

# Synthesis and Characterisation of Poly(aminotrinitrophenylene)

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## ABSTRACT

Poly(aminotrinitrophenylene) (PATNP), a thermally-stable explosive has been synthesised by ring amination of polynitropolyphenylene (PNP) using hydroxylamine hydrochloride in dimethyl formamide in the presence of alcoholic *KOH*. The compound has been characterised by infrared and differential thermal analysis (DTA), which showed an exothermic peak in the range 450-560 °C. Impact and friction sensitivities of PATNP were found to be less than those of PNP. Calorimetric value of the new compound was 3284 J/g.

## 1. INTRODUCTION

With the advent of supersonic aircraft, missiles and space exploration, heat-resistant explosives have acquired great importance. Explosive stores carried externally on high speed aircraft at low altitudes are subjected to aerodynamic heating, resulting in high temperature of the explosive fillings. For such applications, conventional explosives (TNT, PETN, RDX, etc.) have limitations and there is a need for developing thermally-stable explosives (TSEs) which are also insensitive to friction. A number of TSEs are reported in the literature<sup>1-3</sup>. However, thermal stability beyond 350 °C is very uncommon. It is a fact that presence of intramolecular hydrogen bonding increases rigidity of the molecule and favours physical and thermal stability<sup>4</sup>. Polynitropolyphenylene (PNP) is a known compound having aryl-nitro groups in a chain of benzene units. During the search for thermally-stable compounds, an attempt was made to introduce amino group in PNP molecule to enhance

its thermal stability. This paper presents the synthesis, characterisation, and thermal and explosives properties of poly(aminotrinitrophenylene) (PATNP).

## 2. EXPERIMENTAL PROCEDURE

Styphnic acid of 99 per cent purity,  $POCl_3$  (analytical grade) obtained from Riedel de Haen, electrolytic grade copper of 99.5 per cent purity and hydroxylamine hydrochloride of 99 per cent purity were used. All solvents and *KOH* used were of analytical grade.

### 2.1 Synthesis of Polynitropolyphenylene

Polynitropolyphenylene was synthesised<sup>4,5</sup> from styphnic acid in a three-step process according to stage I of the scheme presented in Fig. 1.

- Dipyrindinium styphnate<sup>6</sup> (DPS) was prepared as per the reported method. Pyridine (200 g) was added to styphnic acid (50 g) drop-by-drop in 30 min with continuous stirring. The mixture

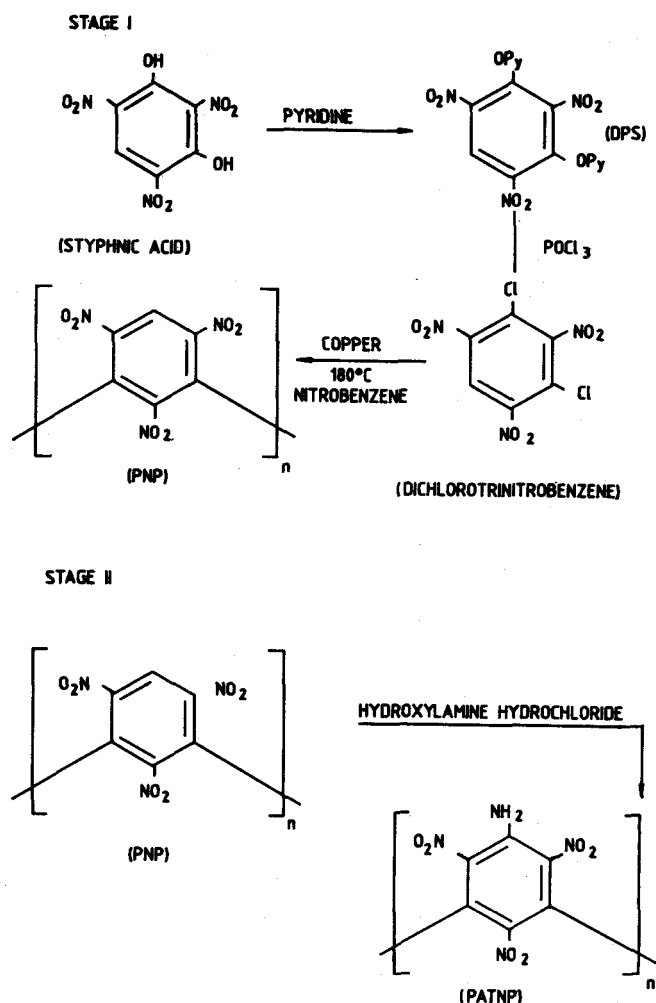


Figure 1. Scheme of synthesis of PATNP

was again stirred for another 30 min and the precipitate obtained was filtered and washed with ether (100 ml) and then air-dried. The yield obtained was 77 g (94 per cent); m.p. 168-170 °C (reported 168-170 °C).

