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Application of [PVI-SO₃H]NO₃ as a novel polymeric nitrating agent with ionic tags in preparation of high-energetic materials†

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In this paper, poly(vinyl imidazole) sulfonic acid nitrate [PVI-SO₃H]NO₃ was synthesized and fully characterized. Then, [PVI-SO₃H]NO₃ was applied for the preparation of energetic materials such as 1,1-diamino-2,2-dinitroethene (FOX-7), pentaerythritol tetranitrate (PETN), 1,3,5-trinitro-1,3,5-triazinane (RDX) and trinitrotoluene (TNT). The major advantages of the presented methodology are mild, facile workup, high yields and short reaction times. [PVI-SO₃H]NO₃ is a suitable nitrating agent for *in situ* generation of NO₂ and without using any co-catalysts of the described nitrating reagent.

Introduction

Nitro materials have widely been used in the preparation of energetic materials, dyes, plastics and pharmaceuticals.[1–4] The most well-known of energetic materials are FOX-7 (1,1-diamino-2,2-dinitroethene), pentaerythritol tetranitrate (PETN), 1,3,5-trinitro-1,3,5-triazinane (RDX) and trinitrotoluene (TNT). Furthermore, these nitro compounds have been applied in dyes, pharmaceuticals, fuels, perfumes, medicine and plastics.[5–7] These materials and derivatives such as pentaerythritol tetranitrate (PETN) were applied in therapy antianginal activity, activator guanylate and active ingredients of pharmaceuticals.[8,9] Also, PETN was used to treat cardiovascular disease through vasorelaxant enzyme release.[10,11]

Architecture of novel renewable and sustainable nitrating reagent in the organic transformation has attracted much attention in the science and industry because of their unique properties, such as efficiency, reusability, reactivity, stability, selectivity, generality and easy separation of the catalyst.[12–18] These methods of preparation of energetic materials were previously reported in the presence of some various nitrating agents, co-catalysts, and solvents, mixed acid of concentrated nitric acid and sulfuric acid, high temperature, long reaction times, and low yields[19–30] (Scheme 1).

Frequently, researcher groups have found that metal nitrates or nitrogen oxides can serve as nitrating reagents. Therefore,

developing green nitrating agents has been growing fast in organic reaction. For this purpose, nitrating agents based on polymeric are highly effective systems. Polymeric nitrating agents have advantages such as (a) easy separation from the reaction mixture, (b) without excess use of nitrating reagents, (c) easy recyclability of nitrating polymer supports, (d) low toxicity, (e) and more stability and selectivity of nitrating polymer supports.[31–34]

In the recent years, development of catalysts and/or reagents based on N-heterocycles with sulfonic acids functional groups is our interest.[35–39] In this regard, we have reported novel nitrating agents [Msim]NO₃, [Py-SO₃H]NO₃ and [Dsim]NO₃ for synthesis of nitro compounds and explosive materials.[40–43] Herein, we wish to introduce poly(vinyl imidazole) sulfonic acid nitrate [PVI-SO₃H]NO₃ as a novel nitrating agent. [PVI-SO₃H]NO₃ was used for the synthesis of energetic materials such as 1,1-diamino-2,2-dinitroethene (FOX-7), pentaerythritol tetranitrate (PETN), 1,3,5-trinitro-1,3,5-triazinane (RDX) and trinitrotoluene (TNT) (Scheme 2).

Experimental

### General procedure for the preparation of poly(vinyl imidazole) sulfonic acid nitrate [PVI-SO₃H]NO₃

At first, poly(vinyl imidazole) (PVI) was synthesized according to the previously reported literature (Scheme 3).[44,45] In a 25 mL round-bottomed flask, a mixture of poly(vinyl imidazole) (PVI) (1.410 g) and chlorosulfonic acid (5 mmol, 0.335 mL) in dry CH₂Cl₂ at 0 °C was stirred for 2 h.[46] Then, nitric acid 100% (5 mmol, 0.20 mL) was added dropwise to [PVI-SO₃H]Cl over a period of 5 minutes at room temperature. After this time, an orange powder appeared to give poly(vinyl imidazole) sulfonic acid nitrate [PVI-SO₃H]NO₃ (Scheme 3).

