

Synthesis and Characterization of Poly(vinyl 2,4,6-trinitrophenylacetal) as a New Energetic Binder

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ABSTRACT: Poly(vinyl alcohol) was modified by an aldehyde acetal reaction with 2,4,6-trinitrophenylacetaldehyde to give a new energetic polymer poly(vinyl 2,4,6-trinitrophenylacetal) (PVTNP). The structure of PVTNP was characterized by elemental analysis, ultraviolet–visible spectroscopy, Fourier transform infrared spectroscopy, and nuclear magnetic resonance spectra. The glass-transition temperature of PVTNP was evaluated by differential scanning calorimetry (DSC), and the thermal stability of PVTNP was tested by differential thermal analysis (DTA)

and thermogravimetric analysis (TGA). DSC traces showed that the PVTNP polymer had one single glass-transition temperature at 105.3°C. DTA and TGA curves showed that the thermooxidative degradation of PVTNP in air was a three-step reaction, and the percentage of degraded PVTNP reached nearly 100% at 650°C. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 1643–1648, 2011

Key words: additives; FTIR; polymer synthesis and characterization; synthesis; thermal properties

INTRODUCTION

With the development of weapons systems, most of single-compound explosives cannot fully meet the requirements of weapons development, and other components, such as energetic binders, need to be added to improve the performance of explosives. Generally, energetic binders are considered to be crosslinked polymers that provide a matrix in which to bind the explosive ingredients together with a particulate particle oxidizer, burning rate catalyst, plasticizer, and so forth; this results in a tough elastomeric three-dimensional network structure capable of absorbing and dissipating energy from hazardous stimuli. This lends the binders well to insensitive munitions applications.^{1–3} In addition to these standard specifications, energetic binders can give a significant contribution to the detonation velocity and propellant impulse thanks to their content of azido groups ($-\text{N}_3$), nitrate esters ($-\text{O}-\text{NO}_2$), nitramines

($-\text{N}-\text{NO}_2$), and aliphatic or aromatic C-nitro groups ($-\text{C}-\text{NO}_2$).

During the past 4 decades, a large number of energetic binders that can, or might, find applications in propellants or plastic-bonded explosives have been synthesized and examined. They include azido polymers,^{3–14} nitrate ester polymers,^{15–20} and aliphatic and aromatic nitro polymers.^{21,22} Nevertheless, almost all of the efforts have been in the investigation of azido polymers and nitrate ester polymers. There have been very few studies reported on the synthesis of aromatic nitro polymers. In this article, we report the synthesis and characterization of an aromatic nitro polymer, poly(vinyl 2,4,6-trinitrophenylacetal) (PVTNP), through the aldehyde acetal reaction of poly(vinyl alcohol) (PVA) and 2,4,6-trinitrophenylacetaldehyde (TNPA or **2**).

