Studies on Some Acrylamido Polymers and Copolymer as Stabilizers for Nitrocellulose

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ABSTRACT: *para*-Phenylene diamine was reacted with diethylmalonate and the product was reacted with acryloyl chloride to obtain the corresponding acrylamido malonanilide monomer. *para*-Nitro aniline was also reacted with acryloyl chloride to obtain the corresponding monomer. The two monomers were homopolymerized and then copolymerized. The obtained homopolymers and the copolymer were mixed with nitrocellulose and evaluated using thermal analysis and Bergmann–Junk techniques as propellant stabilizers in comparison with the common stabilizer, centralite 1. It was found that the homopolymer containing the *p*-nitro group is a superior stabilizer. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 2808–2819, 2002

Key words: monomer synthesis; polymerization; copolymerization; propellant; stabilizers; thermal analysis

INTRODUCTION

The concept of stabilizing propellants is of fundamental importance for long-term service propellants. Propellant stabilizers are those materials that are capable of reacting with the decomposition products of propellants and removing them. They do not prevent decomposition, but they do stop the catalytic action of the decomposition products such as NO, NO_2, HNO_2, and HNO_3. Different classes of organic compounds based on imidazole and pyrazole have been long recognized as stabilizers,[1–6] among which amines are the most important. Compounds possessing the PHN moiety in their structure have also proven to be good stabilizers. Recently, Zayed et al.[7] have prepared and used a series of malonanilides as stabilizers compared against centralite 1 (*N,N′*-diethyldi-phenyl urea; C1), which is the most common stabilizer. They found that some malonanilides were more efficient than C1 and others were equivalent to it. However, polymers and copolymers received considerably less attention as propellant stabilizers. Besides their inherent thermal stability, polymers and copolymers can provide an important feature by offering a large number of phenyl groups that may be capable of reaction with nitric oxide gases, decomposition products of nitrocellulose samples.

In this investigation we reacted acryloyl chloride with 4,4′-diaminomalonanilide and *p*-nitroaniline to obtain the corresponding monomers then homopolymers. The copolymer of the two monomers was also prepared, then the three prepared compounds were used as stabilizers for nitrocellulose compared with centralite 1, the most common propellant stabilizer. Thermal analysis and Bergmann–Junk (B&J) techniques were the main tools used to evaluate the efficiency of the prepared polymers as propellant stabilizers.
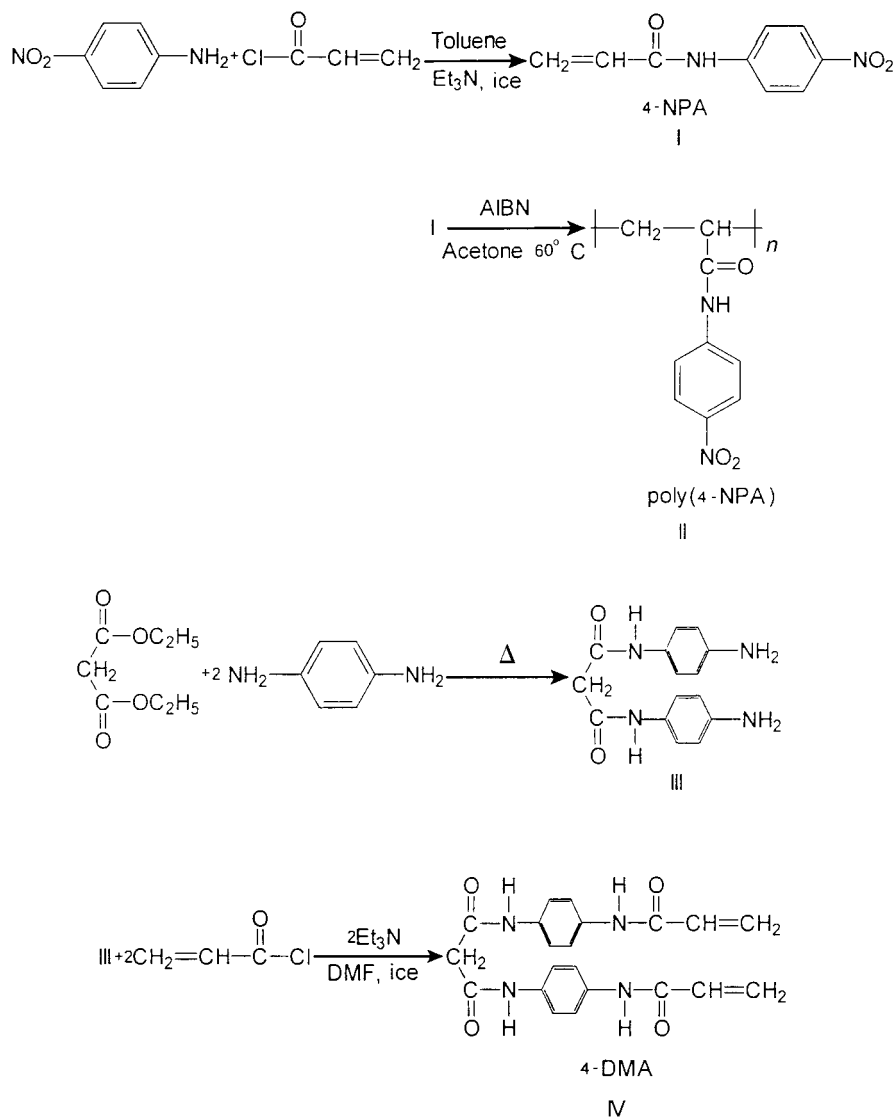
Scheme 1 Synthesis and polymerization of the prepared stabilizers.

