Angewandte
Chemie

Ionic Liquids

Ionic Liquids as Moderators in Exothermic Polymerization Reactions**

R. Vijayaraghavan, M. Surianarayanan, and
*D. R. MacFarlane**

Explosions due to thermal runaway are one of the major safety issues faced by chemical industries.[1–3] A knowledge of the thermokinetics of exothermic reaction systems not only helps in mitigating disastrous events such as catastrophic fires and explosions but also provides the means for designing in-built safety systems. Thermal-hazard assessment basically relies on the identification of dangerous process situations, deviations, and thermal sensitivity of reaction mixtures and products. The conventional hazard assessment methods, namely, hazard and operability limits (HAZOP), failure mode evaluation analysis (FMEA), and fault tree analysis (FTA) will become more precise and effective if thermal stability of relevant chemicals and reaction mixtures are clearly defined.[4] Furthermore, the consequences of runaway reactions have not received much attention compared to the consequences of chemical release from storage and other installations. This is mostly due to an insufficient understanding of the complex behavior of thermal-runaway systems; for example, the consequence analysis (one of the conventional hazard assessment procedures) assumes that the runaway phenomenon is a physical explosion and the forecasted scenario has to be based on the material properties and design pressure of the process vessel. In the absence of information concerning the energy released during runaway reactions, it is indeed difficult to assume that all runaway reactions would lead only to physical explosions. Nevertheless this information is available for most chemical-process reaction systems and continuous efforts are being made to generate thermokinetic data. Inherently safer design approaches,[5] design of emergency relief systems (ERS),[6] and explosion suppression systems (ESS)[7] are a few of the latest methodologies in the chemical industry to deal with thermal runaway. While the concept of inherently safer design approaches can be successfully employed to most of the exothermic reaction systems, ERS and ESS contribute

---

[*] Prof. D. R. MacFarlane
School of Chemistry
Monash University
Clayton, Victoria 3800 (Australia)
Fax: (+61) 3-9905-4597
E-mail: d.macfarlane@sci.monash.edu.au

Dr. R. Vijayaraghavan,[+] Dr. M. Surianarayanan
Department of Chemical Engineering
Central Leather Research Institute
Adayar, Madras 600 020 (India)

[+] Present address: School of Chemistry
Monash University
Victoria 3800 (Australia)

[**] We thank ARC Special Research Centre for Green Chemistry, Monash University for the financial support.

DOI: 10.1002/ange.200460575

significantly to the cost. Furthermore, these systems have to be maintained to function properly and the chance of failure during an emergency is significant. Efforts to synthesize chemical agents that suppress or alter the course of exothermic activity have not proven to be entirely successful as they are system-specific, typically require large quantities, and can be unstable at the temperatures at which runaway occurs, hence contributing to the problem in the event of a catastrophe.[8]

In recent years, ionic liquids (ILs) have been extensively investigated for use as replacement solvents for clean synthesis in a variety of chemical reactions.[9–13] The major advantage of using these ionic liquids is their ability to dissolve a wide range of organic and ionic compounds to an appreciable extent. Their lack of volatility and their high thermal stability are also important features and thus they may prove effective in moderating highly exothermic reactions and hence impeding thermal runaway. For example, vinyl-polymerization reactions are in general highly exothermic in nature (heat of reaction 20 Kcal$\,$mol^{-1}).

The use of ionic liquids as solvents in polymerization reactions has recently been reported[14–17] for free-radical polymerization, transition-metal mediated living free-radical polymerization, charge-transfer, and cationic polymerization. The presence of [bmim][PF_6] (bmim is 1-butyl-3-methylimidazolium) ionic liquid as solvent increased the overall rate of methyl methacrylate[15] polymerization about tenfold compared to the same reaction in benzene. Other advantages of polymers synthesized in ionic liquids have been described in detail.[18] Moderation of the reaction by carrying out the polymerization in solution reduces the heat produced[19] but often the solvents are not stable at high temperatures, the subsequent decomposition and resultant pressure rise causes the system to runaway. Solvent-based systems also pose great challenges in design, scale-up, and their recovery for reuse. Incidents due to thermal runaway of such systems have been widely reported.[19–20] Thus in this case the intrinsic stability and low volatility of ionic liquids should overcome these issues.