EXPERIMENTAL

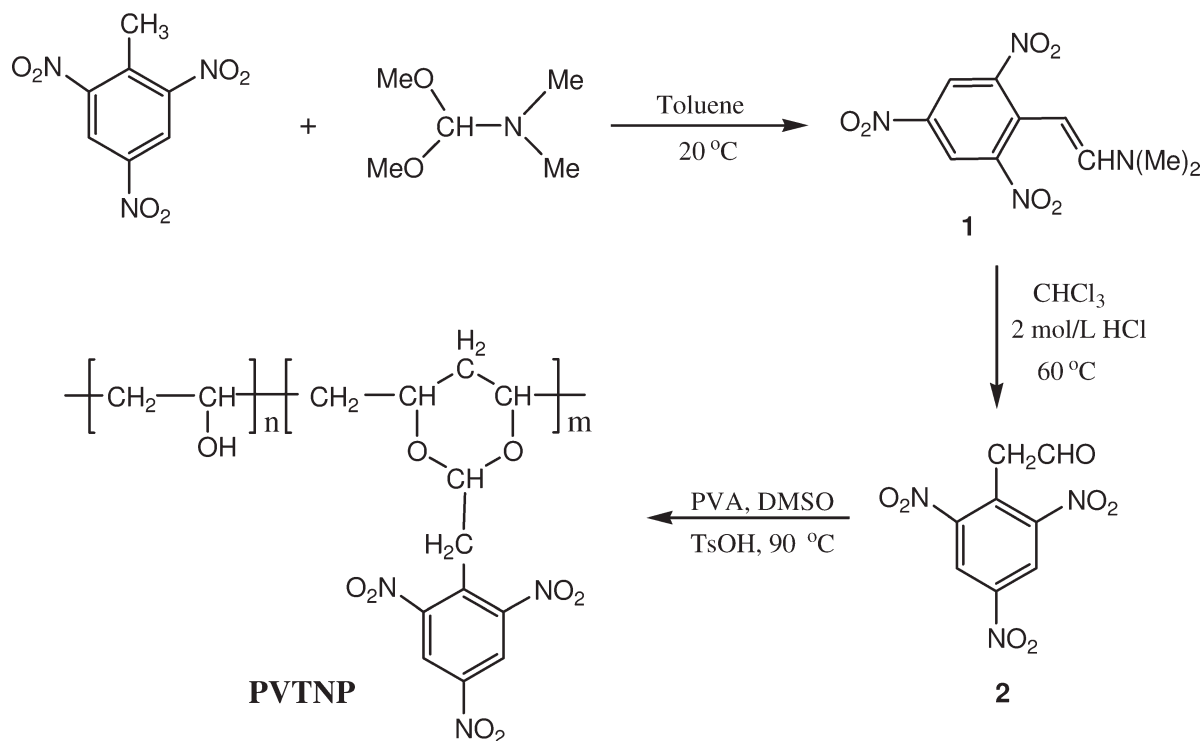
Materials

PVA (mean degree of polymerization = 1700 ± 50 , hydrolysis degree = 99%) was purchased from Chengdu Kelong Chemical Reagents Co. 2,4,6-Trinitrotoluene was afforded by the Institute of Chemical Materials, Chinese Academy of Engineering Physics (Mianyang, Sichuan). Dimethylformamide dimethyl acetal was purchased from Shanghai Jiachen Chemical Co., Ltd. Toluene, chloroform,

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Scheme 1 Synthesis of PVTNP.

petroleum ether, *p*-toluene sulfonic acid, and dimethyl sulfoxide (DMSO) were supplied by Chengdu Kelong Chemical Reagents Co. All solvents for the reactions were analytical grade and were dried before use.

Instruments

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Advance DRX 400-MHz instrument with hexadeuterated DMSO as the solvent and tetramethylsilane as the internal standard. Elemental analyses (EAs) were carried out with a Vario EL CUBE device (Germany). The ultraviolet-visible (UV-vis) spectra were recorded on a UNICON UV-2102 PCS spectrometer with DMSO as the solvent. The infrared spectra were measured on Nicolet 6700 Fourier transform infrared (FTIR) spectrometer (KBr pellet) with a resolution of 4 cm^{-1} in the range $4000\text{--}400\text{ cm}^{-1}$. Differential thermal analysis (DTA) curves were recorded on a WCR-1B analyzer (Beijing Optical Instrument Factory, China) at a heating rate of $10^\circ\text{C}/\text{min}$ under atmosphere with the reference $\alpha\text{-Al}_2\text{O}_3$. Differential scanning calorimetry (DSC) was carried out on a Q200 DSC instrument (TA Instruments) at a heating rate of $10^\circ\text{C}/\text{min}$ under atmosphere. Thermogravimetric analysis (TGA) was performed with a SDT Q600 TGA instrument (TA Instruments) at a heating rate of $10^\circ\text{C}/\text{min}$ under atmosphere.

Synthesis

The chemical structure and the general procedure for the synthesis of the PVTNP are presented in Scheme 1.

