



Effect of new poly 2-acryloyl-*N,N'*-bis (4-nitrophenyl) propandiamide and poly 2-acryloyl-*N,N'*-bis (4-methylphenyl) propandiamide and their synergistic action on the stability of nitrocellulose

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Abstract

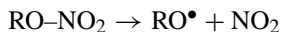
The stability of nitrocellulose can be significantly improved by incorporating two novel polymeric compounds as new stabilizers, each has two *p*-substituted phenyl rings in its repeating unit. The two prepared polymers were used independently and in three different blend ratios in comparison with the conventional propellant stabilizer, diphenylamine. The efficiency of the prepared stabilizers and their synergistic effect were evaluated using thermo gravimetric analysis (TGA), Bergmann–Junk test and differential scanning calorimetry (DSC). It was found that both polymers and their 50%:50% blend ratio are more efficient nitrocellulose stabilizers than diphenylamine.

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1. Introduction

The thermal decomposition of nitrate esters [1,2] in colloidal propellants involves fission of the oxygen–nitrogen bond as the first and rate determining step, leading to the generation dioxide:



The nitrogen dioxide then reacts with the RO^\bullet radical, its degradation products or with other propellant ingredients. Since it is reduced in the process, the final products will

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include nitric oxide, nitrous oxide and nitrogen. Secondary reactions in the propellant lead to the formation of carbon monoxide, carbon dioxide and water as further products [3]. The overall decomposition is autocatalytic and therefore stabilizers are added to react with the initial products of decomposition (nitrogen dioxide nitric oxide and nitrous acid) and reduce the effect of autocatalysis. A variety of organic and heterocyclic compounds have been long recognized as propellant stabilizers [4–10]. However, the low molecular weight propellant stabilizers can be consumed by time and the propellant properties and service life would be affected. Polymeric compounds can therefore be better alternatives although their use as propellant stabilizers has not received much attention of authors. The main potential advantage of a polymeric stabilizer over existing ones is that it would prevent migration problems; in old ammunition the stabilizer can be lost to other components [11]. Also, the gelatinizing effect which polymer can impart would increase the overall activation energy of a propellant mix. In a previous work, the authors [12] have reported that poly *N*-(4-nitrophenyl) acrylamide which has in its repeating unit one phenyl ring *p*-substituted with an NO₂ group has significantly improved thermal stability of nitrocellulose in comparison with the classical propellant stabilizer, diethyldiphenyl urea, centralite 1. The better effect of that polymer was the main drive for more investigations of two acrylamido homopolymers and a copolymer [11] of their monomers. Each repeating unit of the copolymer has two phenyl rings, one is substituted with an electron donating, CH₃ group and the other with an electron withdrawing Cl atom. The results obtained have confirmed the conclusion that remarkable improvement of propellant stability was brought about by using polymeric stabilizers [12], and obviously showed that the superior stabilization effect has been reported for the copolymer. This was owed to the presence of two phenyl rings in each repeating unit of the copolymer, which provides more reactive ring sites to receive the gaseous decomposition products of nitrocellulose. The present work is a sequel to the series of polymer investigations as propellant stabilizers. The aim is to develop, two homopolymeric stabilizers having more reactive ring sites. One of them has in its repeating unit two phenyl rings *p*-substituted with two electron withdrawing NO₂ groups and the other has also two phenyl rings *p*-substituted with two electron donating CH₃ groups. The prepared polymers will be incorporated into propellant mixes independently and in three different blend ratios in order to evaluate their efficiency and the synergistic effect of their action as propellant stabilizers in comparison with the common stabilizer, diphenylamine.

2. Experimental

2.1. Materials

Diethyl malonate, acryloyl chloride and triethylamine were purchased from Merck. *p*-Toluidine, *p*-nitroaniline and diphenylamine were supplied by Aldrich. All solvents were of laboratory grade obtained from Edwic.

2.1.1. Synthesis of 2-acryloyl-*N,N*-bis(4-methylphenyl) propandiamide (2-AMP)

In a molar ratio of 2:1, 5 g of *p*-toluidine were fused with 4 ml of diethyl malonate for 30 min to afford the corresponding malonanilide [13]. Five grams (0.018 mol) of the

obtained malonanilide were dissolved in DMF and mixed with an excess of triethylamine then stirred in ice for 5 min, 1.6 ml (0.018 mol) of acryloyl chloride was added drop wise to the mixture. After addition, the mixture was stirred for 90 min at room temperature until complete addition. The reaction mixture was then poured into distilled water to dissolve the formed triethylamine hydrochloride then filtered to obtained the product which was re-crystallized from chloroform/cyclohexane mixture. The product was dried and the melting point was measured.

2.1.2. Synthesis of 2-acryloyl-*N,N*-bis (4-nitrophenyl) propandiamide (2-ANP)

In a molar ratio of 2:1, 10 g of *p*-nitroaniline were fused with 8 ml of diethyl malonate for 1 h. The mixture was poured into ethanol, left overnight then filtered to obtain 4 g of the corresponding malonanilide as precipitate. Four grams of the obtained malonanilide (0.012 mol) were dissolved in acetone and mixed with an excess of triethylamine then stirred in ice for 5 min, 1.05 ml (0.012 mol) of acryloyl chloride was added dropwise and the reaction mixture was stirred at room temperature for 1 h until complete addition. The mixture was then poured into distilled water to dissolve the triethylamine hydrochloride then filtered. The product was obtained as precipitate and recrystallized from chloroform/cyclohexane mixture then dried and the melting point was determined. The prepared monomers are given in Table 1.