EXPERIMENTAL

Materials

Acryloyl chloride, diethylmalonate, and triethylamine were supplied by Merck (Darmstadt, Germany). Phenylenediame and p-nitroaniline were supplied by Aldrich (Milwaukee, WI). All solvents were of laboratory grade and supplied by Edwic (Egypt).

The synthesis and polymerization of the following prepared stabilizers are graphically presented in Scheme 1.

Synthesis of N-(4-Nitrophenyl) Acryl Amide (4-NPA)

p-Nitroaniline (0.1 mol) in 100 mL of toluene was stirred with 0.1 mol of Et$_3$N in an ice bath. Acry-

loyl chloride (0.1 mol) was added dropwise to this mixture.[8] After addition, the reaction mixture was stirred for 2 h, left overnight, and then filtered. The precipitate was poured into acetone to dissolve the triethylamine hydrochloride, then filtered to obtain the product that was crystallized from the ethanol/water mixture. The product was dried in an oven and the melting point was measured.

Synthesis of 4,4'-Diacrylamido Malonanilide (4-DMA)

Diethylmalonate (0.1 mol) was condensed with 0.2 mol of p-phenylenediamine for 45 min at 240°C. The condensate was poured into ethanol for precipitation and the precipitate was filtered then dried to obtain the corresponding malonani-

poly(4-DMA)

VI

The copolymer
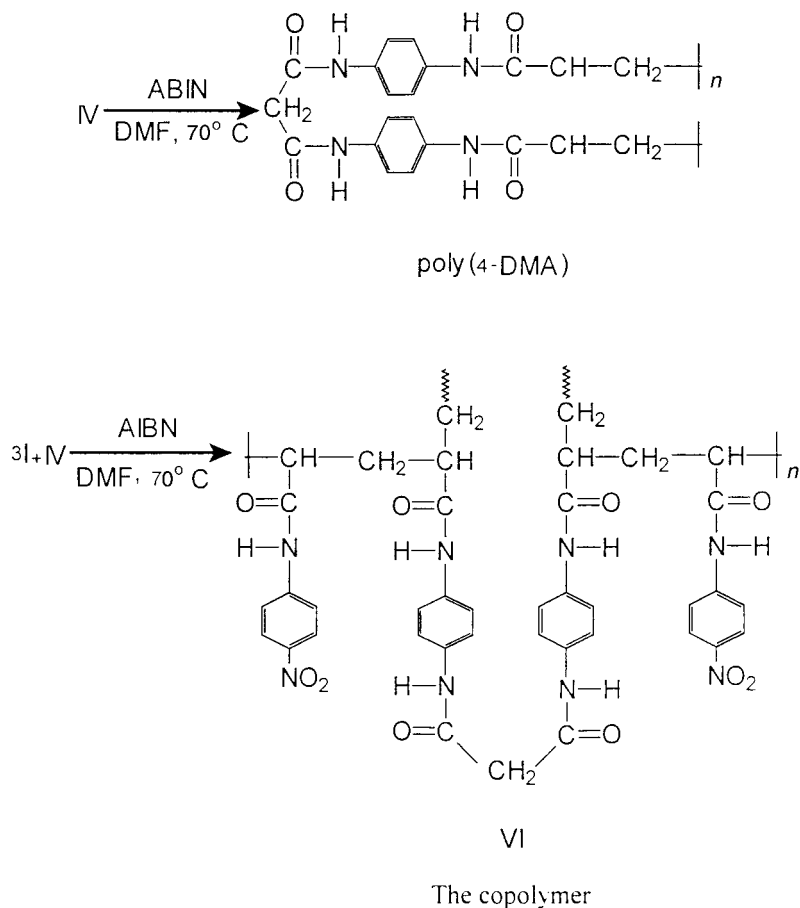
Scheme 1   (*Continued*)

