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Designing Explosive Poly(ionic liquid)s as Novel Energetic Polymers

Binshen Wang,[a] Yongan Feng,[a] Xiujuan Qi,[b] Mucong Deng,[a] Junjun Tian, [a] and Qinghua Zhang*[a]

Abstract: The development of ionic liquids-derived functional materials would be vital for stimulation of the interdisciplinary research in the fields of ionic liquids chemistry and material science. Here, a series of novel poly(ionic liquid)s with explosive capability are designed and prepared by introducing energetic nitrato group and nitro-rich anions, such as nitrate, dinitramide, and nitroform into the polymeric chains. The as-synthesized explosive poly(ionic liquid)s (E-PILs) are fully characterized, and their physicochemical and detonation properties are investigated. All E-PILs show higher detonation performances than state-of-the-art energetic polymers including glycidyl azide polymer (GAP) and poly(glycidyl nitrate) [poly(GLYN)]. Some E-PILs exhibit higher calculated detonation velocities and pressures than 2,4,6-trinitrotoluene (TNT). These E-PILs are promising candidates for applications as new high-performance energetic polymers.

Introduction

In the past decades, ionic liquids (ILs) have undergone a revolutionary development for their applications in the fields of chemistry and material science. Benefiting from a variety of prominent properties, ILs have been investigated as green solvents to replace traditional volatile organic compounds (VOCs) and as safer electrolytes for electrochemistry applications.[1] In recent years, materialization has become the focus of research on ILs, and a broad range of promising applications for ILs-based materials have been explored including high-performing lubricants,[2] energy-storage fluids,[3] environmental sensing fluids,[4] *etc*. However, the inherent lack of mechanical machining properties in some cases (e.g., well-defined morphologies) decreases the applicability of traditional ILs.[5] Hence, a novel class of ILs-based polymer materials, *viz.* poly(ionic liquid)s (PILs), has emerged at the frontiers of ILs chemistry.[6] PILs are the polymeric form of monomeric ionic liquids, which contain the ionic species in each of its repeat units. From monomers to polymers, the majority of special properties of monomeric ILs (e.g., negligible vapor pressure, high thermal stability, and ionic conductivity, etc.) are grafted into the PILs, while the polymer nature enables PILs to be readily processed. The applications of PILs have extended in various fields including stimuli-responsive materials,[7] carbon materials,[8] and antimicrobial materials,[9] *etc*. PILs have certainly provided a platform for the development of novel IL-based functional materials, where the unique properties and function can be designed and fabricated to accomplish a specific task.

Energetic materials represent one of the crucial functional materials which are widely used for constructive as well as destructive purposes in military and civil applications.[10] Modern energetic materials should meet multiple requirements of high energy density, good thermal stability, and high performance. The use of inert polymers as binders and/or plasticizers for explosive formulations brings down the overall energy of such systems. Therefore, one of focuses in the field of energetic materials is the development of energetic or explosive polymers, which can maintain or even improve internal energy and performance of explosives.[11] Some energetic polymers, including glycidyl azide polymer (GAP) and poly(glycidyl nitrate) [poly(GLYN)], have been synthesized. However, their detonation performances are still relatively low, especially in comparison with high explosives. It is important to design new energetic polymers with better detonation performance due to the high energetic requirement of explosives.

Until now, some pioneering studies have focused on the synthesis of hypergolic ionic liquids with energetic property for application as propellant fuels.[12] However, to the best of our knowledge, the study on design and application of PILs in the field of energetic materials has not been reported. As a multidisciplinary material, PILs provide a great potential for the development of new energetic polymers for various applications.