Synthesis of β -dimethylamino-2,4,6-trinitrostyrene (compound 1)

2,4,6-Trinitrotoluene (34.1 g, 0.15 mol) and 18.0 g of dimethylformamide dimethyl acetal (0.15 mol) were dissolved in 100 mL of toluene at 20°C in a round-bottom flask. The reaction mixture was stirred at 20°C for 24 h. The precipitate that formed was filtered off, washed with cold toluene (30 mL), and dried *in vacuo* at 50°C to afford compound 1 in a yield of 30.6 g (72%).

mp = $166\text{--}167^\circ\text{C}$. IR (KBr, ν , cm^{-1}): 3105 ($\nu_{\text{Ar-H}}$); 3074 ($\nu_{\text{C-H}}$); 2956, 2854, 1627 ($\nu_{\text{C=C}}$); 1577 (ν_{Ar}); 1533 [$\nu_{\text{as}}(\text{NO}_2)$]; 1511 (ν_{Ar}); 1451 (ν_{Ar}); 1398, 1323 [$\nu_{\text{s}}(\text{NO}_2)$]; 1286, 1162, 1112, 1087, 875, 795.

Synthesis of compound 2

Compound 1 (28.2 g, 0.1 mol) was dissolved in 175 mL of chloroform in a 1000-mL, three-necked flask with continuous stirring; then, 225 mL of a 2.0 mol/L hydrochloride solution was added at room temperature. The reaction mixture was stirred at reflux temperature for 9 h. After cooling to room temperature, the water layer was removed by liquid-liquid separation, and the chloroform layer was

TABLE I
Condensation Degrees of PVTNP under Different Reaction Conditions

Entry	OH/TNPA ratio	Reaction temperature (°C)	Reaction time (h)	Condensation degree (%)
1	1.8/1	80	10	48
2	2/1	80	10	48
3	2/1	70	10	35
4	2/1	90	10	61
5	2/1	100	10	56
6	2/1	90	3	40
7	2/1	90	7	55
8	2/1	90	24	58
9	2/1	90	48	57

poured on 1000 mL of petroleum ether to afford TNPA (2) in a yield of 21.2 g (83%).

mp = 90–91°C (cf. literature data:²³ 90–91°C). UV-vis [CHCl_3 , maximum absorption (λ_{max}), nm]: 248 (s). IR (KBr, ν , cm^{-1}): 3097 ($\nu_{\text{Ar-H}}$); 2925 ($\nu_{\text{C-H}}$); 2862, 2730 ($\nu_{\text{O=C-H}}$); 1721 ($\nu_{\text{C=O}}$); 1609 (ν_{Ar}); 1541 [$\nu_{\text{as(NO}_2)}$]; 1349 [$\nu_{\text{s(NO}_2)}$]; 1301, 1161, 1112, 1084, 920, 823, 774, 725. $^1\text{H-NMR}$ (CDCl_3 , 400 MHz, δ , ppm): 9.82 (O=C-H, s, 1H), 9.04 (Ar-H, s, 2H), 4.53 (CH_2 , s, 2H). $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz, δ , ppm): 192.32 (C=O); 151.52 (2C); 146.90, 129.61, 123.31 (2C); 42.93 (CH_2). mass spectra (MS) [electrospray Ionisation (ESI), m/z]: 256 [$\text{M}+1$]⁺. ANAL. Calcd for $\text{C}_8\text{H}_5\text{O}_7\text{N}_3$: C, 36.35%; H, 2.12%; N, 16.63%. Found: C, 36.32%; H, 2.14%; N, 16.57%.

Synthesis of PVTNP

PVA (10.0 g, 0.23 mol —OH) and DMSO (150 mL) were introduced into a three-necked flask equipped with a condenser, a mechanical stirrer, and a thermometer. The reaction mixture was heated slowly until the polymer was dissolved in the solvent. To this reaction mixture, 29.3 g of TNPA (2; 0.115 mol) and 0.86 g of *p*-toluene sulfonic acid (0.005 mol) were added. The reaction mixture was stirred at 90°C for 10 h. Thereafter, the reaction solution was poured into 500 mL of distilled water, and the polymer was precipitated and separated out. The polymer was repeatedly washed with chloroform and water until the washings were free from *p*-toluene sulfonic acid and TNPA. The polymer was then dried *in vacuo* at 50°C to afford 26.5 g of PVTNP.