2.2. H-NMR characterization of the prepared monomers

The structure of the new prepared monomers was elucidated by H-NMR spectrometers in DMSO. The spectra of 2-AMP were recorded on Varian Unity 400 MHz Spectrometer Meanwhile, the spectra of 2-ANP were run by Bruker 400 MHz.

2.3. Polymerization of the prepared monomers

Three grams of each of 2-AMP and 2-ANP were dissolved in 50 ml acetone and 0.024 g of azobisisobutyronitrile (AIBN) was added to each experiment as an initiator. The two

Table 1
The prepared monomers and their melting points

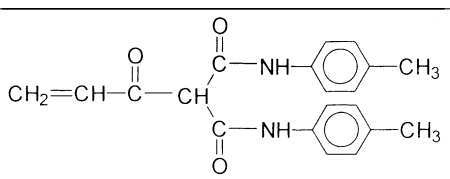
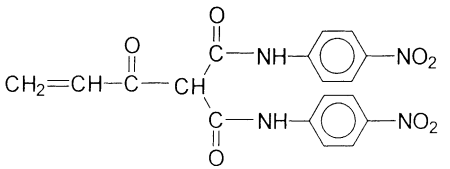
Name	Abbreviation	Structure	m.p. (°C)
2-Acryloyl- <i>N,N</i> -bis (4-methylphenyl) propandiamide	2-AMP		240
2-Acryloyl- <i>N,N</i> -bis (4-nitrophenyl) propandiamide	2-ANP		210

Table 2
Propellant formulations including the prepared polymers as stabilizers

Ingredient	Formulation					
	A1	A2	A3	A4 (75%:25%)	A5 (50%:50%)	A6 (25%:75%)
Nitrocellulose (g)	4.6	4.6	4.6	4.6	4.6	4.6
DBP oil (ml)	0.2	0.2	0.2	0.2	0.2	0.2
Transformer oil (ml)	0.05	0.05	0.05	0.05	0.05	0.05
Stabilizer						
DPA (g)	0.15	–	–	–	–	–
Poly 2-ANP (g)	–	0.15	–	0.1125	0.075	0.0357
Poly 2-AMP(g)	–	–	0.15	0.0375	0.075	0.1125

solutions were homopolymerized at 50 °C for 48 h. The polymers were left to cool then poured into methanol and left for complete precipitation then filtered. The homopolymers were obtained as precipitate and dried.

2.4. Nitrocellulose formulations

Six propellant samples were formulated [11] as 5 g each from nitrocellulose (92%, 4.6 g), dibutylphthalate, DBP (4%, 0.2 ml), stabilizer (3%, 0.15 g) and transformer oil (1%, 0.05 ml). In three formulations (A1–A3), 0.15 g of each of poly 2-ANP and poly 2-AMP as well as diphenylamine, DPA was added as stabilizer. In the other three formulations (A4–A6), the 0.15 g stabilizer was added in three different blend ratios of poly 2-ANP and poly 2-AMP:75%:25%, 50%:50% and 25%:75%, respectively. The formulations are shown in Table 2.

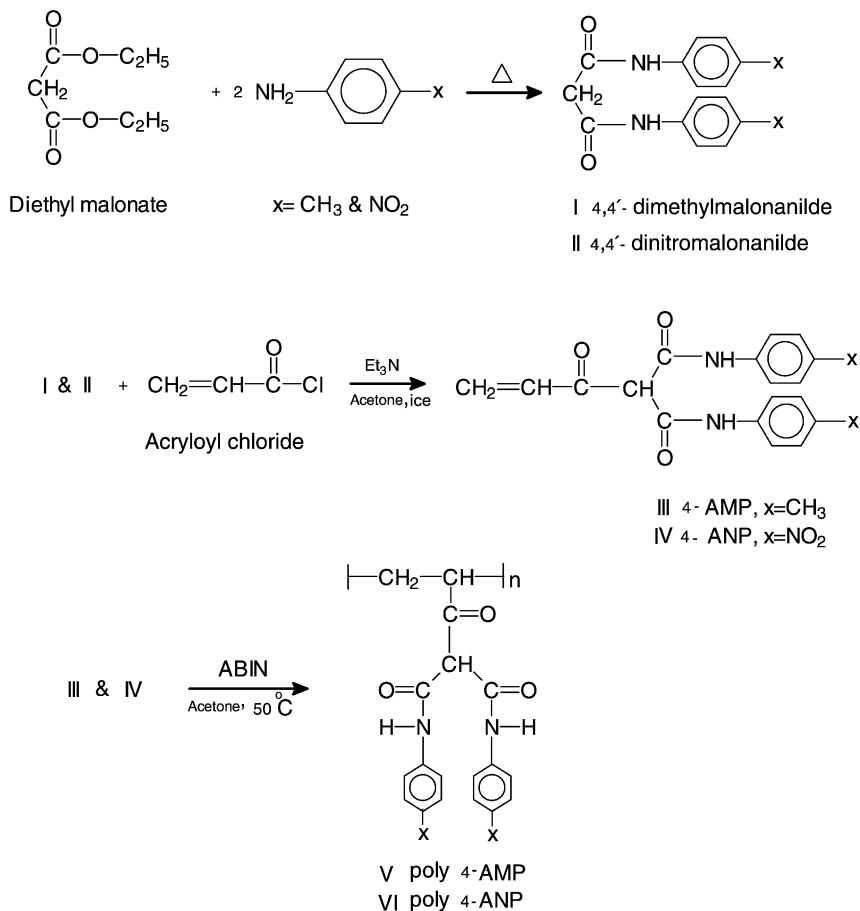
Nitrocellulose was stirred in water and DBP and transformer oils were added successively. Stabilizers were all dissolved in DMF then added dropwise to the mix while stirring. Stirring was continued for 1 h to ensure homogeneity of the mix then samples were dried in an oven at 50 °C for 48 h.