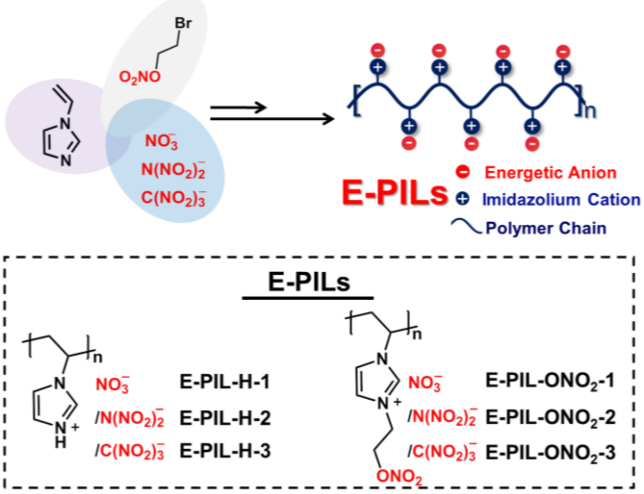

Figure 1. Schematic illustration for synthesis of E-PILs.

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Herein, in continuing efforts to develop novel task-specific ILs[13] and energetic materials,[14] we designed and synthesized a series of explosive poly(ionic liquid)s (E-PILs) by the introduction of energetic nitrato group into the imidazolium cation, in combination with oxidizer-rich nitrate, dinitramide or nitroform energetic anion to the polymer chain (Figure 1). All the prepared ionic polymers were characterized by NMR spectra, IR, elemental analysis, scanning electron microscope (SEM) and X-ray diffraction (XRD), and their physicochemical properties, energetic performance (e.g., detonation velocities and detonation pressures), mechanical sensitivity were extensively studied.

Results and Discussion

Synthesis and characterization

E-PIL-H-1 was prepared by simple two-step reactions, which involved the reaction of 1-vinylimidazole with nitric acid and a subsequent polymerization of 1*H*-3-vinylimidazolium nitrate in the presence of initiator 2,2'-azobis(2-methylpropionitrile) (AIBN) (Scheme S1). Dinitramide-based **E-PIL-H-2** and nitroform-based **E-PIL-H-3** were synthesized via the reaction of 1-vinylimidazole with hydrochloric acid, followed by the polymerization of IL monomer to give chloride anion-based PIL and the metathesis reactions with $KN(NO_2)_2$/$KC(NO_2)_3$. Nitrato group has been demonstrated to be useful in energetic compounds.[15] The introduction of nitrato group into the cationic structure of ILs was through the reaction of 1-vinylimidazole and 2-bromoethyl nitrate. After the polymerization and subsequent metathesis reactions with KNO_3/$KN(NO_2)_2$/$KC(NO_2)_3$, **E-PIL-ONO$_2$-1**, **E-PIL-ONO$_2$-2**, and **E-PIL-ONO$_2$-3** were obtained, respectively. The introduced oxygen-rich group (nitro) could improve the oxygen balance of E-PILs, and led to an enhanced detonation performance.

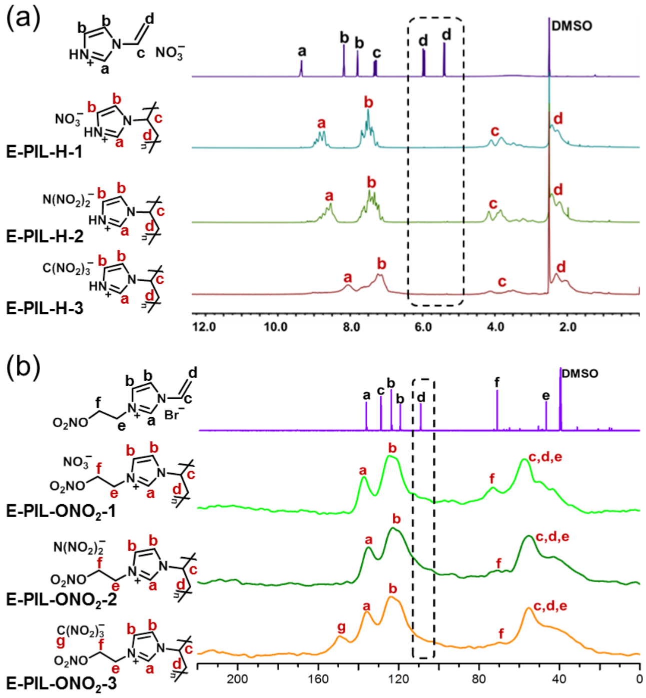

Figure 2. (a) ^1H NMR spectra of 1*H*-3-vinylimidazolium nitrate, **E-PIL-H-1**, **E-PIL-H-2**, and **E-PIL-H-3** in DMSO-d_6. (b) ^{13}C NMR spectrum of 3-(2-(nitrooxy)ethyl)-1-vinylimidazolium bromide in DMSO-d_6, and solid-state ^{13}C MAS NMR spectra of **E-PIL-ONO$_2$-1**, **E-PIL-ONO$_2$-2**, and **E-PIL-ONO$_2$-3**.

