

Synthesis and characterization of PTS and PDATS: Two maiden functionalized energetic polymers having tetrazole and triazine rings

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Abstract: The design of new energetic molecules is based on compounds exhibiting a high density and an elevated heat of formation. These fundamental properties, achieved through the presence of numerous nitrogen atoms. The syntheses of two new energetic polymers containing moieties of tetrazole and diaminotriazine have been carried out in this work. The 4-chloromethyl styrene (CMS) was polymerized by free radical polymerization (FRP) method at 80 °C using α,α -azobis(isobutyronitrile) (AIBN) as an initiator. The PCMS was transformed to PAS by Kornblum's oxidation of methylene chlorides to aldehyde groups in one step. Aldehyde groups of PAS were produced tetrazole and triazine rings in one-pot reaction. The polymers, obtained in quantitative yields, were characterized by FT-IR and ¹H NMR spectroscopy and TGA studies. Thermal properties nitrogen-rich polymers show that explosive thermal degradation takes place at around 230 °C.

Keywords: 4-Chloromethyl styrene, Nitrogen-rich polymers, Energetic polymers, Tetrazole, Diaminotriazine.

Introduction

Explosions are divided into three categories: physical, nuclear and chemical explosion. The chemical explosion relates to the destruction of molecules mid preparation of gases and heat [1, 2]. The burning rate of it determines whether the destruction is just a burning, a deflagration or a detonation [3]. High energy materials are classified into primary and secondary explosives, propellants and pyrotechnics [4, 5]. Primary explosives are very sensitive energetic materials, which can be easily initiated by friction, impact, spark or heat. The high thermal and physical stability of the secondary explosives along with higher detonation velocities are the ingrown discrepancies between the secondary and primary energetic materials. Unlike them, propellants are not meant to detonate, but to deflagrate. Pyrotechnics are classified into three groups, the heat generating, the smoke

generating and the light emitting pyrotechnics [6-11]. Common explosive compositions contain an oxidizer, a fuel and a binder. A close investigation of the explosive mixtures discussed, reveals that in all cases binders without any energetic moieties were applied [12]. Therefore, the performance of the explosive is reduced by the amount of non-energetic material. As a consequence, several energetic polymers were developed [13-17]. Common energetic polymers contain either nitro groups, nitric esters or azide groups [18-20]. The main task of energetic binders in explosive compositions is to keep the different components of the mixture (often powders) together. Despite the existence of several energetic polymers suitable or in use as energetic binders, new polymers are desired. For the preparation of polymers, two methods are generally known – the polycondensation and the radical polymerization [21]. Both methods own their special advantages. The class of tetrazoles [22] and triazines [23] proved to be suitable for the

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preparation of high explosives and energetic polymers. This paper deals with an efficacious preparation and characterization of the nitrogen-rich polymers by the cycloaddition of aldehyde groups to tetrazole and triazine rings. In this work, we first synthesized the homopolymer of 4-chloromethyl styrene (CMS) by radical polymerization. The one-step oxidation of alkyl halides to aldehydes has been performed by convenient procedure [24]. Direct conversion of aldehydes to tetrazoles and triazines has been accomplished by one-pot tandem reactions [25, 26]. Thermal properties of nitrogen-rich polymers were characterized by TGA studies.

Results and discussion

Synthesis of nitrogen-rich polymers due to their energetic applications is very interesting in organic explosive chemistry. There are various methods for these compounds preparation. In the present work, first we synthesized PCMS from by free radical polymerization of 4-chloromethyl styrene (CMS). Then, the PAS synthesized from PCMS by one-step Kornblum oxidation. Finally, we prepared PTS and PDATS by one-pot reaction of PAS with reagents. The structure of products characterized with FT-IR and ^1H NMR analyses.

The molar compositions of units in copolymer PAS were calculated from the ratio integrated intensities of the peaks around 6.74- 7.56 ppm, corresponding to eight protons of benzene rings in units to the area at 9.86 ppm, which was attributed to one proton of aldehyde group. The molar compositions of units were calculated from below two equations where m and n were the mole fractions of converted CMS and CMS, respectively.

$$\frac{m+n=100}{\frac{4m+4n}{m} = \frac{6.116}{1}}$$

$$m = 65.4 \% \quad n = 34.6 \%$$

The molar compositions of units in polymer PTS were calculated from the ratio integrated intensities of the peaks around 6.61- 7.44 ppm, corresponding to twelve protons of benzene rings in all units to the area at 9.76 ppm, which was attributed to one proton corresponding to remained aldehyde groups. The molar compositions of units were calculated from below equations.