2.5. Bergmann–Junk test

After drying, 1 g of each propellant sample was heated in Bergmann–Junk bath for 2 h at 132 °C. Samples were then mixed and shaken well with 50 ml H₂O then titrated against NaOH 0.05 N using methyl red as an indicator [11].

2.5.1. Thermal analysis

Non-isothermal and isothermal (130, 160 and 170 °C) TGA of all propellant samples was carried out by using a Shimadzu–50 thermogravimetric analyzer in nitrogen (purge rate of 30 ml/min) at a heating rate of 10 °C/min. Ten milligram of the samples was used for each experiment. DSC was used to estimate the activation energies of decomposition of propellant samples using Ozawa method [14] at three different heating rates 5, 10 and 15 °C using 3.5 mg samples.



Scheme 1. Synthesis and polymerization of the investigated stabilizers.

3. Results and discussion

3.1. Polymer structure

The route of synthesis and polymerization is given in Scheme 1. H-NMR assignments of 2-AMP were: δ 10.13 (s, 1H), δ 9.8 (s, 1H), δ 7.61 (d, 4H), δ 7.5 (d, 4H), δ 7.15 (d, 4H), δ 7.11 (d, 4H), δ 6.5 (m, 1H), δ 6.3 (m, 1H), δ 5.75 (m, 1H), δ 2.28 (s, 3H), δ 2.27 (s, 3H), and δ 2.06 (s, 3H). From the spectra it can be noticed that more than one signal of CH₃ groups appeared. This might be attributed to the tautomerization of the compound around the C–N bond to become C=N around which rotation cannot take place. Meanwhile the assignments of 2-ANP were: δ 10.4 (s, 1H), δ (10.65 (s, 1H), δ 8.1 (m, 4H), δ 7.75 (m, 4H), δ 7.4 (m, 1H), δ 6.3 (m, 1H) and δ 5.7 (m, 1H). Spectra of 2-AMP and 2-ANP are shown in Figs. 1 and 2, respectively.

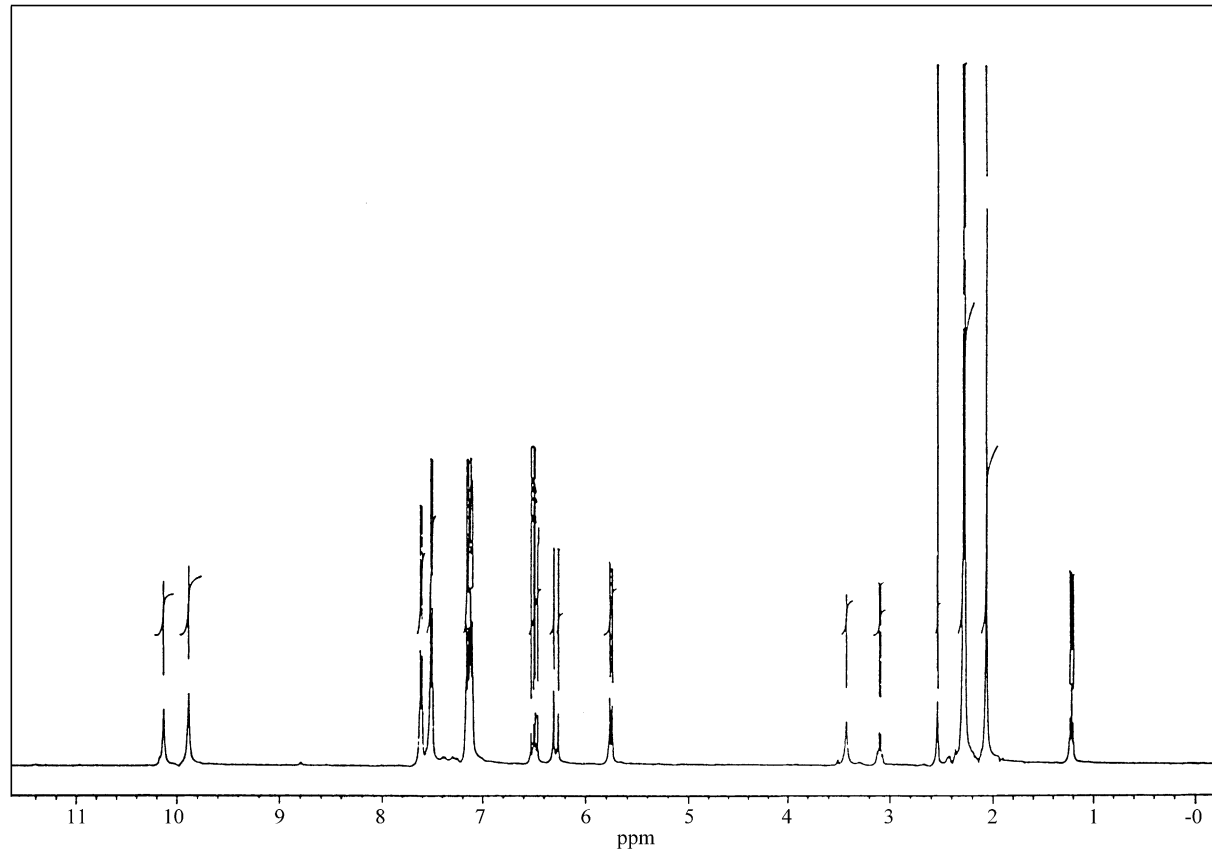


Fig. 1. H-NMR spectra of 2-AMP.