The structures of newly prepared E-PILs were fully characterized. Compared to 1-vinylimidazolium IL monomer, the disappearance of the signals at 5.91-5.96 and 5.36-5.39 ppm in ^1H NMR spectra and the signals at 109 ppm in solid-state ^{13}C MAS NMR spectra indicated a complete polymerization of C=C bonds in the cation of these E-PILs (Figure 2a and b). As shown in Figure 3, IR spectra of **E-PIL-H-1** and **E-PIL-ONO$_2$-1** showed a strong band associated with NO_3^- anion (~1379 cm^{-1}). IR spectra of **E-PIL-H-2** and **E-PIL-ONO$_2$-2** showed a peak associated with $N(NO_2)_2^-$ anion (~1182 cm^{-1}),[16] and IR spectra of **E-PIL-H-3** and **E-PIL-ONO$_2$-3** exhibited a band of $C(NO_2)_3^-$ anion (~1273 cm^{-1}).[17] These results demonstrated the successful introduction of the three kinds of energetic anions [NO_3^-, $N(NO_2)_2^-$, $C(NO_2)_3^-$] into the PILs, respectively (Figure S1). In addition, elemental analysis results confirmed the good purity of E-PILs (Table S1). SEM image showed that the morphology of **E-PIL-H-1** was composed of round-shaped nanoparticles with diameters around 150 nm, while other E-PILs were primarily stacked with sheet structures in greater sizes (Figure S2). Furthermore, XRD pattern of these E-PILs showed diffuse peaks over the angular range 15° to 35° (Figure S3), which were analogous to previous reported poly[3,3'-methylenebis(1-vinyl-1H-imidazolium) bromide].[18] These results indicated amorphous texture of these energetic polymers.

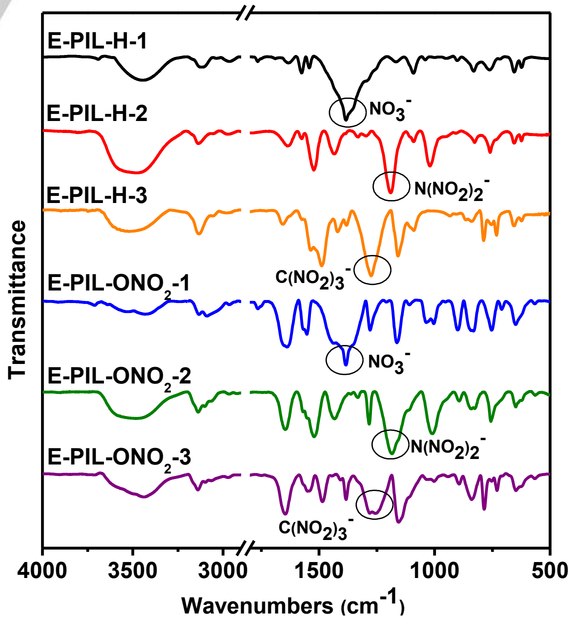

Figure 3. IR spectra of E-PILs with highlighted band positions of their energetic anions.