There are a number of objectives in this study: the main objective is to assess the role of ionic liquids in moderating the thermal polymerization of styrene and acrylonitrile by using an accelerating-rate calorimeter (ARC). Another objective is to explore the possibility of replacing the traditional molecular solvents with an ionic liquid and study their effect in lowering the pressure in the system. Herein we report the thermal polymerization of styrene and acrylonitrile in an ARC with and without the presence of an ionic liquid to establish the role of the ionic liquid as a heat sink. The ionic liquid chosen for this study is *N*-butyl, *N*-methyl pyrrolidinium bis(trifluoromethanesulfonyl)amide, abbreviated as [$P_{1,4}$][tf_2N]. Thermal stabilities of hydrophobic ionic liquids with different anions including bis(trifluoromethanesulfonyl) amide have been studied.[21–23] The study reveals that anions such as bis(trifluoromethanesulfonyl) amide are stable for short periods of time up to 394 °C. The onset of thermal decomposition temperatures are similar for different cations but appear to decrease as the anion hydrophilicity increases. The effect of anion fluorination on thermal stability also reveals the enhanced stability for the [tf_2N]$^-$ ion.[24] Hence this anion is an ideal choice as the component of an ionic liquid for use at high temperatures.

The rate of self-heating versus temperature curve for the thermal polymerization of styrene for neat styrene and for styrene mixed with the IL is shown in Figure 1. The case of neat styrene exhibits several exotherms that correspond to different stages of the reaction, including high-temperature processes around 400 °C. The curves show that the addition of an IL drastically reduces the rate of self-heating at all temperatures compared to the neat monomer. The onset of exothermic activity in the presence of the IL has been postponed to 95 °C. In the case of neat styrene, multiple exotherms are observed with a maximum heat rate of 0.45 °C$\,$min^{-1} at 400 °C, while in presence of IL no exothermic activity is recorded beyond 200 °C and the maximum heat rates are less than 0.03 °C$\,$min^{-1} at 100 °C. Since the IL has very low vapor pressure even at higher temperatures compared to neat styrene, the reaction carried out in IL would not be expected to have a significant rate of decomposition in the vapor phase, hence the absence of multiple exotherms. The vapor-phase decompositions themselves can cause the system to runaway.[25] Hence the use of ionic liquids in this reaction completely avoids one of the significant origins of thermal runaway.

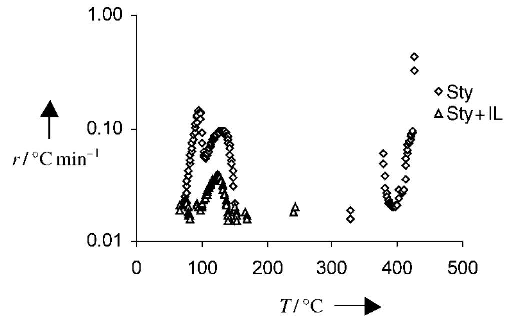

Figure 1. A comparison of ARC rates of self-heating of styrene (Sty) and styrene in IL (Styil); *r* is the heating rate.

At the end of the experiments the bomb was cut open and it was found that there was no trace of monomer. Characterization of the decomposed products is underway.

Similarly the plot of pressure versus temperature (Figure 2) also shows a decrease in the rise in pressure when the reaction is carried out in IL. The absence of exothermic activity and pressure rise beyond 300 °C may be due to the stabilizing effect of the ionic liquid. The higher thermal stability of the IL is thus responsible for the intrinsic safety of the process. The IL present in the system absorbs the heat from the reaction mixture, and because of its high thermal stability it appears to delay or quench polymer decomposition reactions thus further protecting the reaction from runaway. The time available to take safety measures is also significantly increased when IL is present in the system. This is evidenced in the plot of time versus temperature (Figure 3). This plot recorded during an applied constant heating rate shows how the system enters thermal runaway

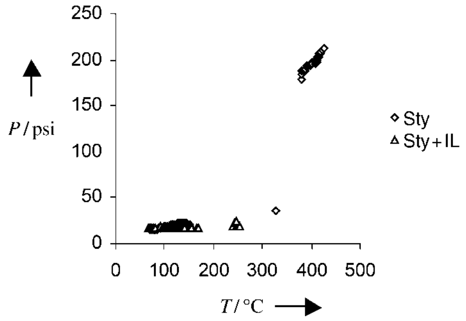

Figure 2. Plots of the temperature versus pressure for the polymerization of styrene and styrene in IL.

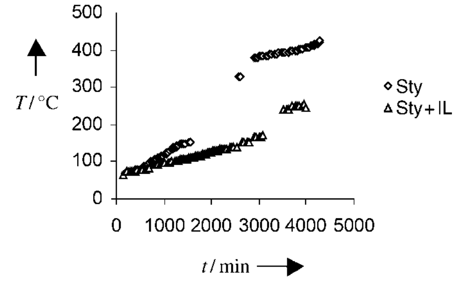

Figure 3. Profiles of time versus temperature for styrene polymerization

and how rapidly the temperature rises during this situation. In the neat system, the temperature rapidly rises from 200 °C to >400 °C with a concomitant rise in pressure that has potentially catastrophic results. On the other hand the IL-based system never exhibits a rapid rise in temperature or pressure and appears to be quite stable up to 400 °C.