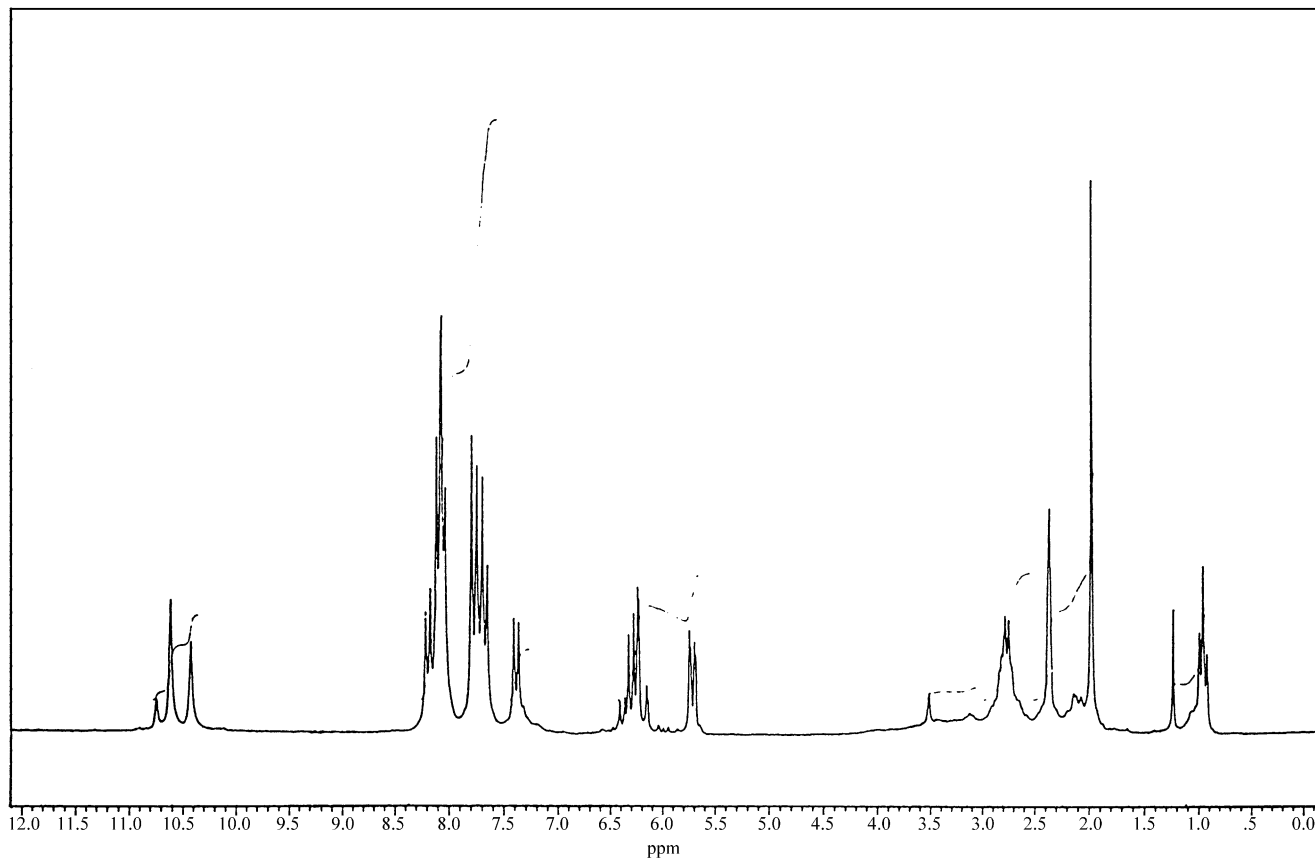


Fig. 2. H-NMR spectra of 2-ANP.

Table 3
Isothermal TGA of nitrocellulose samples containing different stabilizers

Stabilizer	Weight loss percentages after 2 h at isothermal temperatures (°C)		
	130	160	190
A1	5.119	8.893	9.343
A2	3.652	5.375	7.017
A3	3.390	4.416	7.640
A4	3.099	4.567	7.121
A5	3.581	3.020	8.464
A6	2.473	4.899	7.955

3.2. Thermal stability

Thermo gravimetric analysis (TGA) is a reliable and well informing technique used for fast evaluation of the efficiency of propellant stabilizers. Isothermal TGA results of all propellant samples obtained at 130, 160 and 190 °C are given in Table 3. At 130 °C, it can be noticed that propellant samples containing the prepared polymers and their blend ratios have generally showed lower weight loss % than sample A1 containing DPA. The lowest weight loss, 2.5% is recorded for sample A3 incorporated with the blend ratio 25% poly 2-ANP:75% poly 2-AMP. This wt.% is half that shown by sample A1 containing DPA, which means that the efficiency of sample A4 is higher than that of sample A1. On the other hand, the results of samples A2 and A3 containing 100% of the homopolymer are nearly similar and are also highly efficient than sample A1.

At 160 °C, it is evident that the difference in weight loss % between sample A1 containing DPA and those containing the prepared polymeric stabilizers and their blend ratios has become larger, nearly double that observed at 130 °C. Sample A5 containing the blend ratio 50%:50% showed a superior stabilization effect where it lost less than half the wt.% loss shown by the sample A1 containing the classical stabilizer DPA, i.e. sample A5 has more than double the efficiency of sample A6. This means that the best synergistic effect of action of both polymeric compounds is quite apparent at 160 °C when equal proportions of both stabilizers are used. Fig. 3 shows a collective isothermogramal TGA thermogram of all samples at 160 °C as an illustrative example. When the decomposition temperature is raised up to 190 °C, difference in weight loss % between DPA and the rest of samples gets narrow again, nearly 1–2% and the synergistic effect of the blending ratios tends to diminish. This is because of burning near the ignition temperature of nitrocellulose. In spite of that, the best result is recorded for sample A2 containing poly 2-ANP.