lide.[7] A 0.1-mol sample of the obtained malonanilide in 450 mL of DMF was stirred with Et_3N in an ice bath. Acryloyl chloride (0.2 mol) was added dropwise to this mixture. After addition, the reaction mixture was stirred for 3 h, left overnight, and then filtered. The filtrate was poured into distilled water to obtain the crystallized product.[8] The product was filtered and dried, and the melting point was measured. The prepared monomers are shown in Table I.

Table I   The Prepared Monomers and Their Melting Points

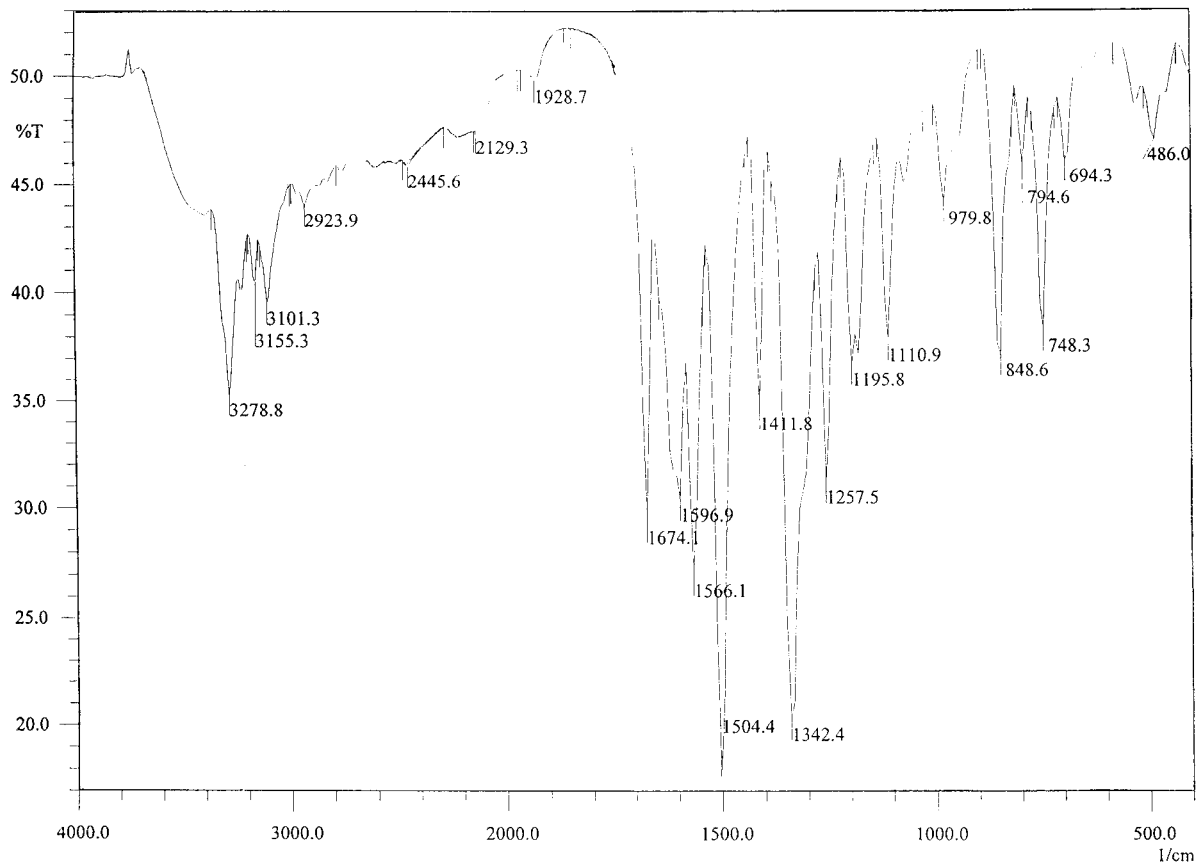| Name	Abbreviation	Melting Point (°C)	Chemical Structure
N-(4-Nitrophenyl) acrylamide	4-NPA	238	
4,4′-Diacrylamido malonanilide	4-DMA	355	

