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Free Radical Polymerization of Acrylonitrile in Green Ionic Liquids

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Summary: Free radical polymerization of acrylonitrile (AN) in ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]), 2,2'-azobisisobutyronitrile (AIBN) as initiator was investigated. Early investigations on polymerizations using ionic liquids indicate that they serve as especially good solvents to achieve high molecular weight polymers. Free radical polymerizations result in higher molecular weight polymers, for ionic liquids have low chain transfer constants and act to stabilize the active radical during the process of polymerization. The thermal stability of polymers synthesized in ionic liquids have be improved obviously than that in traditional solvents.

Keywords: acrylonitrile; ionic liquids; radical polymerization; structure; thermal properties

Introduction

Ionic liquids are salts that are liquids at room temperature. Usually composing of a bulky organic cation such as imidazolium or pyridinium cation and a smaller inorganic ion such as PF_6^- or BF_4^-, they can be customized like organic solvents. However, ionic liquids are consider "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. Moreover, these liquids have interesting properties that may aid industrial synthesis, such as liquid ranges on the order of 300 ℃ and good thermal stability.

Most of Free radical polymerizations are typically operated in volatile organic solvents, which have been blamed for the increasing pollution. The use of room temperature ionic liquids, particularly 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF_6] and 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF_4], as solvents for clean polymerization and

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catalytic processes, particularly those applicable to clean technology, is becoming widely recognized and accepted[1-4]. Many considerable achievements have been received in the field of free-radical polymerzation, including traditional free-radical polymerization,[5,6] nitroxide-mediated stable free-radical polymerization,[7-10] atom transfer radical polymerization (ATRP),[11-16] reverse ATRP,[17-19] and reversible addition-fragmentation chain transfer.[20-23] The excellent room temperature ionic liquid, [bmim][PF_6] as the solvent for the living radical polymerization of methyl methacrylate and acrylates in the presence of a copper(I)/amine catalytic system,[24,25] has been reported.

In this research, we study free-radical polymerization of AN in room temperature ionic liquids, which promises the feasibility that ionic liquids could be used as a green solvent in free radical polymerization. A series of measurements were adopted to analysis effects of ionic liquids and reaction condition on molecule weight, molecular weight distributions and thermal stability.

Experimental Section

Materials

AN (99%) was purchased from Acros Organics and distilled to remove inhibitors by reducing pressure, AIBN (99%) was recrystallized from methanol and dried under vacuum. [bmim][BF_4] were synthesized and purified according to the literature in our lab.[26] Dimethyl formamide (DMF) and methanol were purchased from Acros Organics and used without further purification.

Polymerization

The typical experimental procedure is described subsequently. All polymerizations were carried out under nitrogen gas in order to ensure that systems were oxygen free. The desired amounts of initator (AIBN) and solvent ([bmim][BF_4]) were added into a round-bottom flask with a magnetic stir bar. Then a predetermined quantity of monomer(AN) was poured into the reactor, the system was purged with nitrogen gas for one hour to displace any surplus oxygen. The flask was placed into a preheated water bath and the polymerization was carried out for 1 hour.

PAN samples were dissolved in DMF solvent and formed 2% solution, which were placed over 24hours. As ionic liquids could not dissolve in DMF, the solution divided to two layers and upper layer were poured away. The left solution was taken shapes of film, then put into pure water about 24hours. Membranes were taken out and dried.

Instrumentation

Gel permeation chromatography(GPC) was used to measure molecular weights and molecular weight distributions, M_w/M_n of PAN samples with respect to polyacrylnitrile (PAN) standards . The GPC experiments with flow rate 1ml/min were carried out at 50℃ in DMF using Series 200 model. Sample concentrations were 1% reaction solution in 99% DMF and measured with a refractive index detector.

Solid-state NMR spectrum of polymers by CP/MAS were recorded on a Bruker ARX-400 spectrometer at room temperature. Fourier transform infrared spectroscopic (FT-IR) analysis were performed on NEXUS-670 model(American Nicolet) FT-IR spectrometer with KBr discs.

