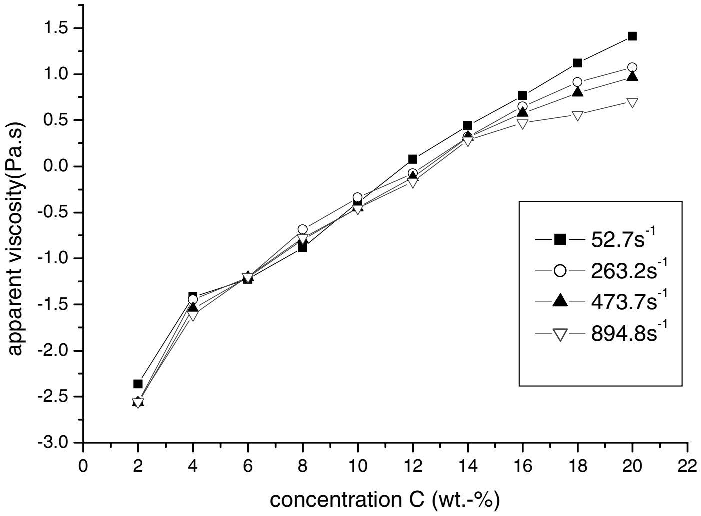

Figure 3. Relationship between apparent viscosity and concentration for PMIA in DMAc/LiCl solutions at different shear rate (80°C)

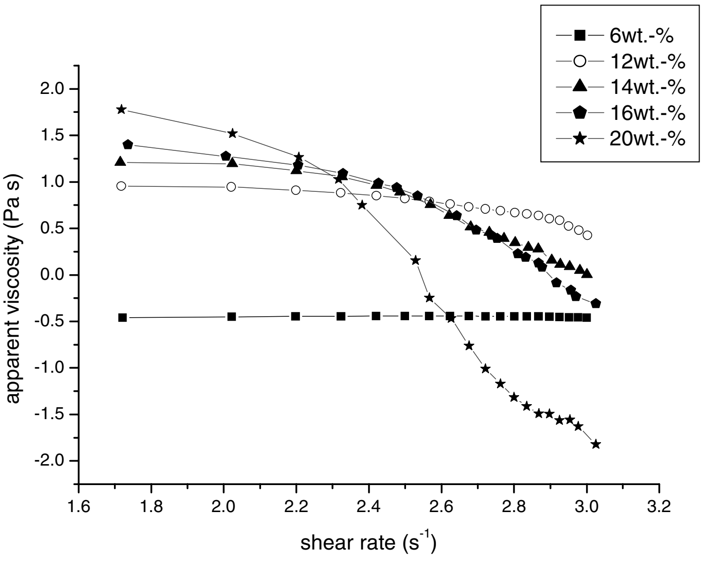

Figure 4. Relationship between apparent viscosity and shear rate for PMIA in [Bmim]Cl with various PMIA concentrations (80°C)

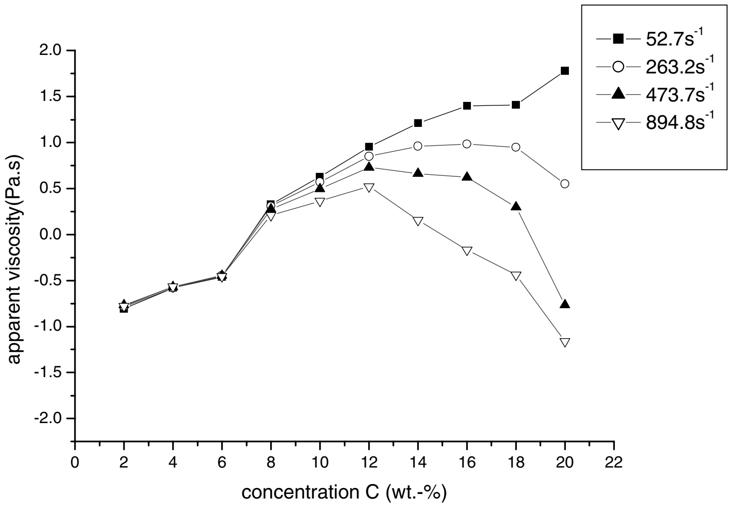

Figure 5. Relationship between apparent viscosity and concentration for PMIA in [Bmim]Cl solutions at different shear rate (80°C)

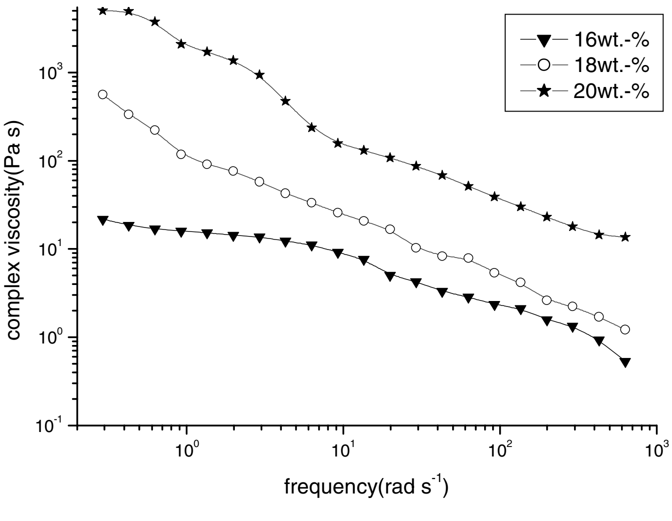

Figure 6. Relationship between complex viscosity and frequency for PMIA in DMAc/LiCl solutions with various PMIA concentrations (80°C)