Figure 1　IR spectra of 4-NPA.
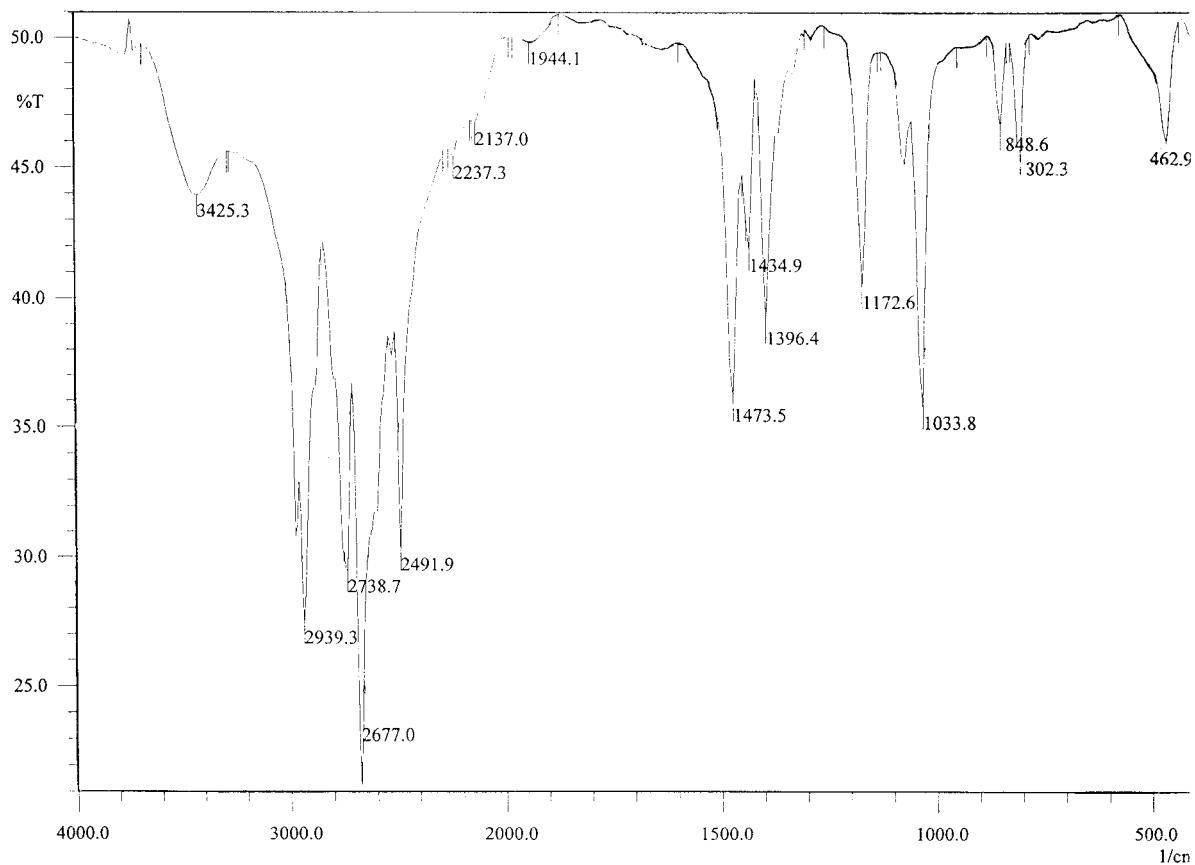

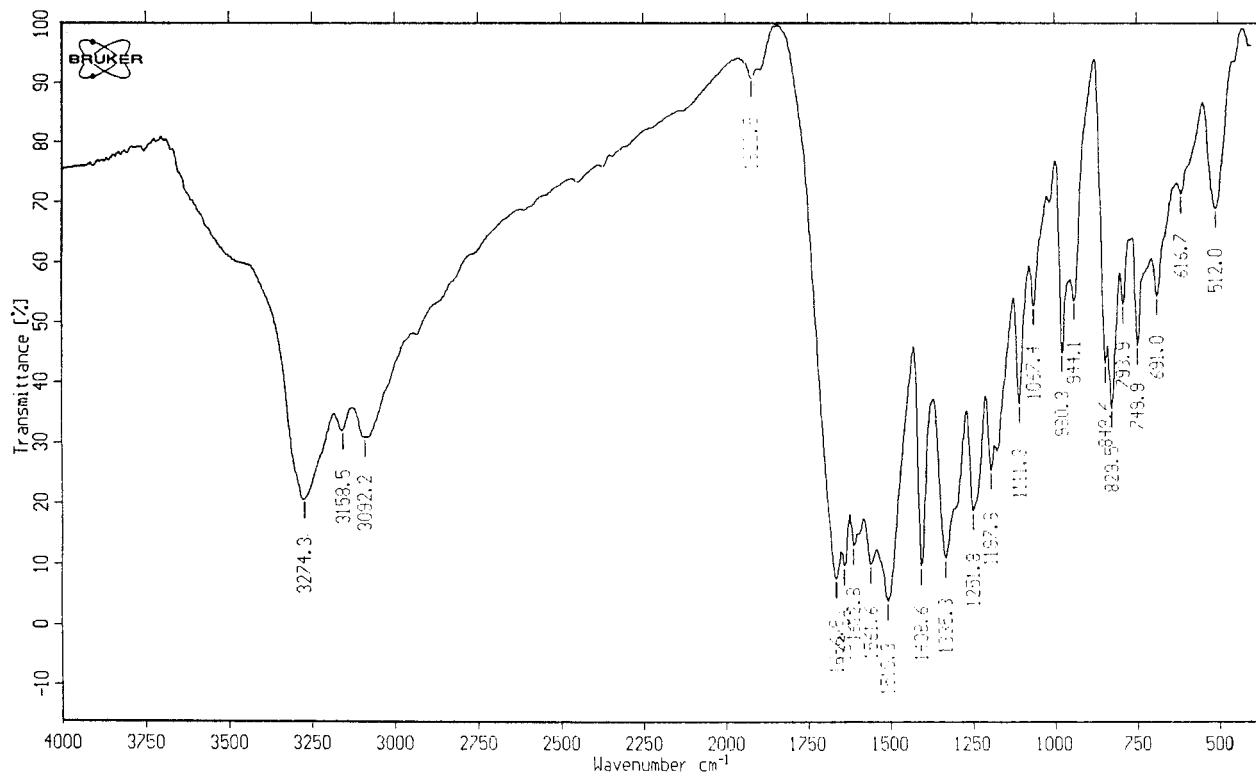**Figure 2**　IR spectra of 4-DMA.