$$m+n=100$$

$$m = p + q = 65.4 \% \quad n = 34.6 \%$$

$$\frac{4p+4q+4n}{p} = \frac{6.383}{0.304}$$

$$p = 19.05 \% \quad q = 46.35 \%$$

The molar compositions of units in polymer PDATS were calculated from the ratio integrated intensities of the peaks around 6.2- 7.49 ppm, corresponding to sixteen protons of benzene rings in all units to the total area between 3.07-3.34 ppm, which were attributed to four protons corresponding to amines in triazine units. The molar compositions of units were calculated from below equations.

$$m+n=100$$

$$m = p + q = p + r + s = 65.4 \% \quad n = 34.6 \%$$

$$p = 19.05 \% \quad r + s = 46.35 \%$$

$$\frac{4p+4r+4s+4n}{4s} = \frac{1.399}{0.372}$$

$$r = 39.7 \% \quad s = 6.65 \%$$

The products solubility was checked and all compounds are soluble in DMSO solvent. The study of composition of products shows that all aldehyde groups of PAS polymer didn't transform to nitrogen-rich rings and the chloride ions of CMS units didn't replace with azide ions, because the produced rings are large and these reactions didn't perform.

Thermal properties of the products:

Thermal properties of polymers were evaluated using the TGA technique and was summarized in Table 1, including the initial decomposition temperature of the polymer (IDT), temperature of 20% weight loss of the polymer (PDT) and the temperature at which the maximum decomposition rate occurred for the polymer (PDT max).

Table 1: Thermal properties of polymers.

Polymer	IDT(°C)	PDT(°C)	PDTmax(°C)
PCMS	144	415	866
PAS	140	322	865
PTS	142	232	866
PDATS	145	241	912

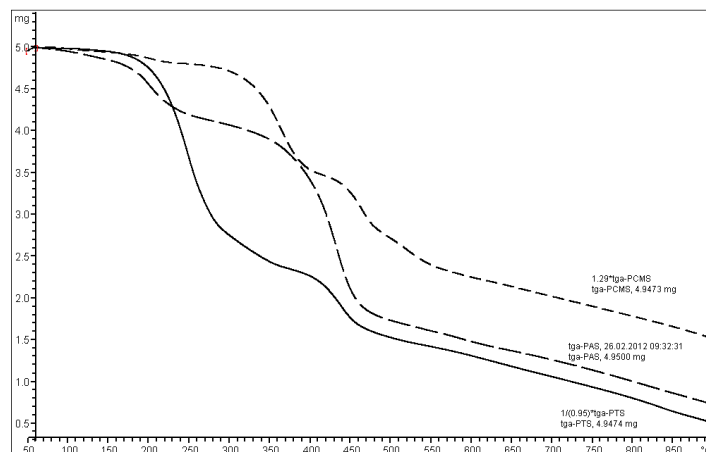


Figure 1: Comparing thermal behaviour of PCMS, PAS and PTS.

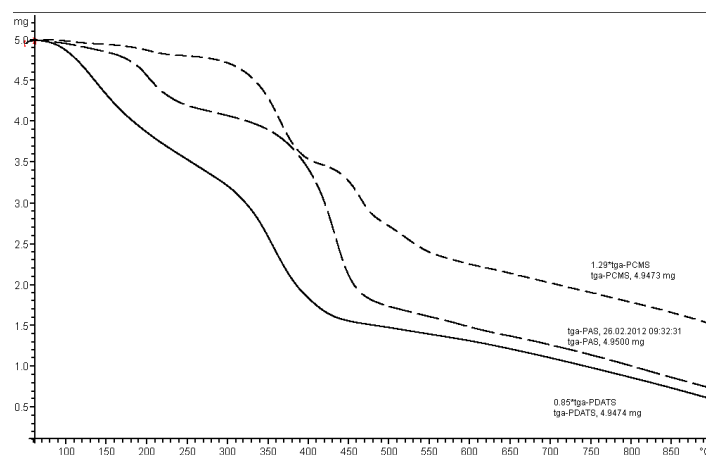


Figure 2: Comparing thermal behaviour of PCMS, PAS and PDATS.

As can be seen from Figures 1 and 2, Two polymer (PCMS and PAS), are completely stable until 320 °C, while the decomposition nitrogen-rich polymers (PTS and PDATS) occurred about 230 °C which that is due to the fact that tetrazole and triazine-rings are both destroyed in this stage.