3.3. Non-isothermal TGA

The results of non-isothermal TGA of all propellant samples are given in Table 4.

The table shows the temperature of starting decomposition and the DTG peak temperatures. When values of these parameters increase, they give an indication on increasing the stability of propellant samples. The descending order of efficiency which can be observed from Table 4 is: A2 ≥ A5 > A3 > A4 > A1 > A6. This order indicates that both prepared polymers and their 50%:50% blend ratio can be used as good stabilizers for nitrocellulose.

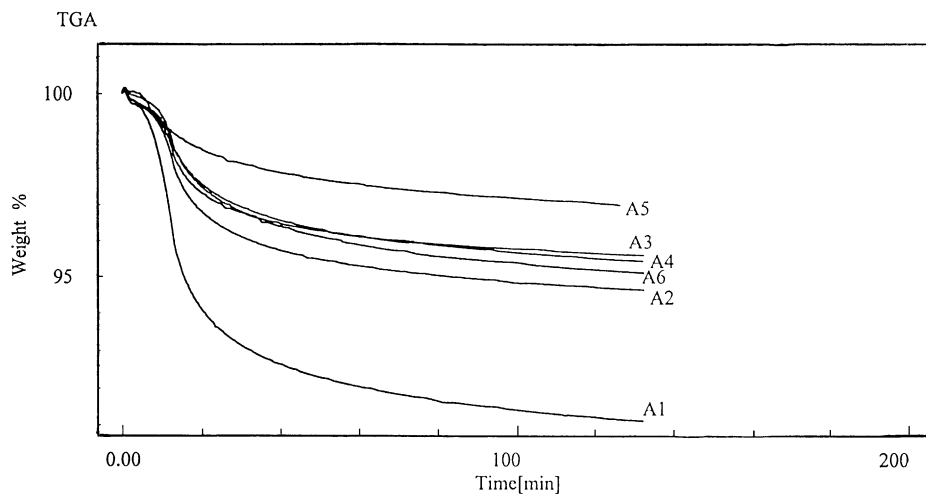


Fig. 3. Collective isothermal thermo gravimetric analysis (TGA) thermogram of nitrocellulose samples stabilized by the polymers prepared in comparison with DPA at 160 °C.

Table 4
Non-isothermal TGA of propellant samples

Samples	Start decomposition (°C)	Peak DTG (°C)	Ash residue (%)
A1	248.00	253.00	1.185
A2	255.88	261.48	0.395
A3	254.00	259.00	0.814
A4	251.00	256.60	1.295
A5	255.83	260.00	0.306
A6	237.88	246.84	0.881

Meanwhile, the order also indicates that the synergistic effect of both polymers at the blend ratio 25%:75% (sample A6) does not offer significantly higher thermal stability to nitrocellulose than DPA. Table 5 also shows the % ash residues remains after burning. When this ash % gets small, it indicates a recommended ignition properties of propellant. The results in Table 5 indicates that sample A5 loaded with the blend ratio 50%:50% and sample A2 loaded with poly 2-ANP have shown the lowest % ash residue. Figs. 4 and 5 representing

Table 5
Bergmann–Junk test

Sample	Stabilizer	NaOH 0.05N (ml)
A1	DPA	2.10
A2	100% poly 4-NAM	1.15
A3	100% poly 4-MAM	0.75
A4	75% poly 4-NAM:25% poly 4-MAM	0.23
A5	50%:50%	1.05
A6	25%:75% poly 4-NAM poly 4-MAM	1.85