Complex viscosity curves of PMIA /DMAc/LiCl solution at various concentration is shown in Figure 6. As shown in Figure 6, complex viscosity increases with the increasing PMIA concentration and is independent of frequency over a frequency range. The complex rheological properties of PMIA in [Bmim]Cl are presented in Figure 7. At low frequency, the complex viscosity of the solutions increases with increasing concentration. When the frequency comes to 66.36 rad · s^{-1}, complex viscosity of the 20wt.% PMIA solution falls below the complex viscosity of the 18wt.% PMIA solution. Then 20wt.% PMIA complex viscosity curve drops greatly

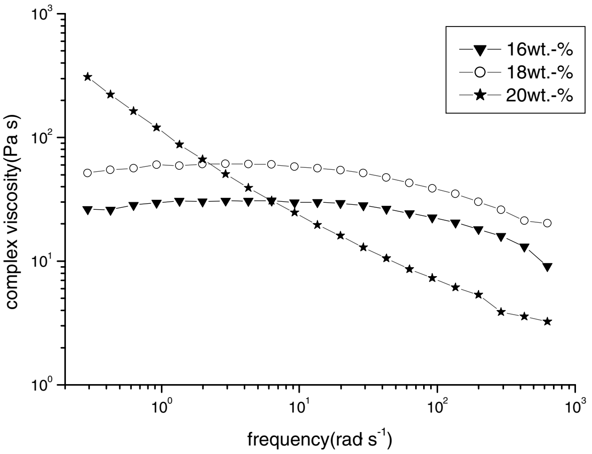

Figure 7. Relationship between complex viscosity and frequency for PMIA in [Bmim]Cl solutions with various PMIA concentrations(80°C)

even below that of the 16wt.% PMIA solution. The complex viscosity-frequency behavior of the PMIA in [Bmim]Cl solutions is similar to that steady-state rheological behavior discussed above.

The rheological behavior of the PMIA in DMAc/3%LiCl is seen as a flexible polymer molecule, while PMIA shows different rheological behavior in [Bmim]Cl, which exhibits maxima in apparent viscosity-concentration plots in the range studied. The behavior is very different from that observed in DMAc/3%LiCl. Based on this phenomenon, rheology shows that PMIA in [Bmim]Cl roughly is parallel to the phase behavior of rodlike polymer solutions[15-17](such as poly(*p*-phenylene terephthalamide)(PPTA, i.e., Kevlar) in sulfuric acid or poly-(benzobisoxazole) (PBO) in methanesulfonic acid) used for solution spinning of high-performance fibers from nematic liquid crystals[18-20]. The distinguishing feature is that PMIA in [Bmim]Cl self-assemble into extremely long strandlike structures and this structure is the basic component of the liquid crystalline phase. The potential reason is extending the ionic strength of the solvent. The solvent power of these solvents can be increased by addition of lyophilic salts. In has been shown in [9] that PMIA preferentially absorbs lithium chloride from solutions in DMF and DMAc. Nonderivitizing solvents for PMIA effect dissolution by disrupting and breaking the intramolecular network. For DMAc/LiCl solvents, complexation of lithium ions by DMAc mobilizes chloride ions which interact with the PMIA amidocyanogen groups. In a typical 3wt.% LiCl/DMAc solution, free chloride ion concentration is about 2.01 mol %. In contrast, [Bmim]Cl has a chloride concentration almost 10 times as high, (approximatedly 20 mol %)[5]. In all these cases, the chloride ions are nonhydrated. We speculate that the high chloride concentration and activity in [Bmim]Cl is highly effective in breaking the extensive PMIA network present. The chloride ions which are strong hydrogen bond acceptors associate with the PMIA amidocyanogen groups, and these association effects leading to supermolecular aggregates in PMIA/[Bmim]Cl solution. 1-butyl-3-methylimidazolium cations which embarrass the PMIA chain conformation make PMIA behavior change from a wormlike chain model to the rodlike chain model[21-23].

Conclusions

In this work, the rheological properties of poly(1,3-phenyleneisophthalamide) have been investigated. The result shows a rich, highly complex behavior in [Bmim]Cl, qualitatively very different from that in DMAc/LiCl solvents. The rheological behavior of poly(1,3-phenyleneisophthalamide) shows its chain stiffness increased in [Bmim]Cl. That amazing rheological behavior could originate from factors such as polymer-IL interaction leading the supermolecular aggregates in PMIA/[Bmim]Cl solution.

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