Conclusion

The PCMS was synthesized by free radical polymerization (FRP). This polymer was transformed to nitrogen-rich polymers (PTS, PDATS) in two steps. The molar compositions of the products were calculated by the ^1H NMR spectral method. The nitrogen-rich polymers show an explosive thermal degradation together with a release of huge heat.

Experimental

Materials:

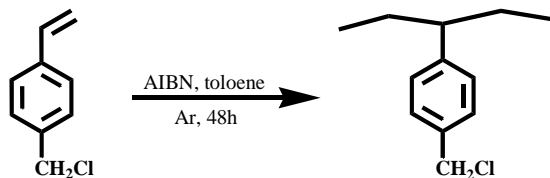
The 4-chloromethyl styrene (Aldrich, 90%) was distilled under reduced pressure to remove inhibitors, before use. The initiator α , α -azobis (isobutyronitrile) (AIBN) (Merck) was purified by crystallization from methanol. The solvents and other reagents were obtained from Merck. All the solvents were distilled and stored over a drying agent. Tetrahydrofuran (THF) was dried by a standard method.

Measurements:

Infrared spectra were recorded with a 4600 Unicam FT-IR spectrophotometer as KBr pellets. ^1H NMR spectra were run on a Bruker 250 MHz spectrometer at room temperature using DMSO-d_6 as a solvent. The TGA curves were obtained on a TGA/SDTA 851 calorimeter at heating and cooling rates of 10 °C/min under N_2 .

Homopolymerization of 4-chloromethyl styrene: PCMS:

For preparing of homopolymer (PCMS), 10 mL of 4-chloromethyl styrene (CMS) was dissolved in 40 mL of toluene and was mixed with AIBN (1% molar) as a radical initiator, in a pyrex glass ampoule. The ampoule was degassed under argon gas, sealed under vacuum, and maintained at 80 ± 1 °C in a water bath, with stirring for about 48 h. After this time, the ampoule was cooled rapidly to room temperature. Then the solutions were poured into cooled methanol. The white precipitates were collected and washed with methanol and dried under vacuum (Scheme 1). ^1H NMR (DMSO- d_6 , ppm): 1.45- 2.09 (aliphatic C-H), 4.66- 4.76 (methylene C-H), 6.51- 6.68 (Ar-H). FT-IR (KBr, cm^{-1}): 3024 (aromatic C-H), 2922 and 2850 (aliphatic C-H), 1611 (aromatic C=C), 1421- 1442 (bending C-H).

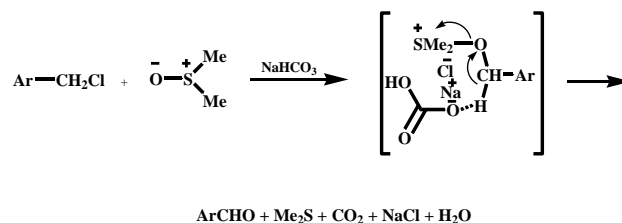


Scheme 1: Polymerization of 4-chloromethylstyrene.

Conversion of $-\text{CH}_2\text{Cl}$ to aldehyde by modified Kornblum's reaction: PAS:

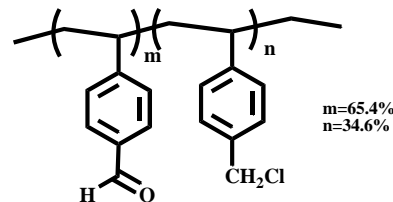
The Kornblum oxidation is a chemical reaction of a primary halide with dimethyl sulfoxide to form aldehyde. Dimethyl sulfoxide (DMSO) is an important highly polar aprotic reagent that has exceptional solvent properties for organic and inorganic substances. The sulfur center in DMSO is nucleophilic toward soft electrophiles and the oxygen is nucleophilic toward hard electrophiles. The known reaction mechanism of the conventional Kornblum oxidation involves an alkoxy-sulphonium ion, which, in the presence of a base, such as sodium bicarbonate,

will eliminate to form the desired aldehyde (Scheme 2) [27].



Scheme 2: Mechanism of Kornblum's reaction.

