ABSTRACT

We report here the extraction of polymers by essentially nonvolatile ionic liquids. The particular molten salts used in this study are 1-ethyl-3-methylimidazolium chloride/aluminum chloride mixtures (EMIC/AlCl₃). This salt is conveniently handled as a liquid at room temperature, and it has negligible vapor pressure for most compositions up to several hundred degrees. This ionic liquid is easy to prepare, and its chemical and physical properties are well described. The compositions of the EMIC/AlCl₃ were basic (EMIC>AlCl₃), neutral (EMIC=AlCl₃), acidic (EMIC<AlCl₃), and in some cases superacidic (acidic EMIC/AlCl₃, HCl added). The polymers tested were nylon 6, plioflex, SMR-GP, high density polyethylene, low density polyethylene, polyvinyl chloride, polystyrene, black rubber, and butyl rubber. Black rubber and polystyrene were selected for further study.

INTRODUCTION

Molten salts with melting temperatures near or below room temperature (now more commonly called “ionic liquids”) are finding use as solvents for organic and inorganic compounds (1). The class of ionic liquid dialkylimidazolium chloroaluminates has been particularly well studied, because of the wide range of Lewis acidity/basicity accessible in them. The most common member of this class is composed of 1-ethyl-3-methylimidazolium chloride (EMIC) and aluminum chloride (AlCl₃), where the acidity or basicity may be selected by choice of the EMIC:AlCl₃ ratio (2).

The acid-base behavior of this ionic liquid is important in the work reported here, so a short explanation of Lewis and Brønsted acidity is appropriate. The EMIC/AlCl₃ mixtures are not binary salts in the usual sense, because there is a chemical reaction between the chloride in EMIC and AlCl₃. If the chloride is in excess (AlCl₃:EMIC ratio < 1, or mole fraction AlCl₃ (N) < 0.5) then the mixture is Lewis basic. Similarly, if the AlCl₃ is in excess (AlCl₃:EMIC ratio > 1, or mole fraction AlCl₃ (N > 0.5) then the mixture is Lewis acidic. In the basic melts the base is largely uncomplexed chloride ion, but in the acidic melts the Lewis acid is the complex anion Al₂Cl₇⁻. The overall acid-base behavior is best summarized by the equilibrium

$$2\text{AlCl}_4^- = \text{Cl}^- + \text{Al}_2\text{Cl}_7^-,$$

which has an equilibrium constant of about $10^{16}$ (3). This means that the Lewis acidity or basicity may be varied over many orders of magnitude. If a strong Brønsted acid, such as HCl, is added to an acidic chloroaluminate melt, then the mixture becomes a superacid (4, 5). Since the concentration of Brønsted acid may be adjusted easily, the
superacidity can be controlled. This clearly would have implications where reaction chemistry involves a protonation step.

The ability for low temperature chloroaluminate ionic liquids to dissolve both organic and inorganic compounds, sometimes in very high amounts, was observed from the very beginning (2, 6, 7). The added feature of an easily and precisely adjustable Lewis or Brønsted acidity make chloroaluminate ionic liquids attractive as reaction solvents. Such experiments were reported in the higher temperature NaCl/AlCl₃ molten salts, then later in EMIC/AlCl₃, where Lewis acid catalyzed Friedel-Crafts reactions proceed very cleanly (8-10). There are now many examples of catalyzed organic reactions that may be run in room temperature ionic liquids.

Green Chemistry is currently a high interest area in Europe and the US. The scope of Green Chemistry was stated by the US Environmental Protection Agency to be, "...the use of chemistry for pollution prevention. More specifically, green chemistry is the design of chemical products and processes that are more environmentally benign. Green chemistry encompasses all aspects and types of chemical processes that reduce negative impacts to human health and the environment relative to the current state of the art.” (14) Low temperature ionic liquids, including non-chloroaluminate ones, fit well as alternatives to volatile organic solvents in process chemistry. Perhaps the strongest proponent of the use of ionic liquids for process chemistry is Kenneth Seddon, who reviewed the field in 1998 (15). Also in 1998 are more generally available article appeared on the subject of ionic liquids and green chemistry (16).

Polymers have a history in the ionic liquids. In the room temperature N-(1-butyl)pyridinium chloride/AlCl₃ melt polypyrrole was synthesized via an electrochemical process (11). Poly(p-phenylene) was prepared by an entirely different process, but in a similar ionic liquid; N-hexadecylpyridinium chloride/AlCl₃ (12). Polyethylene was produced in the EMIC/AlCl₃ melt via Ziegler-Natta polymerization (13). Before Green Chemistry became popular, high temperature molten salts were proposed for use in processing of polymer-containing waste materials, including rubber tires. Larsen et al. used NaCl/AlCl₃, LiCl/KCl and ZnCl₂ molten salt mixtures to pyrolyze rubber from automobile tires (17, 18). Gasification of polymer containing wastes by pyrolysis in molten carbonates was also been reported by Yosim et al. (19, 20).

In this report we describe some experiments where polymers may be separated from more complex materials or devices (such as tires) at moderate temperatures using room temperature ionic liquids.