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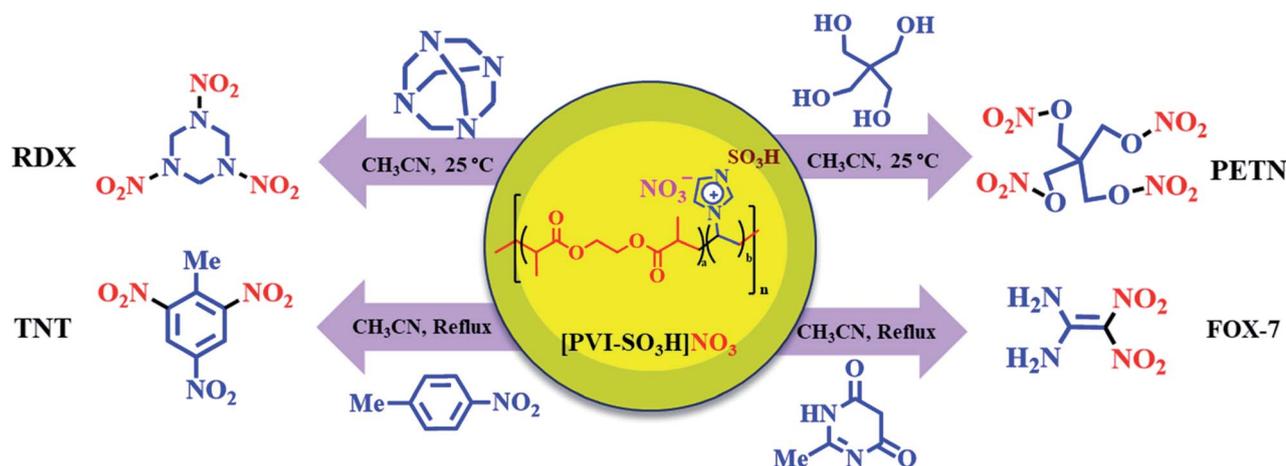
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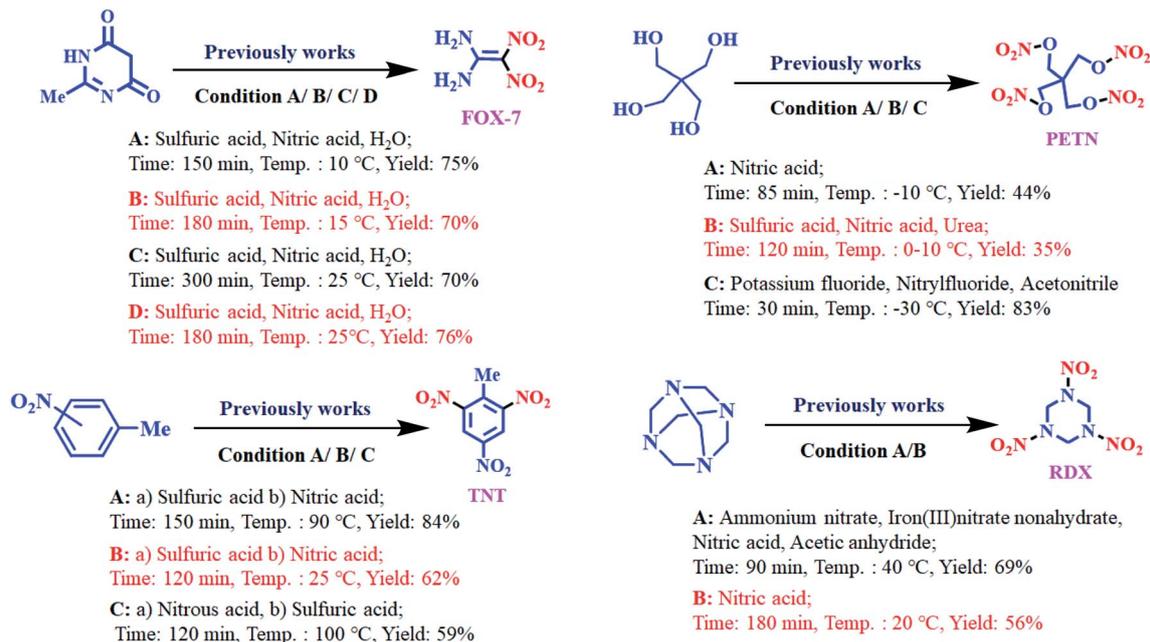
Scheme 1 Synthesis of FOX-7 (1,1-diamino-2,2-dinitroethene), pentaerythritol tetranitrate (PETN), 1,3,5-trinitro-1,3,5-triazinane (RDX) and trinitrotoluene (TNT) according to the previously reports procedures.