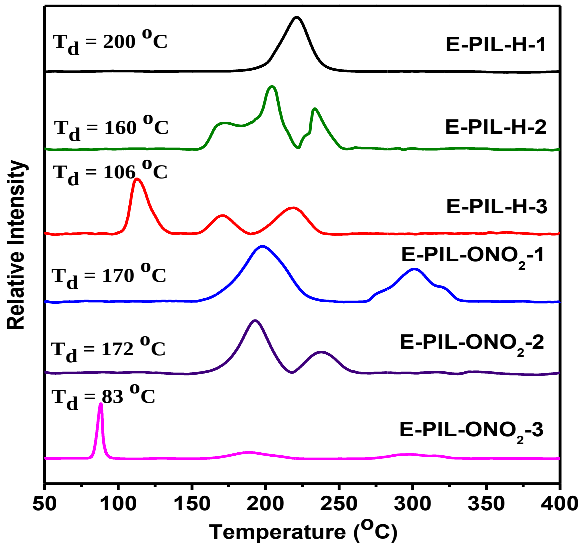

Figure 4. DSC curves of E-PILs measured at a heating rate of 10 °C min^{-1}.

Thermal stability

The thermal stability of E-PILs was analysed using differential scanning calorimetry (DSC) at a heating rate of 10 °C min^{-1}. As shown in Figure 4, **E-PIL-H-1** demonstrated the typical thermal behaviour of explosives,[19] suggesting a onset decomposition temperature of 200 °C. This decomposition temperature is comparable to that of GAP (T_d = 200 °C) and Poly(GLYN) (T_d = 204 °C).[11a] In comparison with a traditional energetic oxidizer ADN (ammonium dinitramide, T_d = 127 °C) containing free dinitramide,[20] onset decomposition temperatures of dinitramide-based **E-PIL-H-2** and **E-PIL-ONO$_2$-2** were increased to 160 and 172 °C, respectively. The significant improvement was probably due to the stabilization of imidazolium cation to the energetic anion. However, nitroform-based **E-PIL-H-3** and **E-PIL-ONO$_2$-3** exhibited relatively low onset decomposition temperatures of 106 and 83 °C, respectively, which were analogous to other reported energetic materials containing nitroform.[21]

Heat of formation and density

Sum of oxygen and nitrogen content of energetic materials is strongly related to the detonation performance. Due to the introduction of energetic anions, these E-PILs had relative high oxygen and nitrogen contents ranging from 57.29% (**E-PIL-H-1**) to 68.24% (**E-PIL-ONO$_2$-3**) (Table 1). The constant-volume combustion energies ($\Delta_c U$) of E-PILs were measured by an oxygen bomb calorimeter, which were ranging from -14636 J/g (**E-PIL-ONO$_2$-3**) to -19253 J/g (**E-PIL-H-1**). After obtaining heats of combustion with a correction for the change in gas volume during combustion, standard enthalpies of formation ($\Delta_f H°$) of E-PILs were back-calculated from heats of combustion on the basis of combustion equations, along with Hess's Law and known standard heats of formation for water and carbon dioxide (Scheme S2). With an exception for **E-PIL-ONO$_2$-1**, other E-PILs had a positive standard enthalpy of formation. Among them, **E-PIL-H-2** showed the highest standard enthalpy of formation of 1.76 kJ g^{-1}, which was higher than that of GAP (1.15 kJ g^{-1}), Poly(GLYN) (-2.71 kJ g^{-1}), and TNT (2,4,6-trinitrotoluene, -0.24 kJ g^{-1}). The density was measured with a helium gas pycnometer at 25 °C. It was found that nitrato functional group was favourable to improve the density of resulting polymers, when comparing the densities of **E-PIL-ONO$_2$-1** (1.60 g cm^{-3}), **E-PIL-ONO$_2$-2** (1.66 g cm^{-3}), **E-PIL-ONO$_2$-3** (1.65 g cm^{-3}) with the same anion-based **E-PIL-H-1** (1.48 g cm^{-3}), **E-PIL-H-2** (1.54 g cm^{-3}), **E-PIL-H-3** (1.61 g cm^{-3}), respectively.

Detonation properties and sensitivity

Based on the obtained enthalpy of formation and experimental densities, the detonation properties of E-PILs were evaluated

Table 1. Physicochemical and energetic properties of E-PILs compared with GAP, Poly(GLYN), and TNT.

