A highly efficient approach for dehydrochlorinating polyvinyl chloride: catalysis by 1-butyl-3-methylimidazolium chloride

Tao Zhao,[a] Qian Zhou,*[a] Xiao-Li He,[a] Sha-Di Wei,[a] Li Wang,[a] Johannes M. N. van Kasteren[b] and Yu-Zhong Wang*[a]

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Highly efficient dehydrochlorination of PVC is feasible using a readily available ionic liquid, 1-butyl-3-methylimidazolium chloride ([Bmim]Cl). The process does not require additional organic solvents, catalysts, or pressure, and the ionic liquid can be recycled (at least 6 time) without appreciable loss of catalytic efficiency. Both anions and cations of the ionic liquids influence upon dehydrochlorination. This ionic influence, combined with the concerted elimination of HCl in a single step, accounts for the faster dehydrochlorination rate.

Introduction

Polyvinyl chloride (PVC) degrades thermally, photochemically, and chemically, by elimination of HCl and formation of a polyene structure.[1,2] Dehydrochlorination of PVC produces dechlorinated PVC (DPVC), with a structure similar to that of polyacetylene, a material with potential applications in chemical and electrochemical areas.[3] Moreover, dehydrochlorination is also an essential step in producing clean fuel oil when recycling PVC-containing waste plastics.[4] With respect to PVC dehydrochlorination, various methods have recently been developed, such as catalytic dechlorination using metal oxides or composite oxides,[5] mechanochemical dechlorination,[6] and hydrolysis in alkaline solutions.[7] The latter method is efficient but requires volatile and toxic solvents, and the resulting by-products, such as KCl, could cause secondary pollution. Although hydrothermal[8] and supercritical[9] dechlorination offer increased efficiency, they also have severe equipment requirements. Therefore, developing efficient and environmentally friendly methods of dehydrochlorinating PVC is of considerable importance.

Poly(ethylene glycol) (PEG) has already been used in our previous work[10] as a reaction medium enhancing PVC dehydrochlorination. Recently, ionic liquids (ILs), *i.e.*, organic salts that melt at or below 100 °C, have been used as solvents or/and catalysts in various reactions, due to their great potential as environmentally benign media: easy to operate, less energy demanding, and environmentally friendly due to chemical and thermal stability, low vapor pressure and ease of reuse.[11] In this paper, we report a novel method for the highly efficient dehydrochlorination of PVC at atmospheric pressure, using an inexpensive and easily accessible ionic liquid, 1-butyl-3-methylimidazolium chloride ([Bmim]Cl).

Results and discussion

Fig. 1 clearly proves the enhancing effects of [Bmim]Cl on PVC dehydrochlorination. At the reaction temperatures (100–220 °C) investigated, PVC/[Bmim]Cl produces a higher degree of dechlorination than without ionic liquids. These enhancing effects are more obvious at higher temperatures (>140 °C): *e.g.*, for PVC the dechlorination efficiency at 180 °C is only 38.1%, while for a PVC/[Bmim]Cl system it increases to as high as 75.8%, with 60.0 wt% of the original chlorine released as HCl.

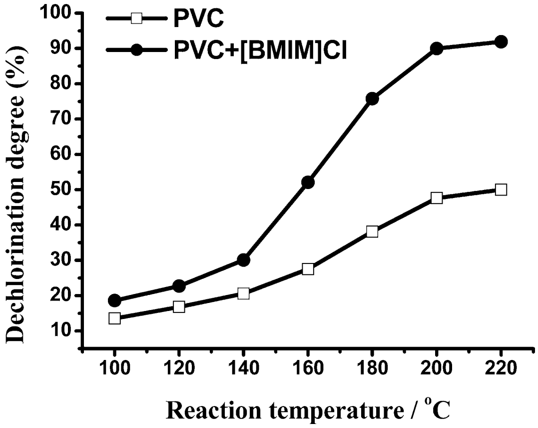

Fig. 1 Effects of reaction temperature on the dechlorination degree of PVC.