Scheme 2 Synthesis of 1,1-diamino-2,2-dinitroethene (FOX-7), pentaerythritol tetranitrate (PETN), 1,3,5-triazinane (RDX) and trinitrotoluene (TNT) by [PVI-SO$_3$H]NO$_3$ as nitrating agent.

## General procedure for the preparation of pentaerythritol tetranitrate (PETN)

In a 25 mL round bottom flask containing 1.9 g of [PVI-SO$_3$H]NO$_3$ as reagent, of the pentaerythritol (1 mmol, 0.136 g) was added. Then, 10 mL of CH$_3$CN was added to the reaction mixture and stirred at room temperature for 30 minutes. The reaction was followed by TLC technique. After completion of the reaction, the reagent residue was separated by filtration. The reaction solvent was evaporated. The mixture was extracted with ethyl acetate/water. The organic layer was dried over anhydrous sodium sulfate, filtered off and the solvent was evaporated. The residue was purified by column

chromatography (silica gel, *n*-hexane: ethyl acetate 6/4) to give the desired product.

General procedure for the preparation of trinitrotoluene (TNT)

In a 25 mL flask containing 1.9 g of [PVI-SO$_3$H]NO$_3$ reagent and 1-methyl-4-nitrobenzene (1 mmol, 0.137 g) was added. Then, 10 mL of CH$_3$CN solvent was added to the reaction mixture and stirred for 45 minutes under the reflux condition. The reaction was followed by TLC technique. After completion of the reaction, the reaction mixture was cooled and the reagent residue was separated by filtration. The reaction solvent was
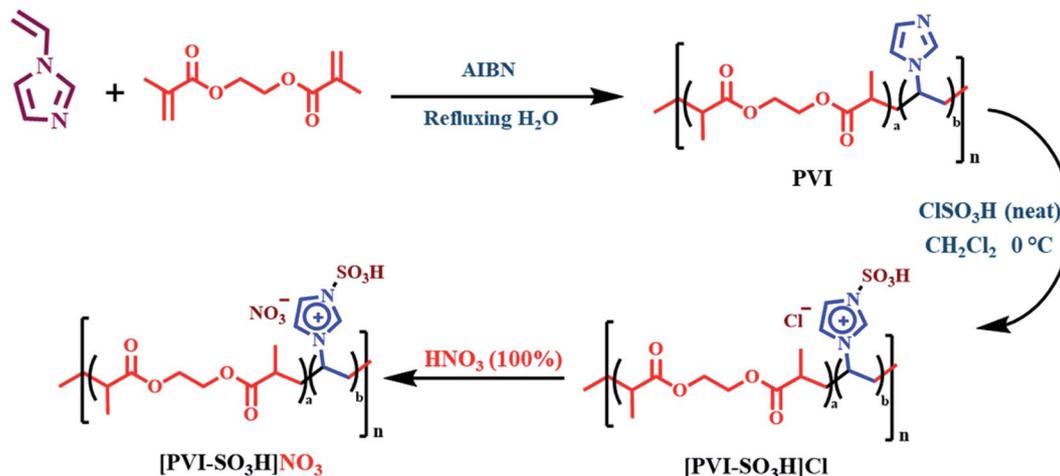
Scheme 3 Preparation of poly(vinyl imidazole) sulfonic acid nitrate [PVI-SO$_3$H]NO$_3$.
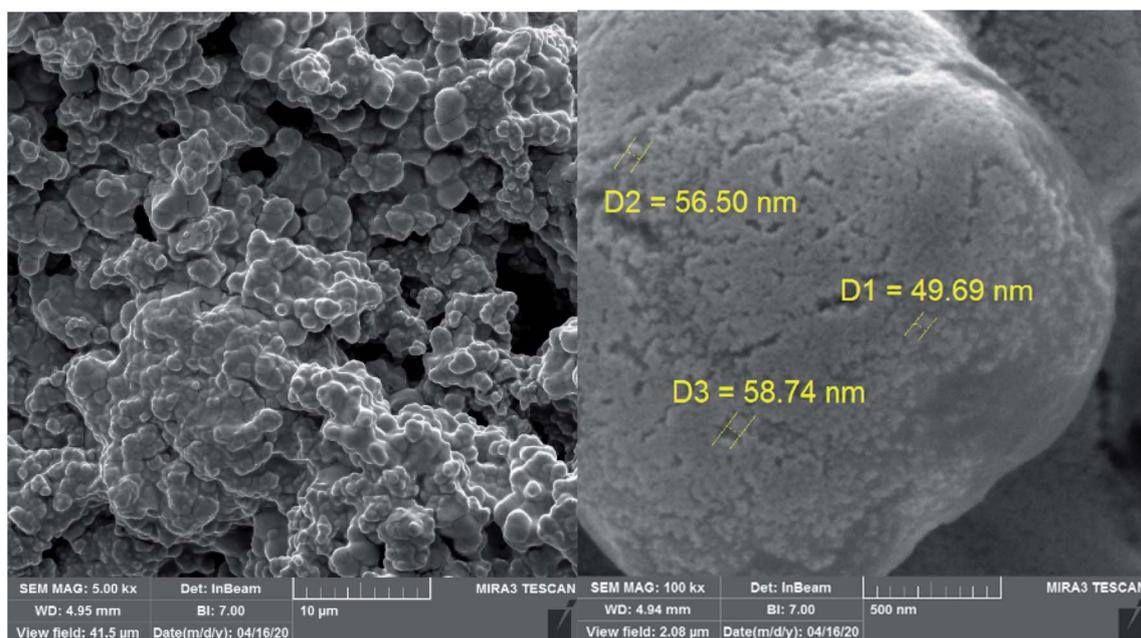