The reaction was carried out in various conditions. In the best condition, while stirring, 6 g PCMS and 24 g sodium bicarbonate were added to 240 mL DMSO, and the mixture was heated at 120 °C for 72 h. After this period of time, the reaction mixture color was converted from yellow to orange. The ampoule was cooled rapidly to room temperature. Then the solution was poured from ampoule into cooled water. The orange precipitate was collected and washed with methanol and dried under vacuum to yield (approximately 90%) of PAS (Scheme 3). ^1H NMR (DMSO- d_6 , ppm): 0.88- 2.41 (aliphatic C-H), 6.74- 7.56 (Ar-H), 9.86 (aldehyde C-H) (Figure 3). FT-IR (KBr, cm^{-1}): 3006 (aromatic C-H), 2922 (aliphatic C-H), 2853 and 2739 (aldehyde C-H), 1699 (C=O), 1573- 1604 (aromatic C=C), 1437 (bending C-H).



Scheme 3: Structure of PAS polymer.

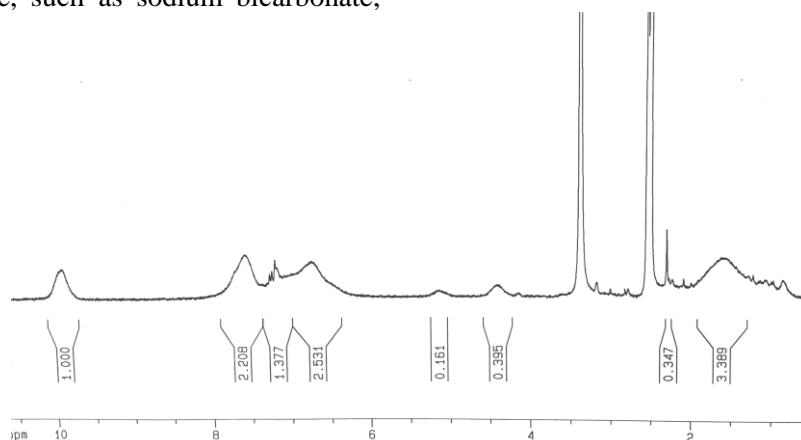
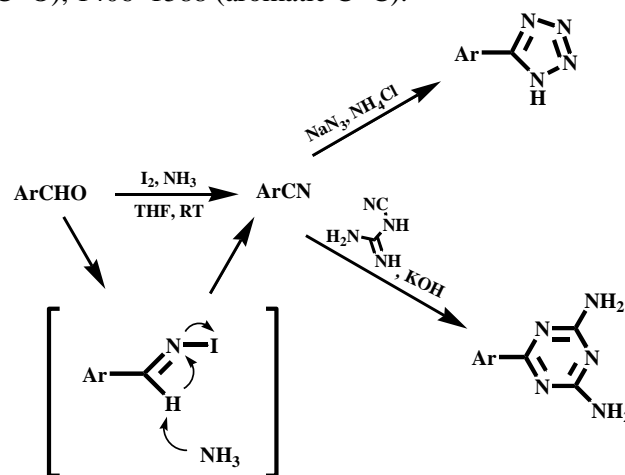


Figure 3: ^1H NMR spectrum of PAS in DMSO- d_6 .

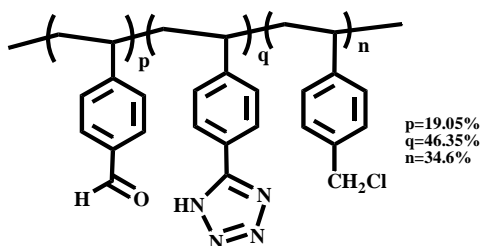
Representative procedure for transformation of aldehydes into tetrazoles: PTS:

Aldehyde groups of PAS reacted with iodine in ammonia water at room temperature to give the nitrile intermediates, which were trapped by addition of sodium azide to produce tetrazoles (Scheme 4) [25, 26]. A solution of PAS (2 g) and iodine (2.8 g) in ammonia water (2 mL of 28% solution) and THF (10 mL) was stirred at room temperature for 2 h. A mixture of NaN₃ (1 g) and NH₄Cl (1.2 g) was then added. The reaction mixture was heated at reflux for 48 h under stirring. HCl (10 mL of 1 M solution) and EtOAc (50 mL) were added, and vigorous stirring was continued until no solid was present and the aqueous layer had a pH=1. The organic phase was concentrated in vacuum, and the remaining solids were rinsed with EtOAc (20 mL) to give a product (Scheme 5). ¹H NMR (DMSO-d₆, ppm): 1.35–1.68 (CH₂-CH), 2.4 (CH₂-Cl), 6.61–7.44 (Ar-H), 9.76 (aldehyde C-H) (Figure 4). FT-IR (KBr, cm⁻¹): 3422 (tetrazole N-H), 3027 (aromatic C-

H), 2984 (aliphatic C-H), 2780 (aldehyde C-H), 1626 (C=O), 1406–1588 (aromatic C=C).