From the SEM photographs (Fig. 2), it can clearly be seen that the dechlorinated PVC film using BmimCl exhibits a rough surface with porous structures, while the DPVC without ionic liquids shows a relatively smooth surface. The porous structure formed by deep degradation of PVC assists in the diffusion of the HCl liberated and thus accelerate the process. Similar results have been observed for PVC/PEG systems.[10]

Ionic liquids are stable at high temperature, with low volatility. According to the ^{1}H-NMR spectrum (Fig. S1), the ionic liquid remains intact after reaction with PVC, without any significant color change, proving that [Bmim]Cl is relatively stable under the

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[a] *Center for Degradable and Flame-Retardant Polymeric Materials (ERCEPM-MoE), College of Chemistry, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu, 610064, China. E-mail: qzhou@scu.edu.cn, yzwang@scu.edu.cn; Fax: +86-28-85410755; Tel: +86-28-85410755*
[b] *Eindhoven University of Technology, TU/e Innovationlab, PO Box 513, 5600 MB, Eindhoven, The Netherlands. E-mail: j.m.n.v.Kasteren@tue.nl*

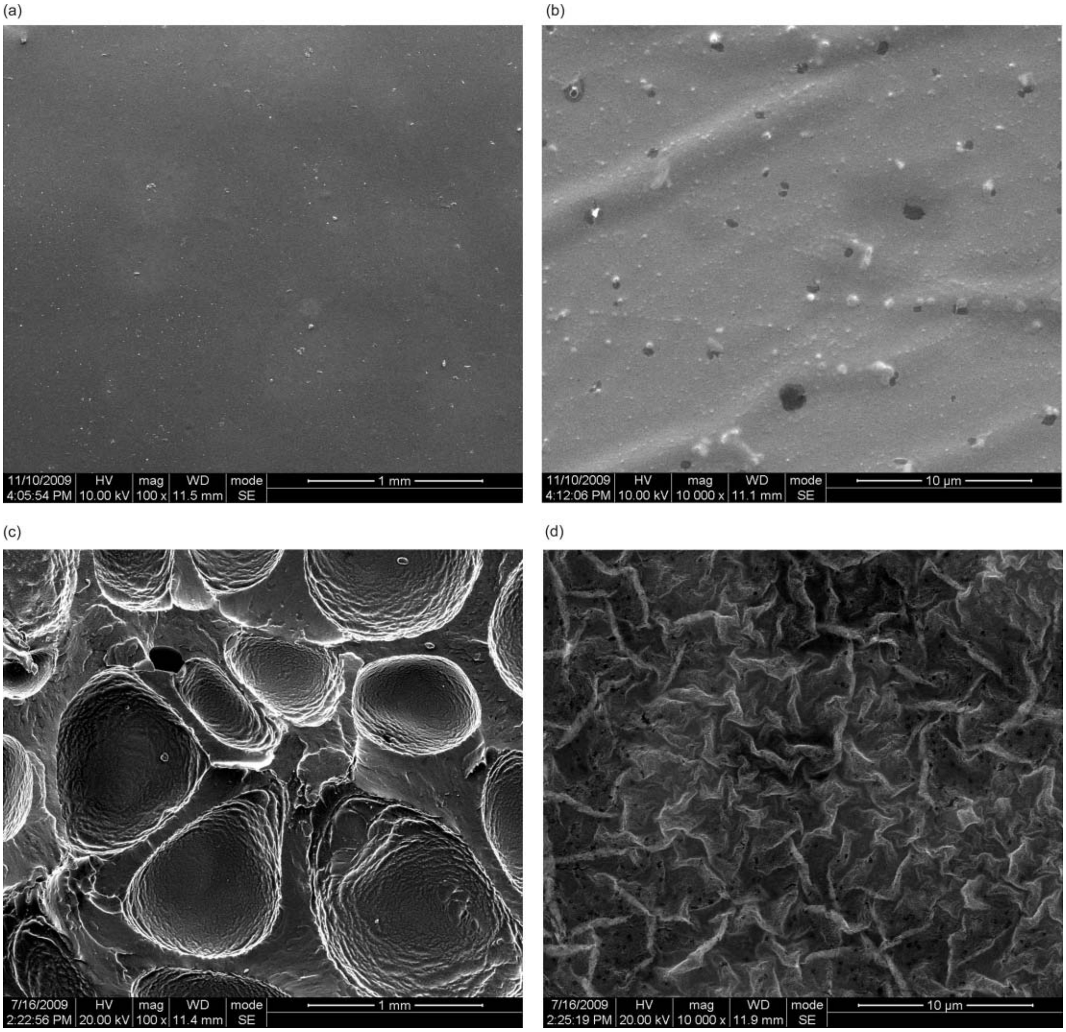


Fig. 2 SEM of DPVC (PVC) at a low magnification (a) and at higher magnification (b) DPVC (PVC/BmimCl) at a low magnification (c) and at higher magnification (d).

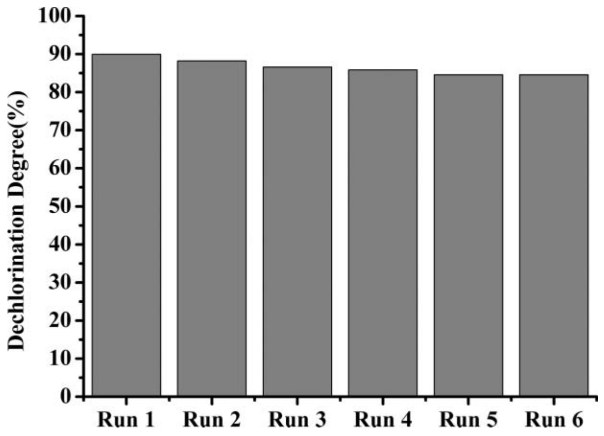