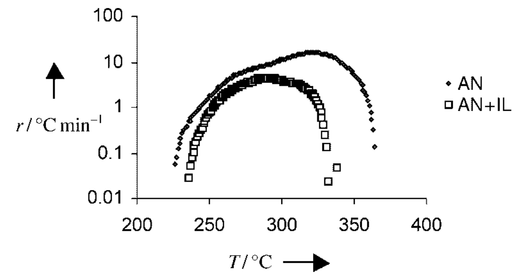

Figure 4. Self-heating profiles for AN polymerization.

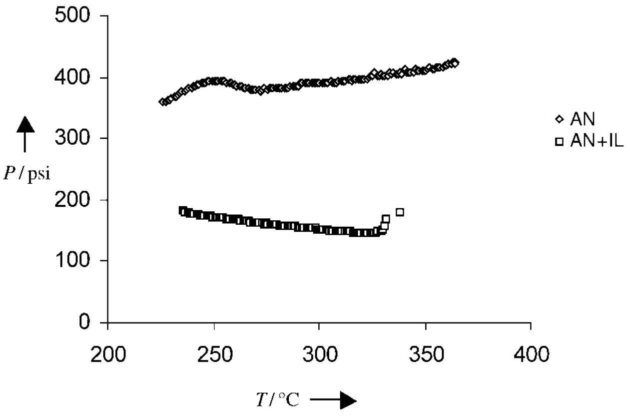

Figure 5. Profiles of temperature versus pressure for AN polymerization.

The plot of the rate of self-heating (Figure 4) for the thermal polymerization of acrylonitrile (AN) also clearly indicates a drastic reduction in the maximum rate of self-heating (10 °C min^{-1} for neat AN and 1 °C min^{-1} for AN in IL) with postponement of the onset of exothermic activity from 226 °C to 235 °C. The adiabatic temperature rise for AN is 138 °C, whereas in the presence of IL it is reduced to 102 °C. This result shows that the IL acts as a heat sink also in this polymerization. The plot of the pressure versus temperature (Figure 5) for pure AN polymerization shows a small peak around around 245 °C followed by a steady increase above 270 °C. This trend is indicative that thermal polymerization proceeds initially in the vapor phase and later the polyacrylonitrile (PAN) thus produced decomposes. In contrast, the pressure profile of AN with IL shows a gradual decrease in pressure, which is indicative of a slow polymerization process that proceeds in the solution phase because the consumption of the monomer reduces the content of volatile species in the mixture. Furthermore, the absence of exothermic activity and an insignificant pressure rise after 340 °C may indicate a quenching of the decomposition reaction, which would otherwise take place.

The profile of time versus temperature (Figure 6) also indicates that the IL-incorporated system provides considerably more time available to take emergency measures in the event of runaway compared to neat AN polymerization. In fact the neat AN system can reach 350 °C from 250 °C in a very short period of time (a few minutes) compared to the IL-based system.

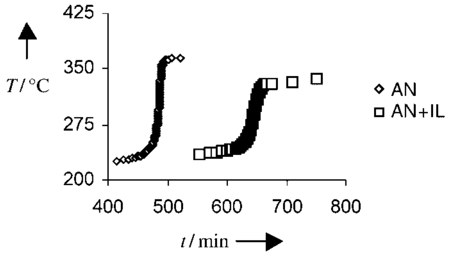

Figure 6. Time versus temperature plots for AN polymerization.

Thus, these studies of the thermal polymerization of styrene and acrylonitrile in ionic liquids provide intrinsically safer processes, especially by considerably reducing the exothermic activity. The studies here show that ILs have the potential to not only reduce the exothermic self-heating but also decrease the exothermic product decomposition, which is a major source of release of toxic gasses. The role of ionic liquids in changing the exothermic decomposition pathways and their mechanistic aspects is the subject of further study. The IL-based polymerization process can be implemented in a closed cycle with respect to the IL by quenching the reaction in methanol, which precipitates the polymer and allows the recovery of the IL from the methanol solution by evaporation of the methanol.

Experimental Section

Analytical grades of styrene and acrylonitrile were used. Styrene was distilled under reduced pressure prior to use. The synthesis of $[P_{1,4}][tf_2N]$ IL followed the procedures previously reported.[26] The sample was dried under vacuum at room temperature for 24 h prior to use; Karl–Fischer determination showed the water content to $< 0.3\%$. Thermal polymerization was carried out in an ARC; this instrument is essentially an adiabatic calorimeter working on the heat–wait–measure principle. Such instruments have been widely employed to investigate thermal runaway of exothermic systems.[27–28] The calorimeter has a very large heat capacity relative to the sample and therefore acts as a near-perfect heat sink for the sample. The instrument detects the instantaneous rate of reaction at each temperature through the heat generated from the sample. This information is used to calculate an instantaneous self-heating rate at each temperature and also to estimate, from a knowledge of the sample mass and heat capacity, the adiabatic temperature rise that the sample would experience if the heat of reaction was retained (as would be the case under normal reaction conditions). To compare the self-heating rates, the experiments were carried out with identical sample weights (same thermal inertia, Φ). The instrument also records the pressure in the head space above the reaction medium in the calorimeter.