The condensation degree of PVTNP was calculated as follows:

$$\text{Condensation degree}(\%) = \frac{88(M_2 - M_1)}{237M_1} \times 100$$

where M_1 is the initial weight of PVA and M_2 is the final weight of the PVTNP.

RESULTS AND DISCUSSION

PVTNP synthesis and characterization

PVA is a polyhydroxylated polymer, and the hydroxyl can be easily modified to afford other functionalization polymers.^{24–31} Through the aldehyde acetal reaction of PVA and TNPA, an aromatic nitro polymer, PVTNP, was obtained. This reaction was carried out from PVA and TNPA with *p*-toluene sulfonic acid as a catalyst. To get the maximum degree of condensation, two different PVA(—OH):TNPA ratios (2 : 1 and 1.8 : 1) were used, but increasing the amount of TNPA did not increase the degree of condensation, as shown in Table I. Likewise, the use of temperatures higher than 90°C did not improve the results. Different reaction times were also tested (3 h, 7 h, 10 h, 1 day, and 2 days), but a noteworthy increase in the condensation degree was only observed at first, and the maximum degree of condensation was reached at 10 h. Longer time did not improve the degree of condensation. This suggests that a plateau (61%) was reached at 90°C for a 10-h reaction.

The EA data of PVTNP are listed in Table II. The calculated components are presented for comparison. As shown in Table II, the measurement results were in agreement with the theoretical values.

The FTIR spectra in Figure 1 show the change in the chemical structure of the original and modified PVA, respectively. As shown in Figure 1(a), the characteristic adsorption peak at 3334 cm^{-1} explained the O—H stretching vibration of PVA, and the bands around 2942, 2912, and 2856 cm^{-1} accounted for the C—H symmetric and antisymmetric stretching vibration of PVA. A weak peak at 1716 cm^{-1} informed about the C=O group present in PVA (vinyl acetate group).³² The FTIR spectrum of PVTNP is presented in Figure 1(b). When compared with the original PVA [Fig. 1(a)], a reduction in the

TABLE II
EA Data of PVTNP

Sample	Carbon (%)		Hydrogen (%)		Nitrogen (%)	
	Calculated	Measured	Calculated	Measured	Calculated	Measured
PVTNP	45.12	45.07	3.84	3.90	11.89	11.85

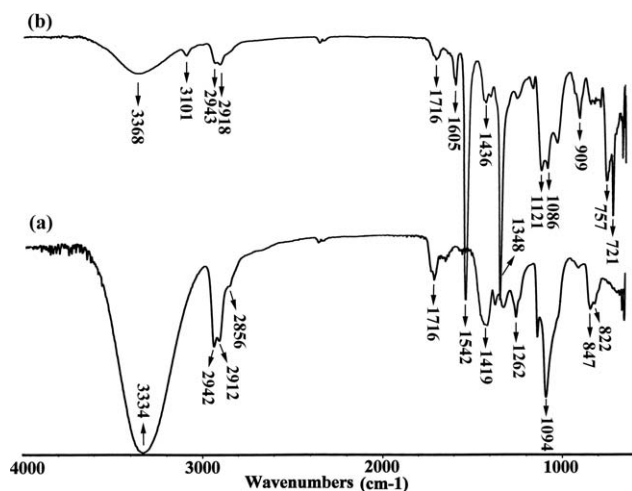


Figure 1 FTIR spectrum of (a) PVA and (b) PVTNP.