Fig. 3 Recyclability of [Bmim]Cl for the dehydrochlorination of PVC (200 °C, 1 h).

reaction conditions. Therefore, good reusability of the [Bmim]Cl system is expected. Fig. 3 shows the dechlorination degree of a PVC sample after consecutive runs with the same ionic liquid. Between every step the ionic liquid is filtered off, washed with water and then vacuum-dried. It can be seen that dechlorination is almost constant for 6 cycles, suggesting that [Bmim]Cl can be reused for the dehydrochlorination of PVC.

In order to correlate ionic liquid structure with PVC dehydrochlorination efficiency, some typical ionic liquids were internally compared (Fig. 4). Although [Bmim]BF_4 and [Bmim]PF_6 hold the same cations as [Bmim]Cl, they do not significantly accelerate dehydrochlorination. Fig. 4 also shows that the

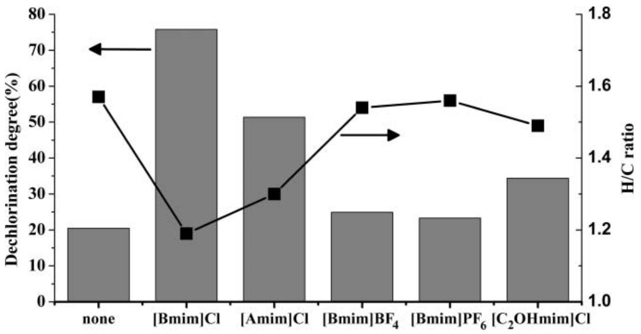


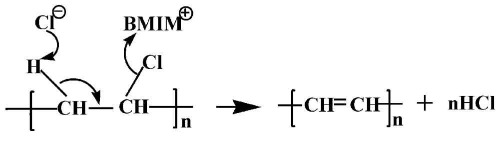
Fig. 4 Effects of ionic liquids on the dechlorination degree of PVC (180 °C).

hydrogen/carbon atomic ratios (H/C) of the DPVC obtained from [Bmim]BF_4 and from [Bmim]PF_6 are similar to that of PVC, while that from [Bmim]Cl is closer to 1.0 (the stoichiometric value of a polyene chain). Since elimination of hydrogen chloride HC from PVC leads to a decrease in H/C molar ratio, these results further prove the higher dechlorination ability of [Bmim]Cl.