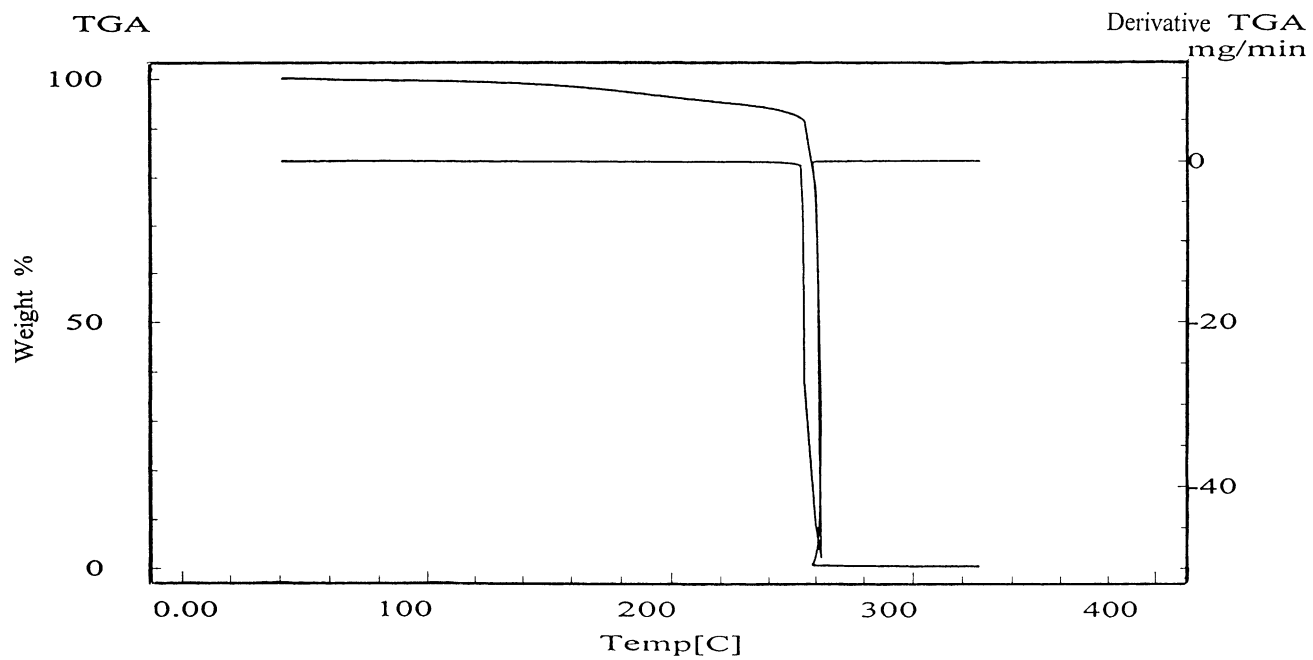


Fig. 4. Non-isothermal thermo gravimetric analysis of the nitrocellulose containing 75% poly 2-ANP:25% poly 2-AMP.

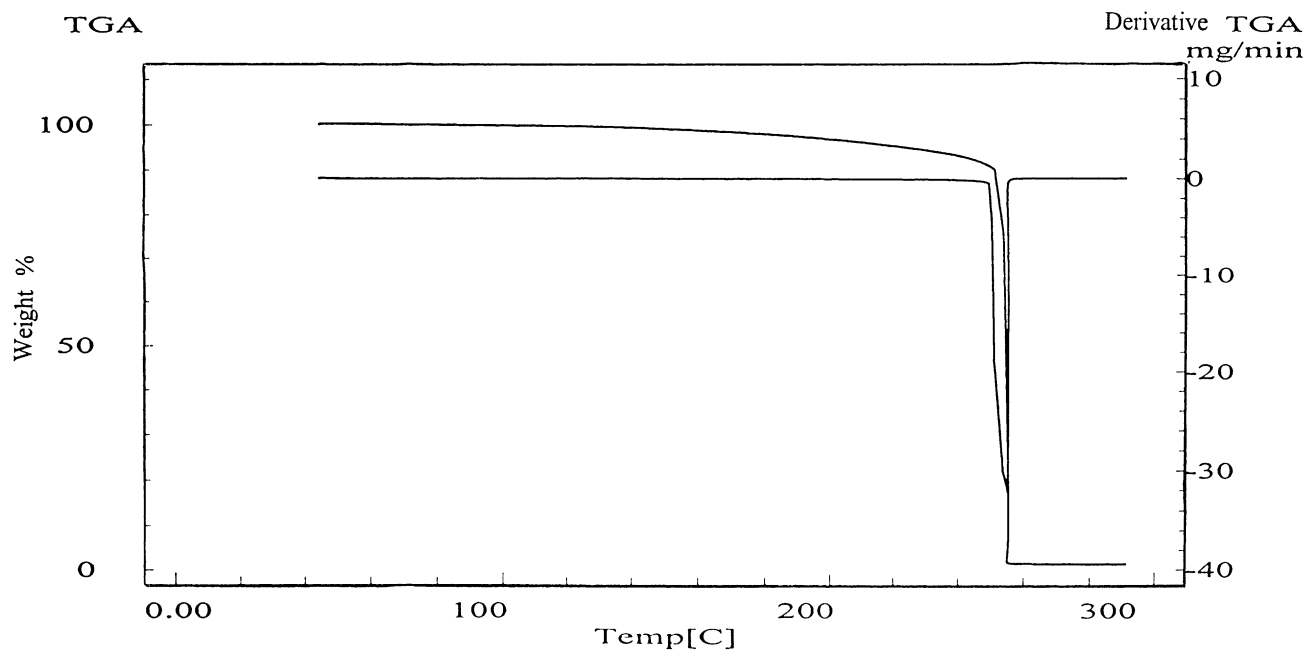


Fig. 5. Non-isothermal thermo gravimetric analysis of the nitrocellulose containing 25% poly 2-ANP:75% poly 2-AMP.

samples A4 and A6, respectively are given as illustrative examples of the non-isothermal decomposition of nitrocellulose.

The amount of nitrogen oxides gases released as a result of nitrocellulose ignition can be titrimetrically estimated and used to predict the stability of propellant mixes. The lower the milliliter consumed of NaOH in the titration, the higher the stability of the propellant is.