Scheme 4: Preparation of PTS and PDATS from PAS.



Scheme 5: Structure of PTS polymer.

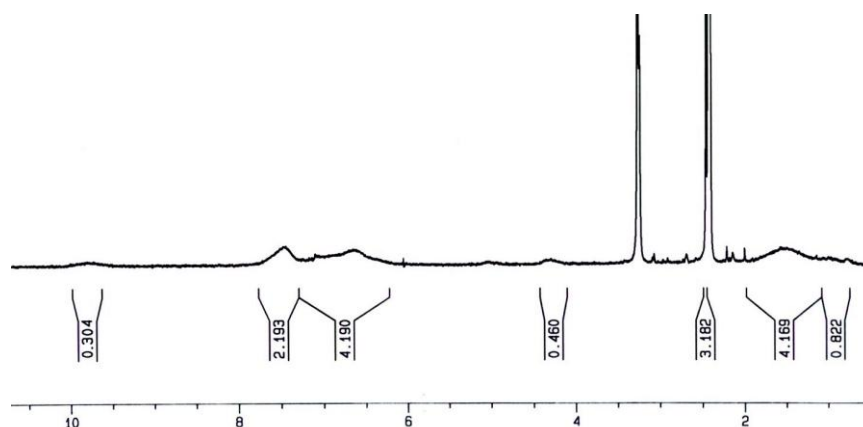


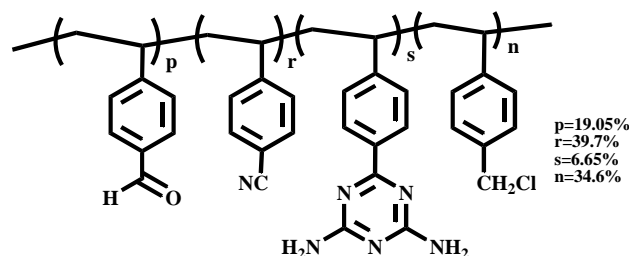
Figure 4: ¹H NMR spectrum of PTS in DMSO-d₆.

Representative procedure for transformation of aldehydes into triazines: PDATS:

A solution of PAS (2 g) and iodine (2.8 g) in ammonia water (2 mL of 28% solution) and THF (10 mL) was stirred at room temperature for 2 h. A mixture of dicyandiamide (1.3 g) and KOH (1.4 g) was then

added. The reaction mixture was heated at reflux for 72 h. The suspended solid products were filtered and rinsed with Et₂O to give a pure diaminotriazine (Scheme 6). ¹H NMR (DMSO-d₆, ppm): 1.9–2.2 (CH₂-CH), 2.6–2.8 (CH₂-Cl), 3.07–3.34 (-NH₂), 6.2–7.5 (Ar-H), 8.83 (aldehyde C-H) (Figure 5). FT-IR (KBr, cm⁻¹

¹): 3421 (-NH₂), 2925 (aliphatic C-H), 2225 (-CN), C=C).
1686 (C=O), 1603 (-C=N-), 1414–1500 (aromatic



Scheme 6: Structure of PDATS polymer.

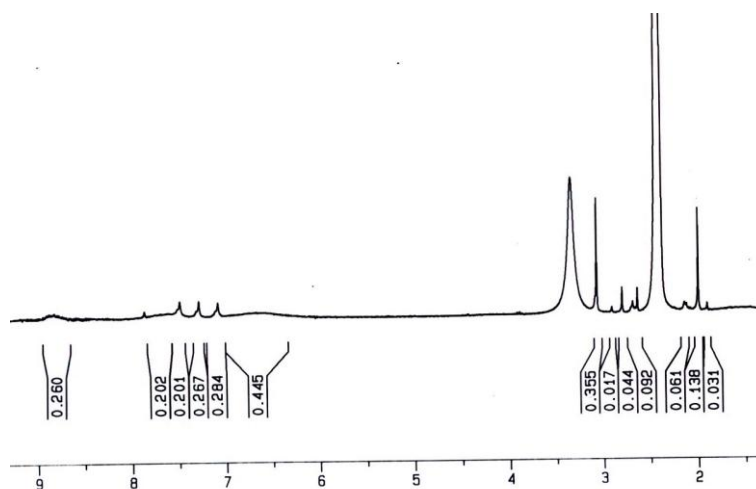


Figure 5: ¹H NMR spectrum of PDATS in DMSO-d₆.

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