It is reported that the hydrogen bond accepting basicity (β) of [C_4mim]-based ILs is as follows: Cl^- (0.95) > BF_4^-(0.55) > PF_6^- (0.44).[12] Therefore, both the role of the chloride anion and its hydrogen bond basicity are crucial in achieving a high dechlorination degree of PVC. On the other hand, with ILs bearing the same anion ion (Cl^-), the dechlorination degree of PVC is as follows: [Bmim]Cl > [Amim]Cl > [C_2OHmim]Cl, suggesting that the structure of the cations of the ILs also influences the dehydrochlorination of PVC.

An ion pair/quasi-ionic mechanism has been proposed for thermal dehydrochlorination of PVC by ionization of chlorine of PVC, followed by rapid elimination of a proton.[13] This mechanism was supported by the increasing degradation rates observed in solutions with increasing polarity of the solvents. However, among the ILs bearing Cl^-, [C_2OHmim]Cl (with the highest polarity) also exhibits the lowest dechlorination rate, suggesting a concerted mechanism instead of a consecutive one. Moreover, the dechlorination rate increases as the amount of IL increases (results not shown here), an observation that also supports the concerted mechanism.

A plausible mechanism for [BMIM]Cl enhanced dehydrochlorination of PVC is proposed in Scheme 1. It is hypothesized that the reaction involves the concerted loss of HCl in a single step, catalyzed by ionic liquids: anions of the ionic liquids such as Cl^- with high hydrogen bond accepting basicity are beneficial in weakening the H–C bond. Similarly, cations can constitute complexes with chlorine atoms of the PVC, weakening the C–Cl bond. Those concerted effects result in a lower energy of activation as well as in faster dehydrochlorination rates. Future work should systematically investigate the effects of the hydrogen bond accepting basicity of anions, the polarity of the IL (compatibility of IL with PVC) and the stability of the IL on the dehydrochlorination of PVC, to identify the optimum cation/anion pair for reactivity.



Scheme 1 Plausible mechanism for [BMIM]Cl-enhanced dehydrochlorination of PVC.

Experimental

Materials

PVC (SG-1), with a chlorine content of 51.5%, was obtained from Xian Chemical Co., China. 1-Butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF_4) and 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim]PF_6) with a purity of 99% were obtained from Hangzhou Chemer Chemistry Co., China. 1-Butyl-3-methylimidazolium chloride ([Bmim]Cl),[14] 1-allyl-3-methylimidazolium chloride ([Amim]Cl)[15] and 1-(2-hydroxyethyl)-3-methylimidazolium chloride ([C_2OHmim]Cl)[16] were synthesized according to reported procedures. All ionic liquids were kept overnight under vacuum at 90 °C before use, to remove water. Fig. 5 shows the chemical structures of these ionic liquids.

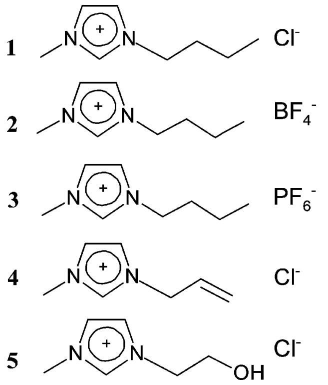


Fig. 5 Chemical structures of the ionic liquids used. 1. [Bmim]Cl; 2. [Bmim]BF_4; 3. [Bmim]PF_6; 4. [Amim]Cl; 5. [C_2OHmim]Cl.

Dehydrochlorination and characterization of PVC

Dehydrochlorination of PVC was carried out in a 100 ml three-necked flask equipped with a thermometer and a nitrogen gas bubbler (30 mL min^{-1}). In a typical experiment, 5 mL [Bmim]Cl and 0.15 g PVC were added to the flask, and then the mixture was reacted at constant temperature for 1 h while stirring. After reaction, the dechlorinated PVC was separated by filtration. After washing thoroughly with water, the resulting DPVC was dried under vacuum for 36 h at 60 °C before characterization. The separated [Bmim]Cl aqueous solution was placed in a flask coupled to a rotary evaporator to remove any remaining water. The resulting recycled [Bmim]Cl was reused for PVC dehydrochlorination to test the reusability of the catalytic solvent in the reaction system.