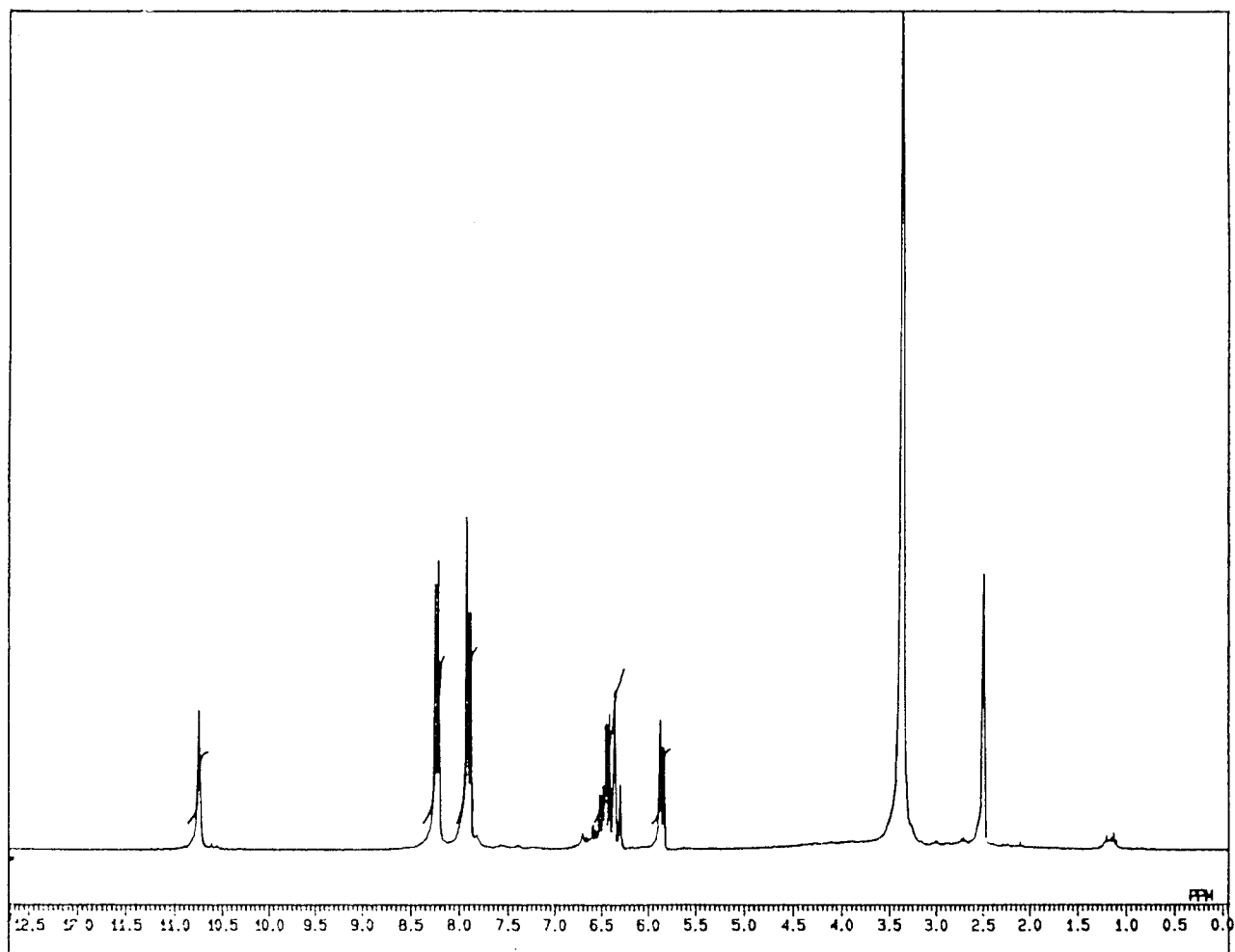**Figure 3** IR spectra of the