intensity of the O—H stretching vibration peak is shown in Figure 1(b); this resulted from the reaction of TNPA with the —OH groups of PVA. The new peaks in Figure 1(b) at 3101 and 1605 cm^{-1} were due to the aromatic ring C—H stretching vibration and the aromatic ring skeleton stretching vibration, respectively. The new bands at 1542 and 1348 cm^{-1} in Figure 1(b) were attributed to the —NO₂ antisymmetric and symmetric stretching vibrations, respectively. The new bands at 909 and 757 cm^{-1} were attributed to the C—N stretching vibration and C—N—O bending vibration, respectively. The new peak at 721 cm^{-1} was due to the aromatic ring C—H out-of-plane bending vibration. Therefore, such results gave strong evidence that the reaction of the PVA with TNPA indeed occurred by the formation of acetal.

The UV-vis spectrum of PVTNP is presented in Figure 2. As shown in Figure 2, the UV-vis spectrum of PVTNP showed an absorption band in the region from 250 to 400 nm, and λ_{max} was at 280 nm.

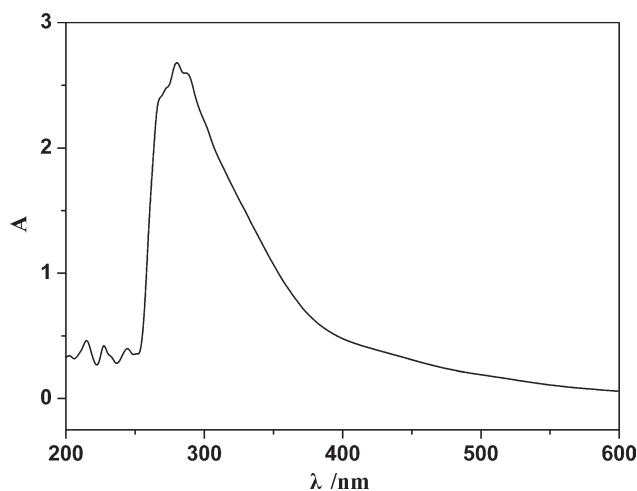


Figure 2 UV-vis spectrum of PVTNP. A = absorbency.

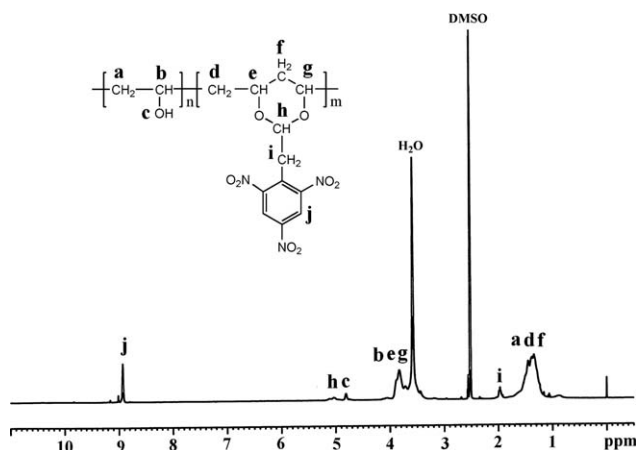


Figure 3 ¹H-NMR spectrum of PVTNP.

Therefore, the absorption in the region from 250 to 400 nm could be considered to be caused by the trinitrophenyl group in the polymer chain.

The ¹H-NMR spectrum of PVTNP is presented in Figure 3. The signals observed at 1.1–1.7 ppm were ascribed to the methylene protons (denoted a, d, and f) of the main chain. The signals at 3.30–4.00 ppm were due to the methine (denoted b, e, and g) of the main chain. The hydroxyl proton (denoted c) of the unmodified PVA appeared in the region 4.75–4.85. In addition to the previously discussed peaks, the characteristic peaks corresponding to the protons of the side chain were observed in their spectra. The peak at 8.93 ppm was attributed to the aromatic ring protons (denoted j), and the peaks at 1.85–2.05 ppm were attributed to the methylene protons (denoted i) of the side chain. The peaks at 4.90–5.20 ppm corresponded to the methine proton (denoted h) of the side chain. These peak positions in the ¹H-NMR spectrum of PVTNP strictly corroborated the UV-vis and IR analyses that the reaction of the PVA with TNPA indeed occurred by the formation of acetal.