EXPERIMENTAL

Materials and Equipment

The EMIC/AlCl₃ ionic liquids were prepared according to a previously published method (2). Superacidic versions of the acidic EMIC/AlCl₃ were prepared by adding EMI HCl2 to an acidic EMIC/AlCl₃ mixture (21). The unvulcanized rubbers (Plioflex and SMR-GP) were donated by a commercial rubber source. The “black rubber” was from a bicycle tire tread or an auto tire tread. The “butyl rubber” was from a used dry-box glove. Low density polyethylene (LDPE), high density polyethylene (HDPE) were purchased from Aldrich. Polystyrene (PS) from a coffee cup was used in the screening.
test, and commercial PS from Aldrich (melt index 1.4, catalog number 9003-53-6) was used for the extraction and characterization experiments.

The melts were prepared in a dry box maintained at <10 ppm combined oxygen and water. All experiments where the melts were exposed to the atmosphere were done in the dry box, except the last step where the melt was added to water. Infrared spectra of KBr pellets of the extracted PS were obtained on a Nicolet Avatar 380 FTIR instrument. Thermal gravimetric analysis of the extracted PS was run on a TA Instruments STD 2960. Differential thermal analysis was done on a TA Instruments DSC 2910.

Screening Tests

Approximately 100 mg of polymer was placed in 4 mL of the desired melt composition in a 10 mm test tube. The samples were heated overnight at 90° C. The determination of solubility was made visually, and the tubes were photographed for the record. In all cases where dissolution occurred, there was also a color change to dark brown or black.

Extractions

The extraction and recovery was done on a larger scale than the screening tests. For example, 1.038 grams of polystyrene was placed in a 50.0 mL beaker and put in the glove box under an inert helium atmosphere. 10.0 mL of acidic (N=0.67) EMIC/AICI3 molten salt was then added to the polystyrene using a graduated cylinder. A stirring bar was then added to the melt, and the 50.0 mL beaker was placed on a stirrer/heatplate and stirred on a low setting and heated for 15 minutes on setting 1 (Approx. 40° C). All of the polystyrene easily dissolved. The 50.0 mL beaker containing the melt was removed from the glove box and placed in the hood. The polymer was extracted by adding the melt to a 500 mL beaker containing 100.0 mL of 0.1 M NaOH. The melt was added approximately 1.0 mL at a time until completion. The polymer precipitated out of solution. Any residual melt left over was washed from the 50.0 mL beaker with distilled water and added to the 500.0 mL beaker containing the NaOH. Once the extraction was complete, the sample was then vacuum filtered, then dried in a vacuum dessicator.

RESULTS AND DISCUSSION

Eight different polymeric materials were tested with four different molten salt compositions. The materials ranged from pure polymers (e.g. polyvinyl chloride) to complex mixtures of polymers and additives (e.g. black rubber). Figure 1 shows the result of a screening test of the eight materials with a basic EMIC/AICI3 melt. The results of that test and similar tests with three other melt compositions are summarized in Table I. The quantity N is the mole fraction of AlCl3 in the ionic liquid. It is clear, and not unexpected, that the acidic melt was most effective in dissolving the widest range of polymers. The superacidic composition, which is both a Bronsted and Lewis acid, appears to be less effective. However, in that experiment we heated the mixture at a lower temperature and for a shorter time in order to avoid losing HCl from the melt.
Table I. Solubility of Polymers in EMIC/AlCl₃ Molten Salts

| Polymer       | N = 0.33 | N = 0.50 | N = 0.67 | N = 0.67 superacidic |
|---------------|----------|----------|----------|----------------------|
| Nylon 6       | I        | I        | SL       | I                    |
| Plioflex SL   | SL       | SL       | S        | SL                   |
| SMR-GP SL     | SL       | SL       | S        | SL                   |
| HDPE I        | I        | I        | S        | SL                   |
| LDPE I        | I        | I        | S        | I                    |
| PVC SL        | SL       | SL       | S        | S                    |
| Black rubber  | S        | S        | S        | S                    |
| Butyl rubber  | S        | S        | S        | S                    |

S = soluble, I = insoluble, SL = slightly soluble

Larger scale extractions were done on polystyrene and black rubber. In these experiments the molten salt containing the dissolved (and perhaps reacted) polymer was added to an excess of basic water to separate the molten salt components and precipitate the polymer. The solid product was filtered and dried. In the case of polystyrene we found the solubility of the polymer to be between 20-25% by weight. The starting polymer was colorless, while the polymer recovered from the melt was dark brown. The melt turned dark brown upon dissolution of the PS, and became deeper in color as more of the polymer dissolved.

The dried extracted PS was characterized by infrared spectroscopy, thermal gravimetric analysis (TGA), and differential scanning calorimetry (DSC). Comparison of the infrared spectrum of the extracted PS in Figure 2 with unreacted PS, shows that most of the bands are unchanged, except the broad absorption centered at 3400 cm⁻¹. This could be due to moisture in the sample, or it could be due to functionalization of the polystyrene. TGA thermograms of unreacted polystyrene may be compared with the extracted PS in Figure 3 EMIC/AlCl₃ molten salt. The extracted PS is clearly more reactive, or much small molecular weight, or both. Since only a small fraction of the weight loss occurs below 100° C, the extracted polystyrene is not simply wet. Some substantial chemistry happened in the acidic molten salt. The differential scanning calorimetry results in Figures 4 and 5 reinforce the results of the TGA experiment. Degradation reaction products escaping from the sample pan caused the erratic response in the DSC thermogram.