- Dichlorotrinitrobenzene (DCTNB) was prepared from DPS. Dipyrindinium styphnate (60 g) was added in small increments to 100 ml POCl<sub>3</sub> (100 ml) in a three-necked flask with constant stirring for 30 min. After the addition was complete, the admixture was heated on a waterbath at 50 °C till all the solid dissolved. It was then poured into ice-cold water and the precipitate formed was filtered, washed with water, methanol and

ether and finally air-dried. The yield obtained was 42 g (100 per cent); m.p. 122-126 °C (reported 122-126 °C).

- PNP was prepared<sup>4</sup> by heating DCTNB (100 g) in nitrobenzene (250 ml) up to 170 °C and adding copper powder in 10 g parts. Initial addition of copper sets in an exothermic reaction. Heating was then stopped but copper powder was continued to be added so as to maintain the temperature at 180-185 °C. In all, copper powder (140 g) was added and the admixture was stirred for an additional 30 min at 180 °C. The mixture was then cooled, diluted with acetone and filtered. The filtrate was then transferred in a rotary evaporator under reduced pressure (5 mm of Hg) to dryness. The residue was treated with steam, foamed with concentrated HNO<sub>3</sub>, left overnight, filtered and washed with 1 per cent ammonia solution and dried in vacuum. The yield obtained was 45 g (60 per cent).

## 2.2 Synthesis of PATNP

According to stage II of the scheme I, PNP (10 g) and powdered hydroxylamine hydrochloride (150 g) were dissolved in dimethyl formamide (1.2 l) contained in a round bottomed flask (3 l capacity) heated on a waterbath maintained at 50-60 °C. 50 g of KOH in 250 ml methanol was then added gradually with vigorous stirring. The colour changed from yellow to orange and KCl was separated. Stirring was continued for an additional hour. The solution was filtered and dimethyl formamide was removed under reduced pressure. Residue was washed with water and methanol and dried. The yield obtained was 6.5 g (60 per cent). High performance liquid chromatography (HPLC) was carried out on a spectrophysics (USA) instrument using a mobile phase of water/tetrahydro furan in the ratio of 30:70. The IR spectra were recorded on a Perkin Elmer FTIR spectrophotometer (Model-1605) using a thin film of the sample. Particle size distribution was determined on a Malvern analyser (Model-26010). Number average molecular weight was determined by Knauer vapour phase osmometer. Differential thermal analysis (DTA) was carried out using a

locally-fabricated apparatus using typical sample (10 mg) at 10 °C/min. Impact (2 kg hammer) and friction sensitivity and calorimetric value were determined using Julius Peter apparatus and Parr adiabatic bomb calorimeter, respectively .

### 3. RESULTS & DISCUSSION

For a thermally-stable explosive with high molecular weight, the thermal stability and insensitivity can be enhanced by introducing amino groups in aryl-nitro compounds. Amorphous nature of the polymer is desirable so that combustion of the explosive does not include a melting process, characteristic of crystalline structure which would also be disadvantageous for desired application (like bonding agent). PATNP is a dark brown amorphous solid. High performance liquid chromatography showed a purity of 99 per cent for PATNP. Volume mean diameter measured for PATNP was 36. Number average molecular weight of PATNP was 5100 and IR spectrum showed *N-H* stretching frequency at 3368  $\text{cm}^{-1}$  and 3233  $\text{cm}^{-1}$  and  $\text{NO}_2$  stretching at 1534  $\text{cm}^{-1}$  and 1344  $\text{cm}^{-1}$  (while in PNP spectrum, the amino group is absent (Fig. 2). PATNP was observed to be much more thermally stable than PNP. Differential thermal analysis curves of PNP and PATNP are shown in Fig. 3. While PNP decomposes in a narrow temperature range with a peak maximum at 306 °C, PATNP shows a broad exotherm with a peak initiation at 460 °C and a peak maximum at 530 °C. Thermogravimetric analysis (TGA) of PATNP could not be carried out due to generation of lot of soot during decomposition. During decomposition the soot deposited back on the sample cup led to erroneous results. As expected, PATNP was found to be less impact and friction sensitive than PNP. The 50 per cent height for PNP and PATNP were 58 cm and 77 cm, respectively and both were friction insensitive up to 24 kg and 36 kg, respectively (The apparatus measures up to 36 kg only). Calorimetric value of PATNP was found to