copolymer of 4-NPA and 4-DMA.
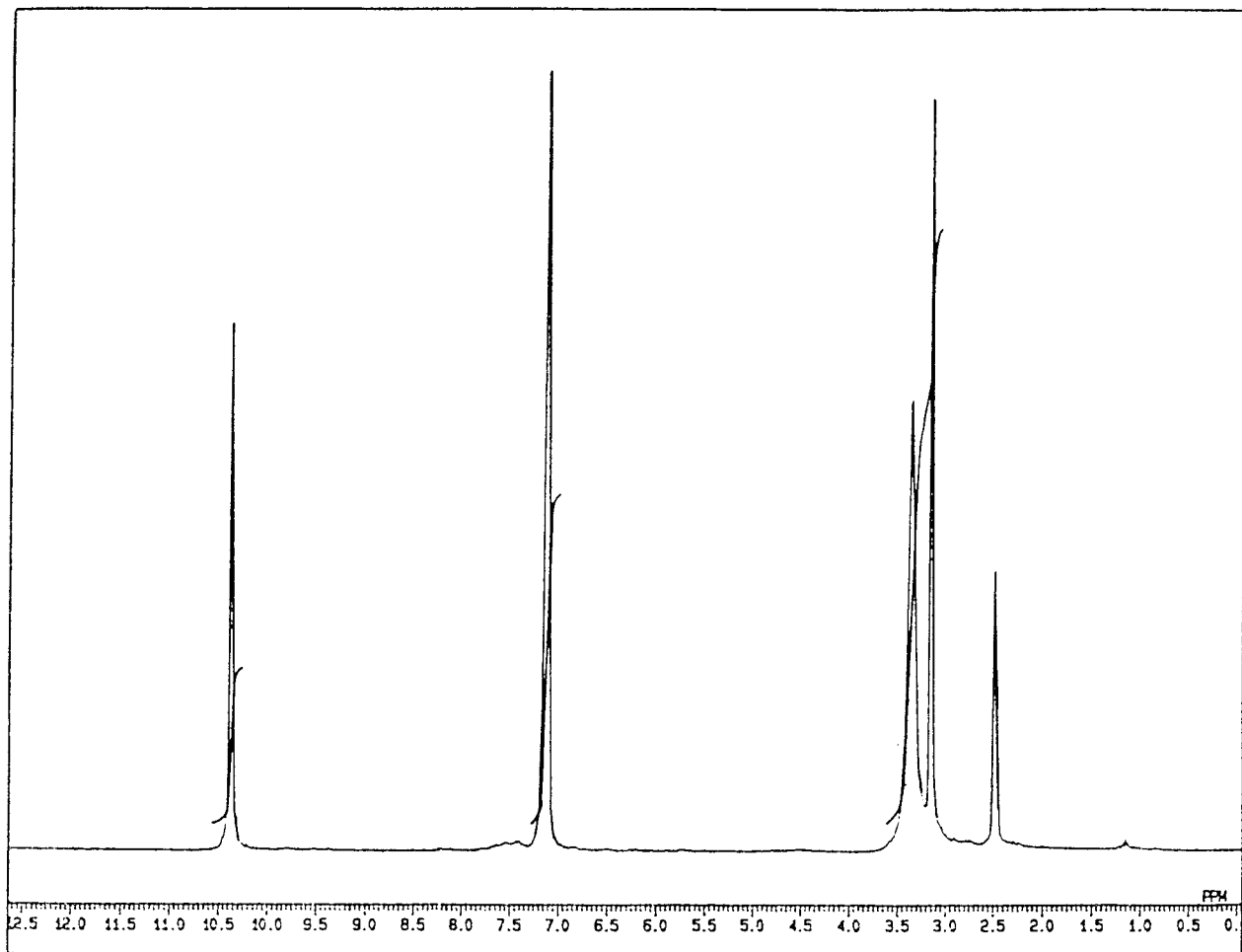