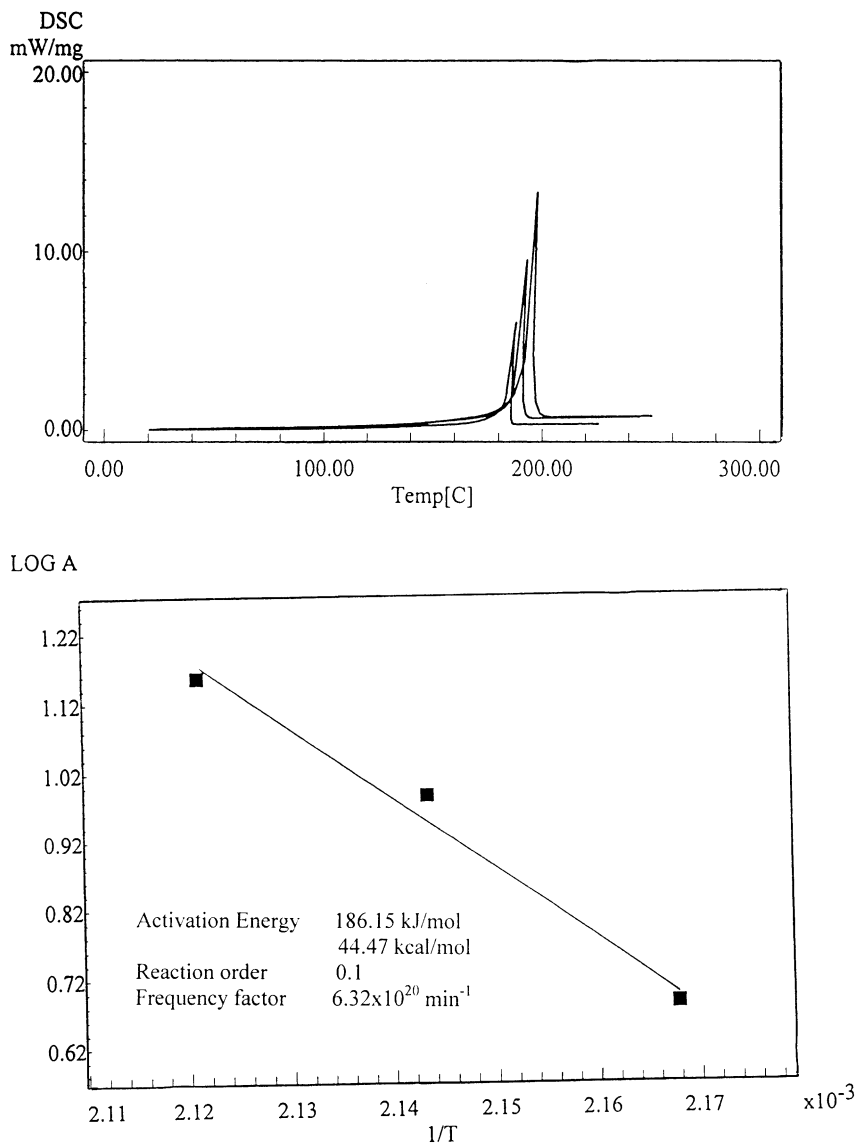


Fig. 6. Differential scanning calorimeter measurements and Ozawa plot of nitrocellulose samples stabilizes by DPA at heating rates 5, 10 and 15°/min.

This is the principal of the famous Bergmann–Junk test. The results of this test are shown in Table 5.

From the table, it can be generally seen that samples incorporated with the prepared polymers either independently or in blend ratios have been titrated with less NaOH than sample incorporated with DPA. The most lowest amount of NaOH consumed is recorded

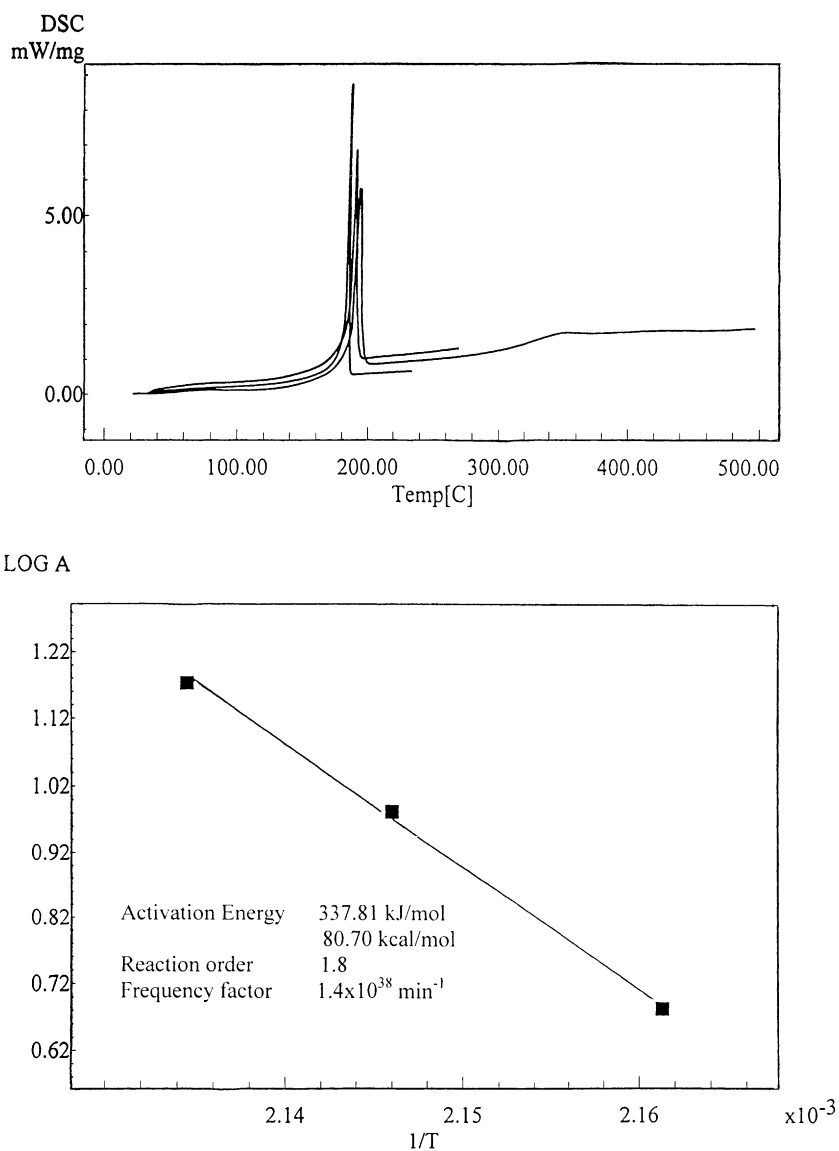


Fig. 7. Differential scanning calorimeter measurements and Ozawa plot of nitrocellulose samples stabilizes by 75% poly 2-ANP:25% poly 2-AMP at heating rates 5, 10 and 15°/min.

for sample A4 (0.23 ml) which indicates that a highly synergistic effect of both polymers can be achieved using the blend ratio 75% poly 2-ANP:25% poly 2-AMP. This means that sample A4 is much more efficient than sample A6 containing DPA which consumed 2.1 ml.