Thermal stability and glass transition temperature(Tg) measurements were operated by DSC and TGA. DSC machine was Mettler-Toledo model DSC822 and heating rate is 10℃/min and 20℃ /min. TG2050 machine from American TA was used to determine the rate of losing weight under nitrogen gas with heating rate 10℃/min, the range of temperature is from room temperature to 500℃.

Results and Discussion

Polymers Purification

PAN samples were formed in both DMF and ionic liquids. Formed polymers had the same physical appearance regardless of the solvent in which they were synthesized. The structure of PAN formed in [bmim][BF_4] was analyzed with infrared spectrum instrument that is the same as sample formed in DMF. Figure 1 shows that there is an obvious absorption peak at 2242cm^{-1}, which is the character absorption peak of -C≡N. This indicates that the structure of PAN in formed in [bmim][BF_4] has combined with the common PAN. However, there exists an obvious difference between the samples A and B. The sample A containing ionic liquids have shorter absorption peak than that B. This could be due to two reasons. Firstly, the polarity of ionic liquids prevents stretching vibration of molecular bonds. As stated earlier, the ionic liquids are highly polar liquids [27,28], which affects the vibration of bonds. Alternatively, existence of ionic liquids in polymers makes better stereo-tacticity than that without ionic liquids, the DSC and TG analysis show the same result.

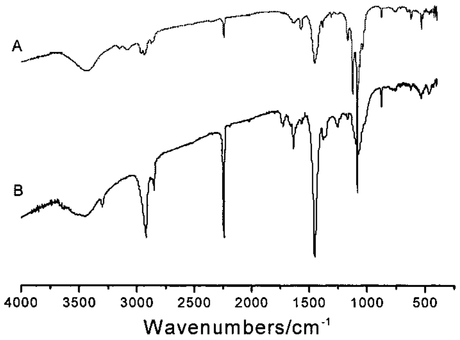

Figure 1. FT-IR spectrum of PAN polymerized in ionic liquids; reaction conditions: T=60℃, polymerization time is 60 minutes, 1 wt% initiator (AIBN), 25wt% AN; The sample A includes ionic liquids and that B does not have ionic liquids.

So polymers purification is crucial to product's viability of any solution polymerization process, for a polymer's thermal and mechanical properties are affected by other elements. As reported earlier, solvents traditionally used are volatile and promised to remove by heating or under vacuum, which is easier than ionic liquids because ionic liquids are nonvolatile. However, the existence of ionic liquids could improve some special properties of polymers.

Molecular Weight and Molecular Weight Distributions

The molecular weights of polymer samples were determined as a function of time for each solvent used. The GPC showed that the number-average molecular weight of the polymer was slightly higher than conventional PAN, but the molecular weight distribution is low from Table 1. Polymerization of PAN is a fast reaction when compared to polymerization in popular solvents. The increase in rate is manifested by a widen of the molecular weight distributions to 3.76. Two main reasons could attribute to this result.[29,30] Firstly, the rate of bimolecular termination by either disproportionation or combination is suppressed which might be due in part to the large increase in viscosity of the action medium. In this case termination would be dominated by chain transfer to either solvent or monomer. The molecular weights observed are consistent with this explanation. Alternatively, the rate constant of propagation, k_P, may be increased in the ionic liquid due to local environment effects. Tadeusz[31] and Carmichael[32] reported the similar result and they also considered that either instantaneous concentration of radicals or the propagation-rate constant is higher than in organic media.

Table 1. Final molecular mass and conversion data for PAN synthesized in this work.

Reaction	Temperature/°C	Time /min	Conversion /%	*Mn*	PDI
1	50	60	90.5	46450	3.65
2	55	60	91.5	44270	3.76
3	60	60	92.2	40760	2.55
4	65	60	93.4	34450	2.32
5	70	60	94.3	32600	3.72

The microstructures of polymer samples were determined by CP/MAS measurements. CP/MAS spectra clearly demonstrates that the polymers were provided with characteristic chemical shifts δ, which could be attributed respectively to $-C\equiv N$ (δ =169.914ppm), -CH- (δ =121.510) and $-CH_2-$ (δ=29.497). Fortunately, it was reported by May[29] that the stereochemistry of the PMMA produced in [bmim][BF_4] is almost identical to that for PMMA produced by free radical polymerization in conventional solvents.