The structure of PVTNP was also confirmed with the ¹³C-NMR spectrum. As shown in Figure 4, the spectrum showed the expected peaks for the methylene carbons of the main chain (denoted a, c, and e), the methine carbons of the main chain (denoted b, d, and f), the methylene carbon of the side chain (denoted h), the methine carbon of the side chain (denoted g), and the aromatic ring carbons of the side chain (denoted i, j, k, and l).

PVTNP thermal properties

It is well known that the thermal stability is an important property for energetic materials and their additives. So, the DTA method was adopted to study the stability of PVTNP. Figure 5 shows the DTA curves of PVA and PVTNP. In Figure 5, the DTA curve of PVA showed one endothermic peak

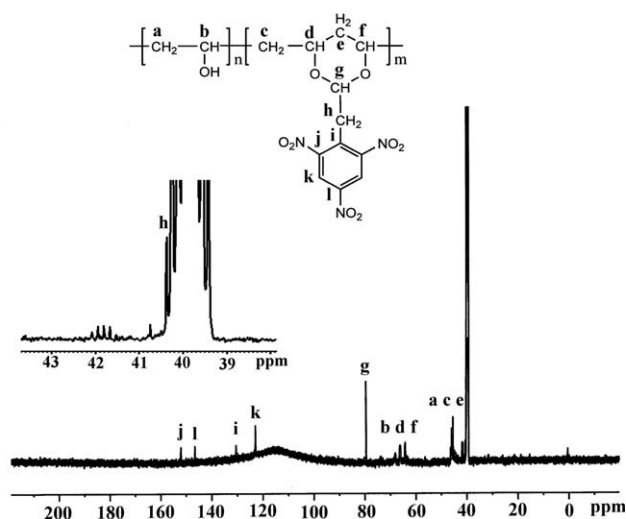


Figure 4 ^{13}C -NMR spectrum of PVTNP.

and three exothermic peaks. The endothermic peak at 221°C was the phase change from solid to liquid.³³ The endothermic peaks at 377 , 426 , and 505°C were caused by the main-chain decomposition reaction of PVA. The DTA curve of PVTNP showed three exothermic peaks. The first peak at 256°C and the second peak at 302°C were caused by the decomposition of the side chain, and the third peak at 532°C was due to the main-chain decomposition of PVTNP.

TGA is one of the commonly used techniques for rapid evaluation of the thermal stability of different materials. The TGA and derivative thermogravimetry (DTG) curves of PVTNP are shown in Figure 6. The first weight loss temperature at 221.5°C corresponded to the stripping of the aromatic ring of the side chain. The second main weight loss at 534.2°C , observed in Figure 6, was due to the main-chain thermal decomposition of PVTNP. The small shoulder between the two main weight losses

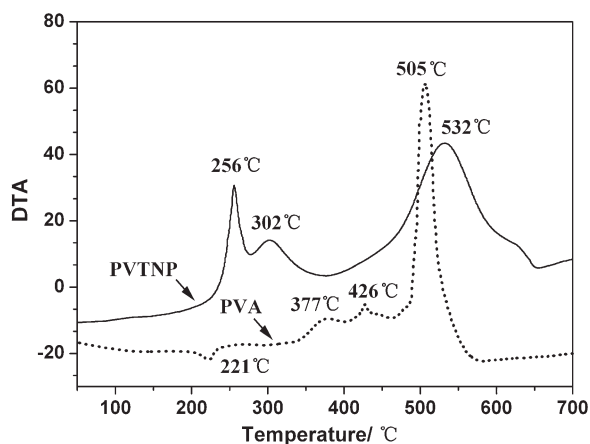


Figure 5 DTA curves of PVA and PVTNP.