Compd.	Formula [a]	O+N% [b]	$\Delta_c U$ [c] [J g^{-1}]	$\Delta_f H°$ [d] [kJ g^{-1}]	d [e] [g cm^{-3}]	P [f] [GPa]	vD [g] [m s^{-1}]	IS [h] [J]	FS [i] [N]
E-PIL-H-1	$C_5H_7N_3O_3$	57.29	-19253	0.27	1.48	16.1	6934	16	192
E-PIL-H-2	$C_5H_7N_5O_4$	66.64	-16604	1.76	1.54	22.0	7705	5	288
E-PIL-H-3	$C_6H_7N_5O_6$	67.73	-15414	1.61	1.61	25.6	7941	4	128
E-PIL-ONO$_2$-1	$C_7H_{10}N_4O_6$	61.75	-16677	-0.41	1.60	20.0	7425	18	216
E-PIL-ONO$_2$-2	$C_7H_{10}N_6O_7$	67.55	-14836	0.33	1.66	24.5	7941	4	128
E-PIL-ONO$_2$-3	$C_8H_{10}N_6O_9$	68.24	-14636	0.85	1.65	26.4	8003	4	120
GAP [j]	$C_3H_5N_3O$	58.56	-	1.15	1.30	11.6	5041	20	324
Poly(GLYN) [j]	$C_3H_5NO_4$	65.50	-	-2.71	1.46	15.8	6755	-	-
TNT [K]	$C_7H_5N_3O_6$	60.76	-	-0.24	1.65	23.5	7459	15	353

[a] Formula of a repeating unit. [b] Oxygen and nitrogen content. [c] Experimentally determined (oxygen bomb calorimetry) constant-volume combustion energy. [d] Experimentally determined (back-calculated from $\Delta_c U$) enthalpy of formation. [e] Density measured using a gas pycnometer at 25 °C. [f] Detonation pressure. [g] Detonation velocity. [h] Impact sensitivity. [i] Friction sensitivity. [j] Ref. 11a, 22. [k] Ref. 23.

with the EXPLO5 program (v6.02). The detonation pressures of E-PILs lie in the range of 16.1 GPa (**E-PIL-H-1**) to 26.4 GPa (**E-PIL-ONO$_2$-3**). All E-PILs demonstrated much higher detonation velocities than GAP (5041 m s^{-1}) and poly(GLYN) (6755 m s^{-1}). It was worth noting that detonation velocities of **E-PIL-H-2**, **E-PIL-H-3**, **E-PIL-ONO$_2$-2** and **E-PIL-ONO$_2$-3** were even superior to that of TNT (7459 m s^{-1}). The calculated detonation velocities were in the following order: nitroform-based E-PILs > dinitramide-based E-PILs > nitrate-based E-PILs. Nitroform-based **E-PIL-ONO$_2$-3** exhibited the highest detonation velocity of 8003 m s^{-1}. The remarkable detonation velocity of **E-PIL-ONO$_2$-3** may be primarily derived from the oxidation of energetic nitrato group in cation and nitroform anion toward its polymer chain. The mechanical sensitivities of these energetic polymers towards impact (IS) and friction (FS) were determined using the traditional BAM method. Nitrate-based **E-PIL-H-1** and **E-PIL-ONO$_2$-1** showed relatively low impact sensitivities of 16 and 18 J, respectively, which were comparable to that of GAP (20 J) and TNT (15 J). However, dinitramide-based and nitroform-based E-PILs exhibited high impact sensitivities of 4-5 J. The friction sensitivities of E-PILs fell within the range of 120 N (**E-PIL-ONO$_2$-3**) to 288 N (**E-PIL-H-2**).

Conclusions

In conclusion, a series of E-PILs composed of nitrato-functionalized cations and nitrate, dinitramide or nitroform energetic anions were prepared. The structures and physicochemical properties of energetic polymers were fully characterized. Their detonation properties were determined by using EXPLO5 program. All as-prepared E-PILs showed higher energetic performances than state-of-the-art energetic polymers including GAP and poly(GLYN). Notably, four of them demonstrated higher detonation velocities than TNT. The highest detonation velocity of as-synthesized E-PILs was up to 8003 m s^{-1}. Among these energetic polymers, **E-PIL-H-1** exhibited a good thermal stability (T_d = 200 °C), a calculated detonation velocity of 6934 m s^{-1} and a detonation pressure of 16.1 GPa, and low sensitivities (16 J of IS and 192 N of FS) to external stimuli such as impact and friction. The good performance makes **E-PIL-H-1** a promising candidate for energetic applications as binders and/or plasticizers for explosive formulations. This work opens avenues to development of novel poly(ionic liquid)s with task-specific explosive capability, and provides a way to prepare high detonation performance energetic polymers.