The extraction of polymers from rubber tire treads was somewhat different. When the molten salt/rubber solution was added to water two fractions formed besides the aqueous one containing the melt components. A dense solid product settled to the bottom, and appeared to contain carbon particles (in the case of the auto tire) or carbon...
plus silica particles (bicycle tire). A phase less dense than water was separated by centrifugation and dried in vacuo. This upper phase was lightly colored material of rubbery consistency, similar to the unvulcanized Plioflex or SMR-GP. We have not completed the analysis of this complicated material, but it appears that the acidic melt devulcanized the polyisoprene in the rubber. The dense carbon and silica particles simply separated from the polymer by density differences.

CONCLUSIONS

Many polymers are soluble in the room temperature molten salt EMIC/AlCl₃, especially acidic compositions. For example, polystyrene and the polyisoprene in black rubber may be extracted and recovered. Some chemical transformations of the polymers occur.

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REFERENCES

1. Richard T. Carlin and John S. Wilkes, in Chemistry of Nonaqueous Solutions, A. Popov and G. Mamantov, Editors., VCH Publishers, New York (1994).
2. John S. Wilkes, Joseph A. Levisky, Robert A. Wilson and Charles L. Hussey, Inorg. Chem., 21, 1263 (1982).
3. Towner B. Scheffler, Charles L. Hussey, John S. Wilkes and Armand A Fannin, Jr., J. Electrochem. Soc., 133, 1389 (1986).
4. G. P. Smith, A. S. Dworkin, R. M. Pagni, and S. P. Zingg, J. Am. Chem. Soc., 111, 525 (1989).
5. G. P. Smith, A. S. Dworkin, R. M. Pagni, and S. P. Zingg, J. Am. Chem. Soc., 111, 5075 (1989).
6. F. H. Hurley and T. P. Wier, J. Electrochem. Soc., 98, 203 (1951).
7. F. H. Hurley and T. P. Wier, J. Electrochem. Soc., 98, 207 (1951).
8. G. Baddeley and R. Williamson, J. Chem. Soc., 4647 (1953).
9. Jeffrey Boon, Joseph A. Levisky, J. Lloyd Pflug and J. S. Wilkes, J. Org. Chem., 51, 480 (1986).
10. John S. Wilkes, in "Molten Salt Chemistry, An Introduction and Selected Applications," G. Mamantov and R. Marassi, eds., D. Reidel Publishing Co., Dordrecht, Holland, 1987, pp405-416.
11. P. G. Pickup and R. A. Osteryoung, J. Am. Chem. Soc., 106, 2294 (1984).
12. D. C. Trevedi, J. Chem. Soc., Chem. Commun., 544 (1989).
13. Richard T. Carlin and John S. Wilkes, J. Molecular Catalysis, 63, 125 (1990).
14. P. Anastas, US EPA Web site http://www.epa.gov/greenchemistry/
15. K. R. Seddon, Molten Salt Forum, 5-6 (Molten Salt Chemistry and Technology 5), 53-62 (1998).
16. M. Freemantle, Chem. Eng. News, 76, 32 (1998).
17. Carey Chambers, John W. Larsen, Walter Li, and Bob Wiesen, Ind. Eng. Chem. Process Des. Dev., 23, 648 (1984).
18. J. W. Larsen and B. Chang, Rubber Chem. Technol., 49, 1120 (1976)
19. R. L. Gay, K. M. Barclay, L. F. Grantham and S. J. Yosim, *Chemtech*, 11, 572-5 (1981).
20. R. L. Gay, K. M. Barclay, L. F. Grantham and S. J. Yosim, ACS Symp. Ser. (Therm. Convers. Solid Wastes Biomass), 130, 227 (1980)
21. R. T. Carlin, P. C. Trulove, and R. A. Osteryoung, *Electrochim. Acta*, 37, 2615 (1992)
Figure 1. Various polymer materials in basic N=0.666 EMIC/AICl$_3$ molten salt. A = Nylon 6, B = Plioflex, C = SMR-GP, D = high density polyethylene, E = low density polyethylene, F = polyvinyl chloride, G = Black rubber, H = Butyl rubber

Figure 2. Infrared spectrum of the product of extraction of polystyrene by N = 0.67 EMIC/AICl$_3$ molten salt

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Figure 3. Thermal gravimetric analysis of polystyrene. Upper curve is unreacted polystyrene. Lower curve is polystyrene extracted by N = 0.67 EMIC/AICl3 molten salt.

Figure 4. Differential scanning calorimetry of polystyrene extracted by N = 0.67 EMIC/AICl3 molten salt. Compare with Figure 5.
Figure 5. Differential scanning calorimetry of unreacted polystyrene. Compare with Figure 4.