Thermal Stability Measurements

Thermal stability is one of important characters for process. The glass transition is important in design of polymeric materials because it marks the transition between hard, glassy properties at lower temperature and rubbery behavior at higher temperatures. It shows by Figure 2 and 3 the polymers with ionic liquids have better thermal stability than those without ionic liquids. Figure 2 shows the T_g of PAN 1 contained ionic liquid dropped significantly, with little change without ionic liquid. Further, the rate of sample 1 losing weight is lower than others without ionic liquid as shown in table 1, which demonstrates ionic liquid could strength thermal stability of polymers. Generally, molecule chains of polar polymers form many physical crosslinked points since polar groups or hydrogen bonds interact strongly. When ionic liquid enter molecular chains, the polar groups of ionic liquid produce effect with that of molecules each other, so which destroy polymers' crosslinked points achieve high sub-chain activity. The procedure could be simulated by following model.

Table 2. The data of rate of PAN TGA.

Sample	1#	2#	3#	4#
Rate of losing weight	22%	28%	33%	43%

1#: PAN with ionic liquids polymerized in [bmim]BF_4, monomer concentration 25%(w/w).
2#: PAN polymerized in [bmim]BF_4, monomer concentration 25%(w/w).
3#: PAN polymerized in [bmim]BF_4, monomer conce ntration 40%(w /w).
4#: PAN polymerized in DMF monomer concentration 25%(w/w).

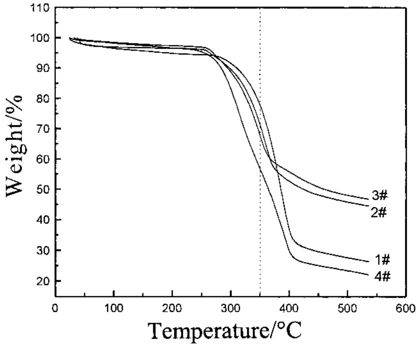

Figure 2. TGA curves of polymers; reaction condition was the same as demonstrated in Table 1.

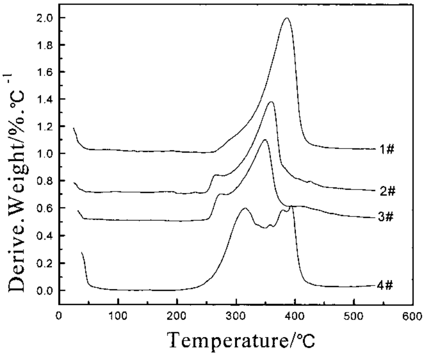

Figure 3. DSC resualts of polymers; reaction condition was the same as demonstrated in Table 1.

Besides, Mark[33] and Cadogan[34] considered that ionic liquids containing imidazolium cations are similar to some conventional plasticizers, containing an aromatic core and pendant alkyl groups. Ionic liquids perform many characteristics similar to plasticizers, such as reproducibility, and wide thermal range being some of the greatest advantage over conventional plasticizing agents. One of the most important characteristics of plasticizer compounds is low volatility so that the polymer can remain flexible over a long lifetime without becoming brittle and failing. Ionic liquids are particularly intriguing in this aspect, as they typically have no detectable vapor pressure, which could enable the formation of flexible materials with significantly extended lifetimes.These results indicate that ionic liquids as plasticizers could strengthen thermal stability of polymers.

Conclusion

PAN was synthesized in [bmim][BF_4] using AIBN as initiator, a green alternative to traditional volatile solvents. The effects of reaction parameters on molecular weight and molecular weight distributions of the polymer formed in room temperature ionic liquid are the same as for that observ in traditional solvents.

The polymerization products were characterized by GPC, NMR, FT-IR, DSC, and TGA. The FT-IR analysis shows that the structure of production is the same with the common PAN, however polarity of ionic liquid confines the stretching vibration of molecular bonds. Thermal stability of PAN with ionic liquids is improved obviously because ionic liquids break polymers' crosslinked points, also ionic liquids containing imidazolium cations are similar to some conventional plasticizers.

This investigation of polymerization in ionic liquids sheds light on the potential to develop environmentally-friendly processes and gain an understanding of the reaction behavior to make materials with reduced emission that also have technically superior properties.

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