Fig. 1 Scanning electron microscope (SEM) images of [PVI-SO$_3$H]NO$_3$.

evaporated. The mixture was extracted with ethyl acetate/water. The organic layer was dried over anhydrous sodium sulfate, filtered and the solvent was evaporated. The residue was purified by column chromatography (silica gel, *n*-hexane: ethyl acetate 9/1) to give product.

General procedure for the preparation of 1,1-diamino-2,2-dinitroethene (FOX-7)

In a 25 mL flask containing 1.9 g of [PVI-SO$_3$H]NO$_3$ reagent and 2-methylpyrimidine-4,6(1*H*,5*H*)-dione (1 mmol, 0.126 g) was added. Then, 10 mL of CH$_3$CN solvent was added to the reaction mixture and stirred for 60 minutes under the reflux condition. Reaction progress was followed by TLC technique (*n*-hexane: ethyl acetate 3/7). After completion of the reaction, the reagent

was separated by filtration and 10 mL water was then added to the reaction mixture to perform the hydrolysis (for 10 minutes). The pure product was then recrystallized in water solvent.

General procedure for the preparation of 1,3,5-trinitro-1,3,5-triazinane (RDX)

In a 25 mL flask containing 1.9 g of [PVI-SO$_3$H]NO$_3$ reagent and hexamethylenetetramine (1 mmol, 0.140 g) was added. Then, 10 mL of CH$_3$CN solvent was added to the reaction mixture and stirred at room temperature for 20 minutes. The reaction was followed by TLC technique and after completion of the reaction, the reagent was separated by filtration. The reaction solvent was evaporated. The mixture was extracted with ethyl acetate/water. The organic layer was dried over anhydrous sodium sulfate,

filtered and the solvent was evaporated. The residue was purified by column chromatography (silica gel, *n*-hexane: ethyl acetate 6/4) to give product.
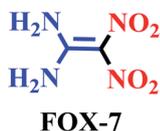
PETN
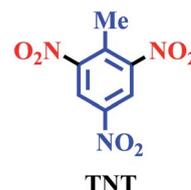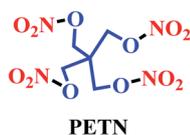
2,2-Bis((nitrooxy)methyl)propane-1,3-diyl dinitrate

White solid; Mp (°C): 142–145; FT-IR (KBr, cm^{-1}): 3029, 2983, 1646, 1271, 868. ^{1}H NMR (600 MHz, DMSO) δ: 4.70 (s, 8H). ^{13}C NMR (101 MHz, DMSO) δ: 70.1, 40.6.