Experimental Section

Materials

Sodium nitrate (AR), nitric acid (AR), and hydrochloric acid (AR) were obtained from CHRON CHEMISCALS Co. Ltd. 2,2'-Azobis(2-methylpropionitrile) (AIBN, 98%) was purchased from ENERGY CHEMICAL Co. Ltd. 1-Vinylimidazole (99%) was obtained from ALADDIN Co. Ltd. 2-Bromoethyl nitrate, potassium dinitramide, and potassium nitroform were prepared according to the previous literature studies.[24]

Instrumentation and analytical methods

^{1}H and ^{13}C NMR spectra were recorded on a Bruker 600 AVANCE spectrometer (600 and 151 MHz, respectively). ^{13}C solid-state MAS NMR spectra were recorded at a frequency of 100 MHz, a spinning rate of 9.0 kHz, and a recycling delay of 4 s using a VARIANVNMRS-400WB spectrometer under one pulse conditions. IR spectra were recorded on PerkinElmer Spectrum Two IR Spectrometers. Elemental analysis was performed on a Vario Micro cube elemental analyzer. SEM was operated on a Hitachi S-4800 microscope. XRD analyses were collected on Bruker D8 ADVANCE with Cu-Kα radiation, λ=1.5418 Å. Thermal property measurements were performed on a TGA/DSC Mettler Toledo calorimeter at a scan rate of 10 °C min^{-1}. Densities were measured on a Micromeritics Accupyc II 1340 gas pycnometer at ambient temperature. Impact and friction sensitivities were determined by employing a standard BAM Fallhammer and a BAM friction tester.

Synthesis of E-PILs

Preparation of E-PIL-H-1: To 1-vinylimidazole (3.291 g, 35 mmol) was added an equivalent amount of 10% nitric acid. The reaction mixture was stirred for 2 h. After washing with diethyl ether and ethyl acetate, and drying under vacuum, 1*H*-3-vinylimidazolium nitrate was generated. Subsequently, the 1*H*-3-vinylimidazolium nitrate, AIBN (0.148 g, 0.9 mmol), and methanol (16 mL) were charged into a Schlenk flask equipped with a magnetic stirrer, and the mixture was refluxed under nitrogen for 24 h. After polymerization, the polymers were cooled to room temperature, washed with ethyl acetate and methanol, drying under vacuum to afford the product. Yield: 68%.

Preparation of E-PIL-H-2 and E-PIL-H-3: To 1-vinylimidazole (3.291 g, 35 mmol) was added an equivalent amount of 10% hydrochloric acid. The reaction mixture was stirred for 2 h. After washing with diethyl ether and ethyl acetate, and drying under vacuum, 1*H*-3-vinylimidazolium chloride was generated. Subsequently, the 1*H*-3-vinylimidazolium chloride, AIBN (0.181 g, 1.1 mmol), and methanol (20 mL) were charged into a Schlenk flask equipped with a magnetic stirrer, and the mixture was refluxed under nitrogen for 24 h. After polymerization, the polymers were cooled to room temperature, washed with diethyl ether and ethyl acetate, drying under vacuum to afford poly(1*H*-3-vinylimidazolium chloride).

To a solution of potassium dinitramide (2.174 g, 15 mmol) in distilled water (30 mL), poly(1*H*-3-vinylimidazolium chloride) (0.650 g, 5 mmol based on monomer) was added in small portions. After the reaction mixture was stirred for 0.5 h, precipitate was collected by centrifugation, washed with distilled water and drying under vacuum to afford the **E-PIL-H-2**. Yield: 47%.