Activation energies of decomposition of all propellant samples were calculated and the results are shown in Table 6.

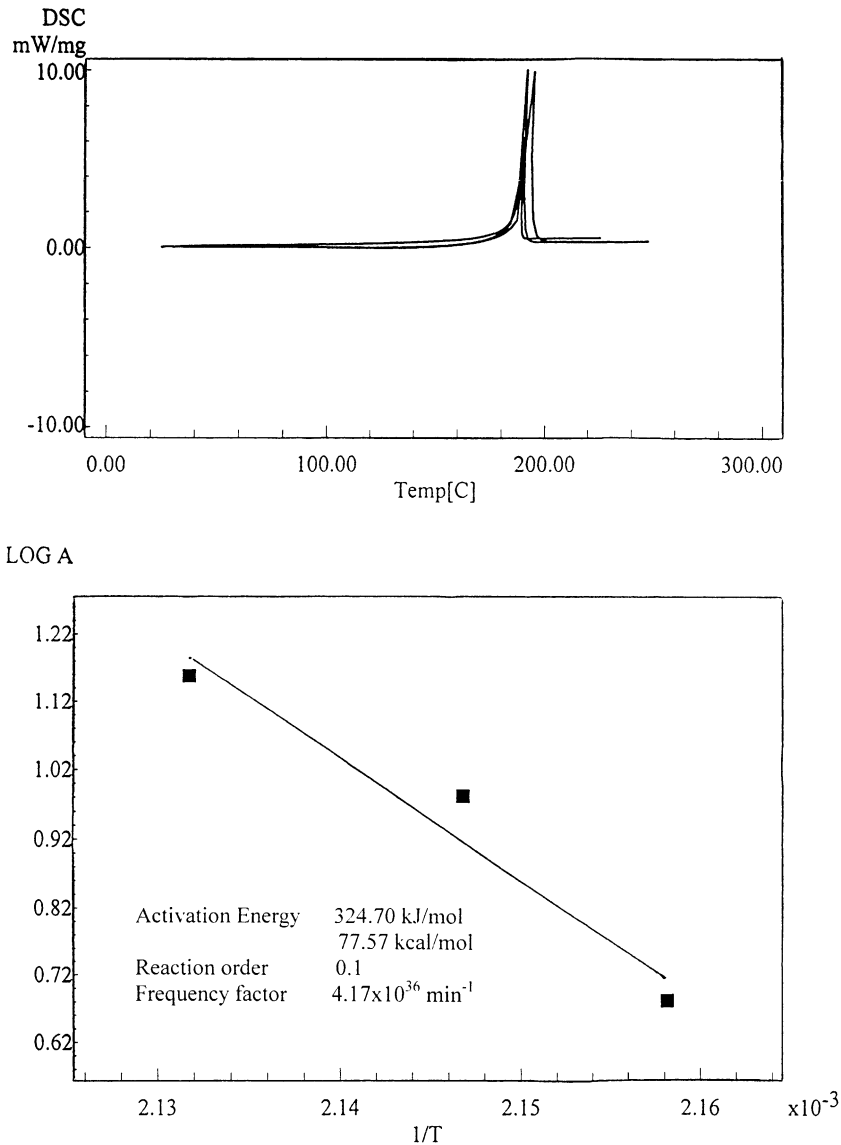


Fig. 8. Differential scanning calorimeter measurements and Ozawa plot of nitrocellulose samples stabilizes by 50% poly 2-ANP:50% poly 2-AMP at heating rates 5, 10 and 15°/min.

Table 6
Activation energy of decomposition of all propellant samples

Sample	Composition of stabilizer	E_a (KJ/mol)
A1	DPA	186
A2	100% 2-ANP	257
A3	100% 2-AMP	272
A4	75%:25%	337
A5	50%:50%	324
A6	25%:75%	196

It was previously reported [11] that, the higher the activation energy of decomposition, the higher the stability of the propellant is. From Table 6, it can be seen that the activation energies are descending in the order: A4 > A5 > A3 > A2 > A6 > A1 >. This order shows clearly that the best stabilization effect has been reached by the synergistic action of both prepared polymers in the blend ratios 75% poly 2-ANP:25% poly 2-AMP and 50%:50%. However, the synergistic action of both polymers in the ratio 25:75, has shown a slightly more increase in thermal stability than DPA which showed the lowest stabilization action. Furthermore, the activation energy of sample A3 containing poly 2-AMP is higher than that of sample A2, containing poly 2-ANP. This means that the electron donating effect of the two CH₃ groups existing in each repeating unit of poly 2-AMP may be more stronger in activating the phenyl rings than the electron withdrawing effect of the two NO₂ groups existing in each repeating unit of poly 2-ANP when each polymer is used independently. In Figs. 6–8, in which log heating rate is plotted against 1/*T* where *T* is the peak temperature at each heating are representing samples A1, A4 and A5 and are shown as illustrative examples. These results are in good agreement with the results obtained by Bergmann–Junk test given in Table 5.

4. Conclusions

1. The prepared polymers are generally more efficient stabilizers for nitrocellulose than diphenylamine.
2. The best synergistic effect of poly 2-ANP and poly 2-AMP as nitrocellulose stabilizers can be reached at blend ratios 50%:50% and 75%:25%, respectively.

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