RDX

1,3,5-Trinitro-1,3,5-triazinane

White solid; Mp (°C): 203–205; FT-IR (KBr, cm^{-1}): 3074, 3065, 3001, 1573. ^{1}H NMR (600 MHz, DMSO) δ: 6.11 (t, $J = 4.5$ Hz, 6H). ^{13}C NMR (101 MHz, DMSO) δ: 61.1.

FOX-7

2,2-Dinitroethene-1,1-diamine

Yellow solid; Mp (°C): 235–238; FT-IR (KBr, cm^{-1}): 3424, 3332, 3300, 1637, 1521. ^{1}H NMR (600 MHz, DMSO) δ: 9.00 (s, 2H), 8.58 (s, 2H). ^{13}C NMR (101 MHz, DMSO) δ: 158.0, 127.7.

TNT

2-Methyl-1,3,5-trinitrobenzene

Brown solid; Mp (°C): 83–85; FT-IR (KBr, cm^{-1}): 3096, 1602, 1617, 1538. ^{1}H NMR (600 MHz, DMSO) δ: 9.03 (s, 2H), 2.57 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ: 150.7, 145.6, 132.9, 122.5, 14.8.

Results and discussion

As above said, during three decades our investigations on the field of nitration of organic compounds,[35–43] herein we report poly(vinyl imidazole) sulfonic acid nitrate [PVI-SO$_3$H]NO$_3$ as a novel polymeric nitrating agent for preparation of four energetic materials (Scheme 3). After synthesis of described [PVI-SO$_3$H]NO$_3$ its structure was fully characterized by FT-IR, energy dispersive X-ray spectroscopy (EDX), SEM-elemental mapping, scanning electron microscope (SEM), thermal gravimetric (TG) and derivative thermal gravimetric (DTG). Then, [PVI-SO$_3$H]NO$_3$ was applied for the preparation of energetic materials such as 1,1-diamino-2,2-dinitroethene (FOX-7), pentaerythritol tetranitrate (PETN), 1,3,5-trinitro-1,3,5-triazinane (RDX) and trinitrotoluene (TNT) (Scheme 2).

The comparison FT-IR spectrum of [PVI-SO$_3$H]NO$_3$ and [PVI-SO$_3$H]Cl were showed in (Fig. S1 see in ESI†). As it is shown in Fig. S1,† a broad peak was displayed at about 2400–3500 cm^{-1} related to OH of SO$_3$H groups. The peak at about 1376 cm^{-1} is corresponded to asymmetric and symmetric vibration of O–N= O. Also, the peak at about 1722 cm^{-1} was attributed to C=O
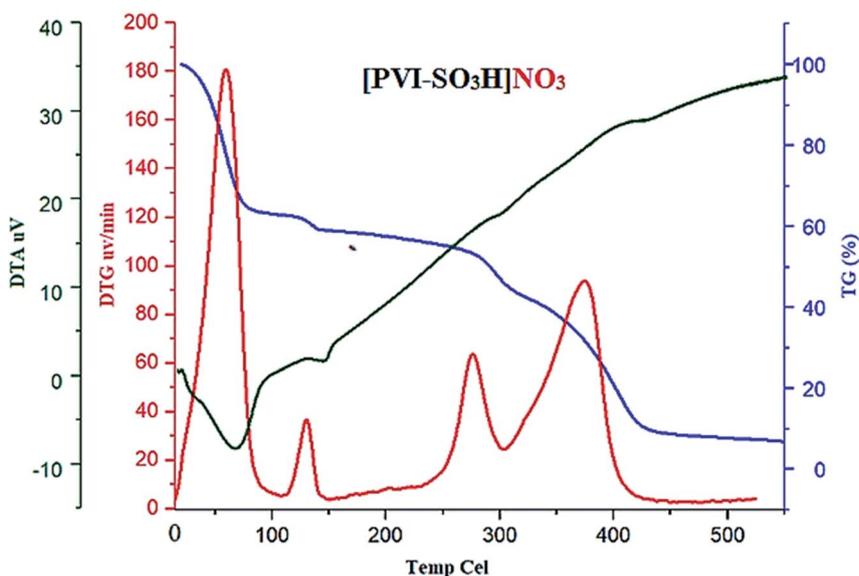

Fig. 2 Thermal gravimetric (TG), derivative thermal gravimetric (DTG), as well as the differential thermal analysis (DTA) of [PVI-SO$_3$H]NO$_3$.