To a solution of potassium nitroform (2.834 g, 15 mmol) in distilled water (80 mL), poly(1*H*-3-vinylimidazolium chloride) (0.650 g, 5 mmol based on monomer) was added in small portions. After the reaction mixture was stirred for 0.5 h, precipitate was collected by centrifugation, washed with distilled water and drying under vacuum to afford the **E-PIL-H-3**. Yield: 42%.

Preparation of E-PIL-ONO$_2$-1, E-PIL-ONO$_2$-2, and E-PIL-ONO$_2$-3: Under vigorous stirring, 1-vinylimidazole (3.291 g, 35 mmol) was added dropwise to 2-bromoethyl nitrate (8.869 g, 52.5 mmol). After 72 h at room temperature, resulting liquid was washed with diethyl ether and ethyl acetate, drying under vacuum to give 3-(2-(nitrooxy)ethyl)-1-vinylimidazolium bromide. Subsequently, the 3-(2-(nitrooxy)ethyl)-1-

vinylimidazolium bromide, AIBN (0.164 g, 1.0 mmol), and methanol (17 mL) were charged into a Schlenk flask equipped with a magnetic stirrer, and the mixture was refluxed under nitrogen for 24 h. After polymerization, the polymers were cooled to room temperature, washed with ethyl acetate and methanol, drying under vacuum to afford poly(3-(2-(nitrooxy)ethyl)-1-vinylimidazolium bromide). Yield: 77%. Anion exchange reactions were carried out according to the literature procedure with a minor modification.[25]

Poly(3-(2-(nitrooxy)ethyl)-1-vinylimidazolium bromide) (1.315 g, 5 mmol based on monomer) was added to saturated sodium nitrate aqueous solution (15 mL). Precipitate was collected by filtration after stirring the reaction mixture for 24 h, and then was added to a new saturated sodium nitrate aqueous solution (15 mL). After repeating the same procedure six times, the precipitate was collected by filtration, drying under vacuum to afford **E-PIL-ONO$_2$-1**. Yield: 72%.

Poly(3-(2-(nitrooxy)ethyl)-1-vinylimidazolium bromide) (1.315 g, 5 mmol based on monomer) was added to a solution of potassium dinitramide (2.174 g, 15 mmol) in distilled water (30 mL). Precipitate was collected by filtration after stirring the reaction mixture for 24 h, and then was added to a new solution of potassium dinitramide (2.174 g, 15 mmol) in distilled water (30 mL). After repeating the same procedure two times, the precipitate was collected by filtration, drying under vacuum to afford **E-PIL-ONO$_2$-2**. Yield: 88%.

Poly(3-(2-(nitrooxy)ethyl)-1-vinylimidazolium bromide) (1.315 g, 5 mmol based on monomer) was added to a solution of potassium nitroform (2.834 g, 15 mmol) in distilled water (80 mL). Precipitate was collected by filtration after stirring the reaction mixture for 24 h, and then was added to a new solution of potassium nitroform (2.834 g, 15 mmol) in distilled water (80 mL). After repeating the same procedure two times, the precipitate was collected by filtration, drying under vacuum to afford **E-PIL-ONO$_2$-3**. Yield: 87%.

Acknowledgements

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Keywords: Polymers • Ionic liquids • Energetic materials • Thermal stability • Detonation performance

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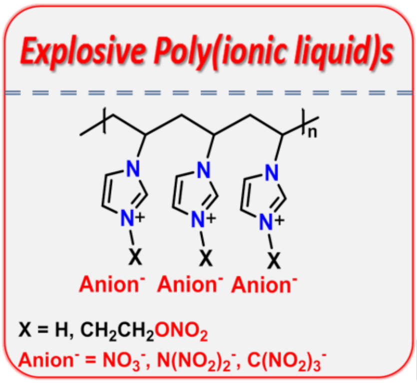
FULL PAPER

A series of novel explosive poly(ionic liquid)s (E-PILs) are designed and prepared by introducing energetic nitrato group and nitro-rich anions into the polymeric chains. All E-PILs show higher detonation performances than state-of-the-art energetic polymers. The E-PILs are promising candidates for applications as binders and/or plasticizers for explosive formulations.



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Designing Explosive Poly(ionic liquid)s as Novel Energetic Polymers