Figure 4 ^{1}H-NMR spectra of 4-NPA.

Figure 5 ^{1}H-NMR spectra of 4-DMA.

Polymerization of 4-NPA

A solution polymerization technique with a monomer/initiator ratio of 50 : 1 was used. A 4-g sample of 4-NPA was polymerized in 40 mL DMF at 60°C for 24 h using 0.032 g of azobisisobutyronitrile (AIBN) as an initiator. The solution was left to cool, then poured into distilled water to precipitate the polymer. The polymer was obtained as a yellow powder, purified by reprecipitation, then dried.

Polymerization of 4-DMA

The same solution polymerization technique with the same monomer-to-initiator ratio was used. A 4-g sample of 4-DMA was polymerized in 100 mL DMF at 70°C for 20 h using 0.032 g of AIBN as an initiator. The solution was left to cool, then poured into methanol to precipitate the polymer. The solution was filtered and the polymer was

obtained as a brownish powder, then purified by reprecipitation.

Copolymerization of 4-NPA and 4-DMA

A 9-g sample of 4-NPA was added to 3 g of 4-DMA in a ratio of 3 : 1, then dissolved in 250 mL DMF. The solution was copolymerized at 70°C for 36 h using 0.096 g AIBN as an initiator. The solution was left to cool, then poured into methanol to precipitate the homopolymer of poly(4-DMA), then filtered. The filtrate was poured into distilled water to precipitate both copolymer and the homopolymer of 4-NPA, then filtered. The precipitate was then poured into acetone to dissolve the homopolymer of 4-NPA, then filtered to obtain the copolymer as precipitate.

Characterization of the Prepared Polymers

IR spectroscopic data were performed on a Bruker 1600 FTIR spectrophotometer (Bruker Instru-
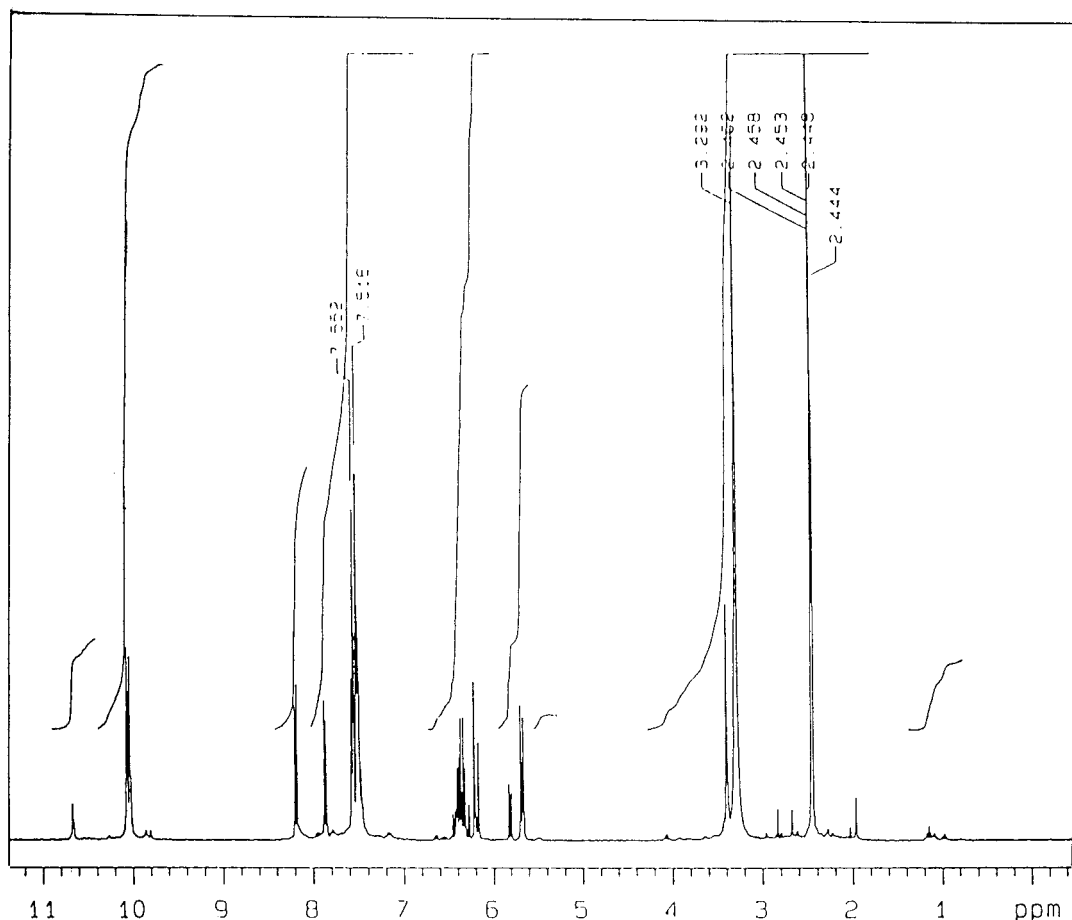
Figure 6   ^{1}H-NMR spectra of the copolymer of 4-NPA and 4-DMA.