Table 1 Effect of different temperature and solvent on the synthesis of explosive materials

Entry	Solvent	Temp. (°C)	Amount of reagent (g)	Time (min)	Yield (%)			
					PETN	RDX	FOX-7	TNT
1	EtOH	Reflux	1.9	120	—	—	—	—
2	MeOH	Reflux	1.9	120	—	—	—	—
3	*n*-Hexane	Reflux	1.9	120	—	—	—	—
4	Acetone	Reflux	1.9	120	28	34	—	17
5	CHCl$_3$	Reflux	1.9	120	32	38	28	30
6	H$_2$O	Reflux	1.9	120	—	—	—	—
7	DMF	100	1.9	120	—	15	40	38
8	CH$_2$Cl$_2$	Reflux	1.9	120	45	50	15	35
9	EtOAc	Reflux	1.9	120	—	—	—	—
10	Toluene	Reflux	1.9	120	15	—	—	32
11	**CH$_3$CN**	**25**	**1.9**	**30**	**85**	—	—	—
		Reflux	1.9	60	—	—	82	—
		25	1.9	20	—	75	—	—
		Reflux	1.9	45	—	—	—	70
12	CH$_3$CN	—	1.5	—	62	58	72	62
			1.3	—	48	43	38	40
			1	—	—	—	—	—
			0.5	—	—	—	—	—
			—	—	—	—	—	—

group. Furthermore, peaks at about 1234 and 1239 cm^{-1} were corresponded to N–SO$_2$ and O–SO$_2$ bonds respectively.
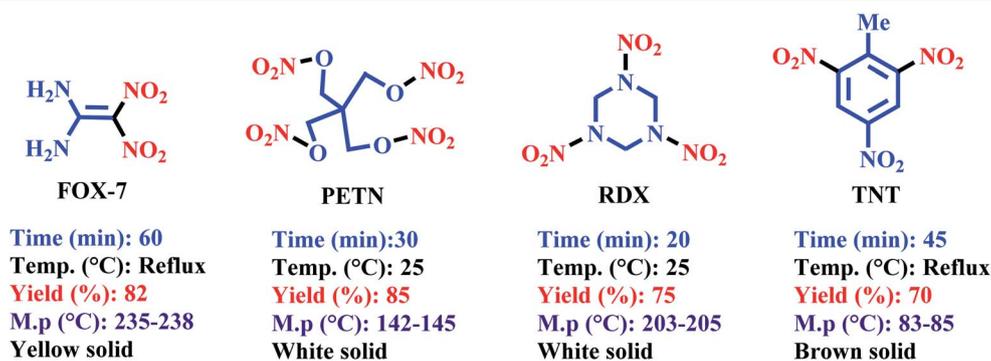
The structure of the [PVI-SO$_3$H]NO$_3$ was also approved by SEM-EDS analysis (Fig. S2 see in ESI†). The existence of C, O, N and S atoms was verified the structure of the described nitrating agent [PVI-SO$_3$H]NO$_3$. Then, SEM-elemental mapping (C, O, N and S) in the reagent with a well-dispersed over the reagent surface was confirmed (Fig. S2 see in ESI†).
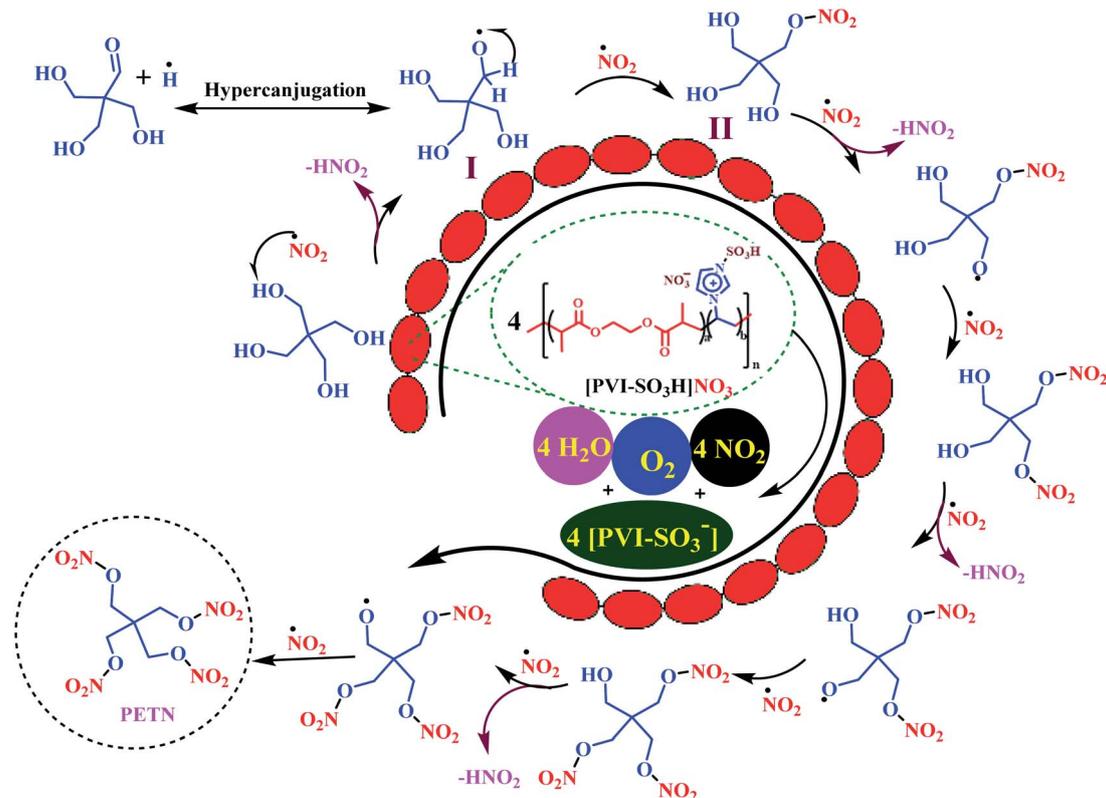
The scanning electron microscopy (SEM) micrographs of [PVI-SO$_3$H]NO$_3$ was shown in Fig. 1. As can be seen from SEM micrographs, the morphology of reagent indicating a complete surface morphology change caused by adding of HNO$_3$ to [PVI-SO$_3$H]Cl.[46] However, the shape of particles is cauliflower and nano-scales.