The monomer, styrene or acrylonitrile (typically 0.85 g), was taken along with the IL (0.36 g) in the ARC titanium bomb. Similar quantities of monomers were taken separately in another set of experiments without the addition of IL. These experiments were performed to study the effect of IL and to compare the system with traditional thermal polymerizations. The self-heating rate and pressure data were recorded as a function of temperature and time.

Received: May 7, 2004

Keywords: calorimetry · green chemistry · ionic liquids · polymerizations · thermodynamics

---

[1] M. Surianarayanan, Y. Iizuka, A. Miyake, A. Itoh, T. Ogawa, *Kayaku Gakkaishi* **2002**, *63*, 316–322.

[2] J. L Gustin , *J. Phys. III* **1991**, *1*, 1401–1405.

[3] R. N. Laudau , *Chem. Eng. Prog.* **1993**, *89*, 66–70.

[4] M. Surianarayanan, R. Vijayaraghavan, G. Swaminathan, P. G. Rao, *Curr. Sci.* **2001**, *6*, 738–747.

[5] T. Kletz, *Inherently Safer Chemical Processes*, CCPS of AICHE, New York, **1996**.

[6] H. K. Fauske, *Chem. Eng. React. Des.* **1989**, *67*, 199–201.

[7] K. Chatrathi, S. Richard, *Chem. Eng. Prog.* **1996**, *92*, 22–24.

[8] W. Kordylewski, J. Amrogowicz, *Combust. Flame* **1992**, *90*, 344–345.

[9] P. Wasserscheid, K. Keim, *Angew. Chem.* **2000**, *112*, 3926–3945; *Angew. Chem. Int. Ed.* **2000**, *39*, 3772–3789.

[10] J .F Brennecke, E. J. Maginn, *AIChE J.* **2002**, *47*, 2384–2389.

[11] T. Welton, *Chem. Rev.* **1999**, *99*, 2071–2083.

[12] K. R. Seddon, *J. Chem. Technol. Biotechnol.* **1997**, *68*, 351–356.

[13] R. Sheldon, *Chem. Commun.* **2001**, 2399–2400.

[14] M. Hongyang, W. Xinhua, C. Xiaofang, Zhou, Q. Feng, *J. Polym. Sci. Part A* **2003**, *41*, 143–151.

[15] K. Hong, H. Zhang, J. W. Mays, A. E. Vissar, Christopher, *Chem. Commun.* **2002**, *13*, 1368–1369.

[16] R. Vijayaraghavan, D. R. MacFarlane, *Aust. J. Chem.* **2004**, *57*, 129–133.

[17] R. Vijayaraghavan, D. R. MacFarlane, *Chem. Commun.* **2004**, 700–701.

[18] P. Kubisa, *Prog. Polym. Sci.* **2004**, *29*, 3–12.

[19] T. Uchida, M. Surianarayanan, M. Wakakura, H. Tomioka, *J. Chem. Eng. Jpn.* **1998**, *31*, 960–968.

[20] L. Bethrick, *Hand Book of Reactive Chemical Hazards*, **1987**, Butterworths, London, **1987**, p. 15.

[21] P. Bonhote, A. P. Dias, N. Papageogiou, K. Kalyanasundaram, M. Gratzel, *Inorg. Chem.* **1996**, *35*, 1168–1178.

[22] J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker, R. D. Rogers, *Green Chem.* **2001**, *3*, 156–164.

[23] K. Baranyai, G. B. Deacon, D. R. MacFarlane, J. M. Pringle, J. L. Scott, *Aust. J. Chem.* **2004**, *57*, 145–147.

[24] J. M. Pringle, J. Golding, K. Baranyai, C. M. Forsyth, G. B. Deacon, J. L. Scott, D. R. MacFarlane, *New J. Chem.* **2003**, *27*, 1504–1510.

[25] I. G. Britton, D. A. Taylor, D. C. Wobser, *Plant/Oper. Prog.* **1986**, *5(4)*, 238–251.

[26] M. Forsyth, J. Huang, D. R. MacFarlane, *J. Mater. Chem.* **2000**, *10*, 2259–2265.

[27] Y. Iizuka, M. Surianarayanan, *Ind. Eng. Chem. Res.* **2003**, *42*, 2987–2995.

[28] D. I. Townseed, J. C. Tou, *Thermochim. Acta* **1980**, *37*, 1–30.