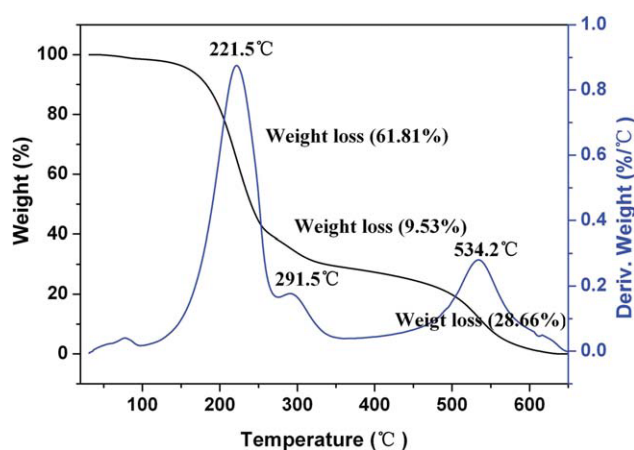


Figure 6 TGA and DTG curves of PVTNP. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

observed in the DTG curve of PVTNP arose from the slight overlapping of the first-stage weight loss peak of the aromatic ring and the weight loss peak of $-\text{CH}_2\text{CHO}-$ group of the side chain.

To understand the thermal behavior of PVTNP well, the glass-transition temperature (T_g) of PVTNP was recorded by DSC. Figure 7 shows the DSC curve of PVTNP from -50 to 150°C . It is shown that PVTNP had a single T_g at about 105.3°C .

CONCLUSIONS

In this study, a new energetic polymer, PVTNP, was synthesized through the aldehyde acetal reaction of PVA and 2,4,6-trinitrophenylacetal. The structure of PVTNP was confirmed, and their thermal properties were studied. The important points are presented here as conclusions. A peak at 3101 cm^{-1} in FTIR spectroscopy confirmed the C—H stretching vibration of the aromatic ring, and two peaks 1542 and 1348 cm^{-1} in FTIR spectroscopy confirmed the

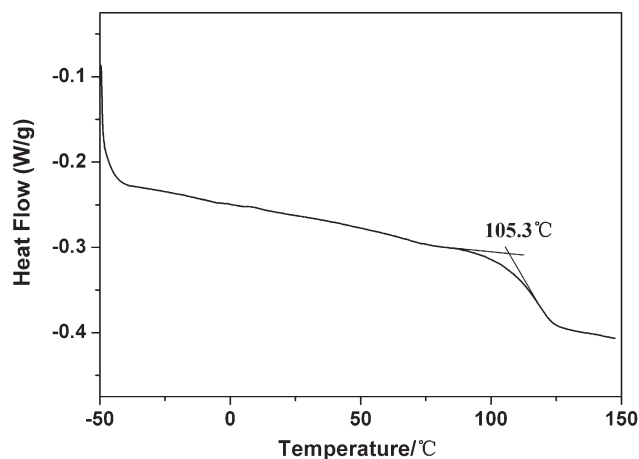


Figure 7 DSC curve of PVTNP.

—NO₂ antisymmetric and symmetric stretching vibrations, respectively. The aromatic ring protons peak of PVTNP appeared at 8.93 ppm in ¹H-NMR, and the aromatic ring carbon peaks of PVTNP appeared at 152.08, 146.62, 130.56, and 123.03 ppm in ¹³C-NMR. The *T_g* of the polymer PVTNP could be seen at 105.3°C. The thermooxidative degradation of PVTNP in air was a three-step reaction. The first decomposition occurred at 221.5°C, and about 61.81% of the polymer was degraded. The second degradation occurred at 291.5°C, and about 9.53% of the polymer was degraded. The third decomposition occurred at 534.2°C, and about 28.66% of the polymer was degraded. The percentage of degraded PVTNP reached nearly 100% at 650°C. Further experiments will be carried out to demonstrate its capacity for a new energetic binder.

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