The chlorine content of the DPVC was measured by the oxygen–combustion–chlorine-selective electrode method. The evolved HCl appeared: (i) in the trace of condensed water that was originally dissolved in the ionic liquid, (ii) in the ionic liquid itself; and (iii) in the aqueous NaOH used for HCl trapping. The HCl from (i) and (iii) was analyzed by the chloride ion selective electrode (ISE) method, and that from (ii) was calculated by comparing the difference between the chlorine content of the ionic liquid before and after reaction.

The dechlorination degree (DD) of PVC was calculated as:

$$\text{DD }(\%) = \left(1 - \frac{\text{Cl content in DPVC}(\text{g})}{\text{Cl content in PVC polymer}(\text{g})}\right) \times 100$$

The H/C ratio of the DPVC was determined with an elemental analyzer (Thermo electron Flash EA1112, USA).

PVC film was prepared using a solvent (THF) casting method. Dechlorinated PVC films were obtained by reacting PVC with or without [Bmim]Cl under nitrogen atmosphere at 200 °C for 1 h.

The surfaces of DPVC films were observed using a JEOLJSM-5009LV scanning electron microscope (SEM) operating at an accelerating voltage of 20 kV.

Conclusions

This procedure using an ionic liquid is a novel, green and efficient method for PVC dehydrochlorination. Significant advantages of this method are: operational simplicity, high dechlorination efficiency, greenness of procedure (by avoiding hazardous organic solvent, additional catalysts, and toxic waste byproducts), and satisfactory recyclable properties. It holds great promise for application in other dehalogenation processes.

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References

1 S. H. Kim, S. Y. Kwak and T. Suzuki, *Polymer*, 2006, **47**, 3005–3016.
2 R. Bacaloglu and M. Fisch, *Polym. Degrad. Stab.*, 1995, **47**, 33–57.
3 E. D. Owen, M. Shah, N. J. Everall and M. V. Twigg, *Macromolecules*, 1994, **27**, 3436–3438.
4 T. Bhaskar, T. Matsui, J. Kaneko, M. A. Uddin, A. Muto and Y. Sakata, *Green Chem.*, 2002, **4**, 372–375.
5 Q. Zhou, W. Lan, A. Du, Y. Wang, J. Yang, Y. Wu, K. Yang and X. Wang, *Appl. Catal., B*, 2008, **80**, 141–146.
6 X. Xiao, Z. Zeng and S. Xiao, *J. Hazard. Mater.*, 2008, **151**, 118–124.
7 S. M. Shin, T. Yoshioka and A. Okuwaki, *Polym. Degrad. Stab.*, 1998, **61**, 349–353.
8 M. J. P. Slapak, J. M. N. van Kasteren and B. Drinkenburg, *Polym. Adv. Technol.*, 1999, **10**, 596–602.
9 Y. Takeshita, K. Kato, K. Takahashi, Y. Sato and S. Nishi, *J. Supercrit. Fluids*, 2004, **31**, 185–193.
10 Y. H. Wu, Q. Zhou, T. Zhao, M. L. Deng, J. Zhang and Y. Z. Wang, *J. Hazard. Mater.*, 2009, **163**, 1408–1411.
11 J. G. Huddleston, H. D. Willauer, R. P. Swatloski, A. E. Visser and R. D. Rogers, *Chem. Commun.*, 1998, 1765–1766.
12 R. Lungwitz, M. Friedrich, W. Linert and S. Spange, *New J. Chem.*, 2008, **32**, 1493–1499.
13 W. H. Starnes Jr, *Prog. Polym. Sci.*, 2002, **27**, 2133–2170.
14 R. P. Swatloski, S. K. Spear, J. D. Holbrey and R. D. Rogers, *J. Am. Chem. Soc.*, 2002, **124**, 4974–4975.
15 H. Zhang, J. Wu, J. Zhang and J. He, *Macromolecules*, 2005, **38**, 8272–8277.
16 L. C. Branco, J. N. Rosa, J. J. M. Ramos and C. A. M. Afonso, *Chem.–Eur. J.*, 2002, **8**, 3671–3677.