In another investigation, structural and thermal stability of [PVI-SO$_3$H]NO$_3$ was also determined using thermal gravimetric (TG), derivative thermal gravimetric (DTG), as well as the differential thermal analysis (DTA) (Fig. 2). Initial stage weight losing is about 100 °C, associated with the removal of possible solvents (organic and water) which was used in the course of reagent preparation. Then, the loss of weight of the reagent at 160 °C was related to release of NO$_2$. Also, another step of weight losing was occurred about 300 °C which is the onset of the structural degradation of [PVI-SO$_3$H]NO$_3$.

After the synthesis and full characterization of [PVI-SO$_3$H]NO$_3$ it was applied for the preparation of high-energetic materials such as FOX-7 (1,1-diamino-2,2-dinitroethene), pentaerythritol tetranitrate (PETN), 1,3,5-trinitro-1,3,5-triazinane (RDX) and trinitrotoluene (TNT). The mentioned nitro materials derivatives were synthesized *via* a nitration reaction of the corresponding starting materials (pentaerythritol, 1-methyl-4-nitrobenzene, 2-methylpyrimidine-4,6(1*H*,5*H*)-dione, hexamethylenetetramine) in the presence of [PVI-SO$_3$H]NO$_3$. The nitration of starting materials (1 mmol) and [PVI-SO$_3$H]NO$_3$ as

Table 2 Synthesis of 1,1-diamino-2,2-dinitroethene (FOX-7), pentaerythritol tetranitrate (PETN), 1,3,5-triazinane (RDX) and trinitrotoluene (TNT) by [PVI-SO$_3$H]NO$_3$

FOX-7	PETN	RDX	TNT
Time (min): 60	Time (min): 30	Time (min): 20	Time (min): 45
Temp. (°C): Reflux	Temp. (°C): 25	Temp. (°C): 25	Temp. (°C): Reflux
Yield (%): 82	Yield (%): 85	Yield (%): 75	Yield (%): 70
M.p (°C): 235–238	M.p (°C): 142–145	M.p (°C): 203–205	M.p (°C): 83–85
Yellow solid	White solid	White solid	Brown solid

Scheme 4 A plausible mechanism for the preparation of PETN.

a nitrating agent was optimized. As shown in Table 1, the worthy results were obtained when the reaction was achieved in CH$_3$CN as solvent (Table 1, entry 11). No improvement was detected in the yield of reaction using different solvent and temperature (Table 1, entry 1–10). The results are summarized in Table 1. As shown in Table 1, no improvement the best yield for the synthesis of high-energetic materials were obtained

using other molar ratios of [PVI-SO$_3$H]NO$_3$ at room temperature or refluxing CH$_3$CN (Table 1, entry 12).