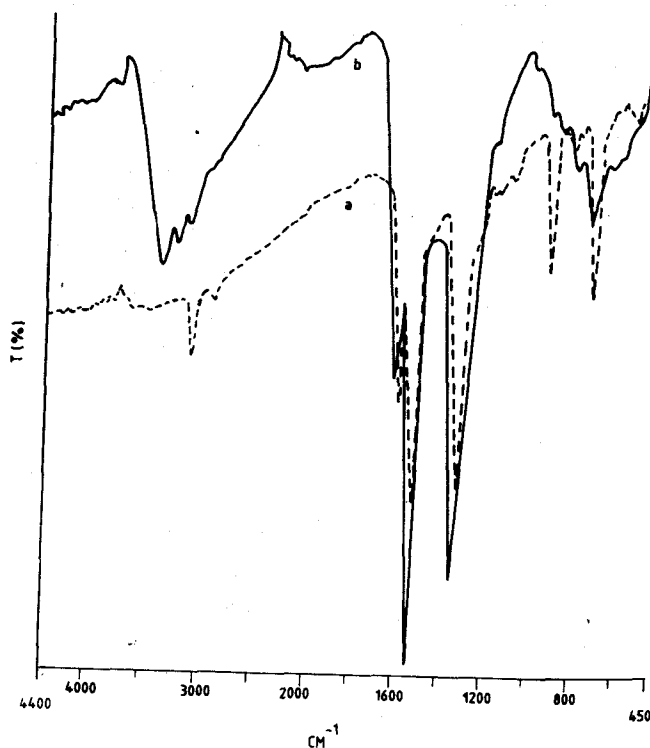


Figure 2. FTIR of PNP (dotted) and PATNP (solid)

be 3284 J/g, suggesting its high energy content. This aspect is relevant for its potential application as an energetic ingredient in propellant formulations.

### 4. CONCLUSION

PATNP is one of the highest thermally-stable explosive reported so far and is also insensitive to friction. It has potential applications as energetic binder and as a coating material for sensitive high energy materials in propellants, explosive formulations and pyrotechnics.

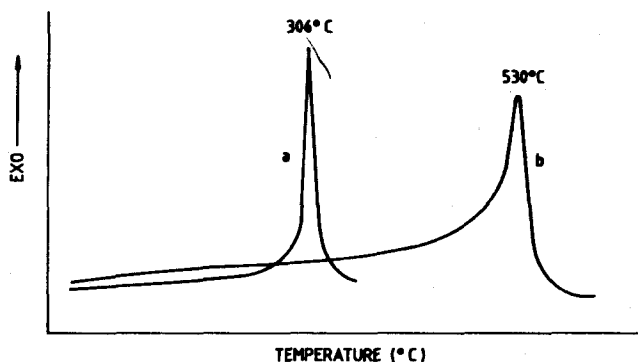


Figure 3. DTA curves of (a) PNP and (b) PATNP

## REFERENCES

1. Kilmer, E.E. Heat-resistant explosives for space application. *J. Spacecraft Rockets*, 1968, 5(10), 1216-19.
2. Schwarz, A.C. Application of hexanitrostilbene (HNS) in explosive components. Sandia National Laboratories, Albuquerque, New Mexico, 1972. Report No. Sc-PR-71-0673.
3. Coburn, M.D.; Harris, B.W.; Lee, K.Y.; Stinecipher, M.M. & Hayden, H.H. Explosives synthesis at Los Alamos. *Ind. Eng. Chem. Prod. Res.*, 1986, 25, 68-72.
4. Hagel, R. & Redecker, K.H. Dynamit nobel attengesellschaft: polymers obtained from polynitroaromatic compounds. USA Patent 4,250, 294. February 1981.
5. Redecker, K.H. & Hagel, R. Polynitro-polyphenylene, a high temperature-resistant, noncrystalline explosive. *Prop. Explos. Pyrotech.*, 1987, 12, 196-201.
6. Warman, M. & Siele, V.L. *J. Org. Chem.*, 1961, 26, 2997.
7. Horning, E.C. (Ed). *Organic synthesis*, Vol. 3. John Wiley & Sons. Inc., London, 1960. p. 664.

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