CAUTION: During the synthesis of high-energetic materials the temperature of the reaction should be slowly increased and on workup, shock, heat, friction, and impact on the product must be avoided.

Table 3 Comparison of the performance of [PVI-SO$_3$H]NO$_3$ for the synthesis of explosive materials with other nitrating reagents

Entry	Nitrating system	Solvent	Time (min)	Yield (%)			
				PETN	RDX	FOX-7	TNT
1	HNO$_3$/AIBN	—	120	52	43	32	28
2	Cr(NO$_3$)$_3$. 6H$_2$O/HNO$_3$	—	120	20	—	Trace	—
3	Cr(NO$_3$)$_3$·6H$_2$O	CH$_3$CN	120	—	Trace	—	Trace
4	Cu(NO$_3$)$_2$·3H$_2$O	CH$_3$CN	120	—	—	—	—
5	Fe(NO$_3$)$_3$·9H$_2$O	CH$_3$CN	120	Trace	Trace	—	—
6	SSA/NaNO$_3$ (ref. 47)	CH$_3$CN	120	—	20	25	—
7	HNO$_3$	—	120	38	32	18	27
8	SSA/HNO$_3$ (ref. 47)	—	120	Trace	22	—	20
9	[Msim]NO$_3$	—	120	56	60	48	40
10	Fe(NO$_3$)$_3$·9H$_2$O/FeCl$_3$	CH$_3$CN	120	Trace	—	—	—
11	Ce(HSO$_4$)$_3$·7H$_2$O/HNO$_3$	—	120	28	15	Trace	20
12[a]	[PVI-SO$_3$H]NO[a]	CH$_3$CN	30	85	—	—	—
			60	—	—	82	—
			20	—	75	—	—
			45	—	—	—	70

[a] This work.

After the optimization of the reaction conditions (Table 1), the best result for the synthesis of explosive materials such as 1,1-diamino-2,2-dinitroethene (FOX-7), pentaerythritol tetranitrate (PETN), 1,3,5-trinitro-1,3,5-triazinane (RDX) and trinitrotoluene (TNT) were obtained using [PVI-SO$_3$H]NO$_3$ 1.9 g at room temperature and refluxing CH$_3$CN (Table 2).

Plausible mechanisms for the preparation of explosive materials were show in Scheme 4 here and Schemes S1–S3 in the ESI.† At first, starting materials (pentaerythritol, 1-methyl-4-nitrobenzene, 2-methylpyrimidine-4,6(1H,5H)-dione, hexamethylenetetramine) reacts with the *in situ* generated NO$_2$ radical released from [PVI-SO$_3$H]NO$_3$ to produce intermediate **I** and nitrous acid (HNO$_2$). Then, intermediate **I** reacts with the NO$_2$ radical (released from [PVI-SO$_3$H]NO$_3$) to afford intermediate **II**. Then, these processes are repeated to obtain the final products.

To compare the performance of [PVI-SO$_3$H]NO$_3$ for the synthesis of desired nitro materials such as 1,1-diamino-2,2-dinitroethene (FOX-7), pentaerythritol tetranitrate (PETN), 1,3,5-trinitro-1,3,5-triazinane (RDX) and trinitrotoluene (TNT), we have used various organic and inorganic nitrating reagents. As Table 3 indicates, [PVI-SO$_3$H]NO$_3$ is the best of choice for the synthesis of explosive materials (Table 3).

Conclusion

We have prepared poly(vinyl imidazole) sulfonic acid nitrate [PVI-SO$_3$H]NO$_3$ as a novel polymeric nitrating agent for preparation of four energetic materials. [PVI-SO$_3$H]NO$_3$ successfully used for the preparation of FOX-7 (1,1-diamino-2,2-dinitroethene), pentaerythritol tetranitrate (PETN), 1,3,5-trinitro-1,3,5-triazinane (RDX) and trinitrotoluene (TNT). Also, major advantages of the described methodology are high yield of products without using any co-catalysts, low temperature, short reaction times and generality for the preparation of energetic materials.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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