ments, Billerica, MA) using KBr. ^{1}H-NMR spectra of the two prepared monomers were obtained on a JEOL 270 (JEOL, Peabody, MA), whereas that of the copolymer was obtained on an Oxford 400 (Oxford Instruments, Oxford, UK) using DMSO, to elucidate the structure and to ensure the purity of the prepared compounds. Spectra of

IR and ^{1}H-NMR are shown in Figures 1–3 and 4–6, respectively.

Propellant Mixing

Propellant samples were prepared by a solventless method by mixing nitrocellulose (92%), dibu-

Table II   IR and ^{1}H-NMR Assignments of The Prepared Monomers and Their Copolymer

Compound	IR	^{1}H-NMR
4NPM	C=O, amides I and II, 1473.5 and 1434 cm^{-1} –NH amide, 3425 cm^{-1}	Amide, N–H (s) = 10.7 δ Ar–H (dd) = 7.9–8.2 δ
4-DMA	The two types of C=O, amides I and II, 1674, 1546 and 1666, 1504 cm^{-1}	Amide, N–H (s) = 10.4 δ Ar–H, (dd) = 7.2 δ
Copolymer	–NH, 3274.3 cm^{-1}, C=O of both monomers, 1669–1510 cm^{-1}	Amide, N–H of 4-NPA (s) = 10.65 δ Amide, N–H of 4-DMA (d) = 10.1 δ Ar–H of 4-NPA and 4-DMA (m) = 7.4–8.2 δ

Table III   Decomposition Temperatures of Nitrocellulose Samples Containing Different Stabilizers

Stabilizer	Temperature of Starting Decomposition (°C)	DTG Peak Temperature (°C)	Time Difference Between Starting Decomposition and DTG Peak (min)
Poly(4-NPA)	185.00	312.00	13.97
Copolymer	189.00	293.00	10.58
Poly(4-DMA)	181.26	268.84	8.16
Centralite 1	172.00	263.00	8.81

tylphthalate (4%), stabilizer (3%), and transformer oil (1%). Samples were dried before use in an oven at 60°C for 16 h.

Thermal Analysis

Nonisothermal and isothermal (150, 160, and 170°C) TGA and DSC analyses were carried out using a Shimadzu 50 (Shimadzu, Kyoto, Japan) to examine the decomposition behavior of the stabilized nitrocellulose samples. All the thermal analysis experiments were carried out using 10-mg samples, under inert nitrogen atmosphere at a heating rate 10°C min^{-1}.

Bergmann–Junk Test

Propellant samples were heated in a B&J bath for 2 h at 132°C. Samples were then titrated against 0.05N NaOH using methyl red as an indicator.[9]

RESULTS AND DISCUSSION

Polymer Structure

IR and ^{1}H-NMR spectra of the two prepared monomers, 4-NPA and 4-DMA, and their copolymer were consistent with the assigned structures. Assignments are given in Table II.

TGA was carried out under nonisothermal conditions, the obtained results of which are shown in Table III.

It can be seen that the prepared polymers have generally imparted nitrocellulose higher stability than that imparted by the common stabilizer C1. This is obvious from the starting decomposition temperatures, which descend in the order: copolymer > poly(4-NPA) > poly(4-DMA) > C1. This order clearly shows that starting decomposition has been delayed 17, 15, and 9.8°C, respectively, in the case of using the prepared polymers rather
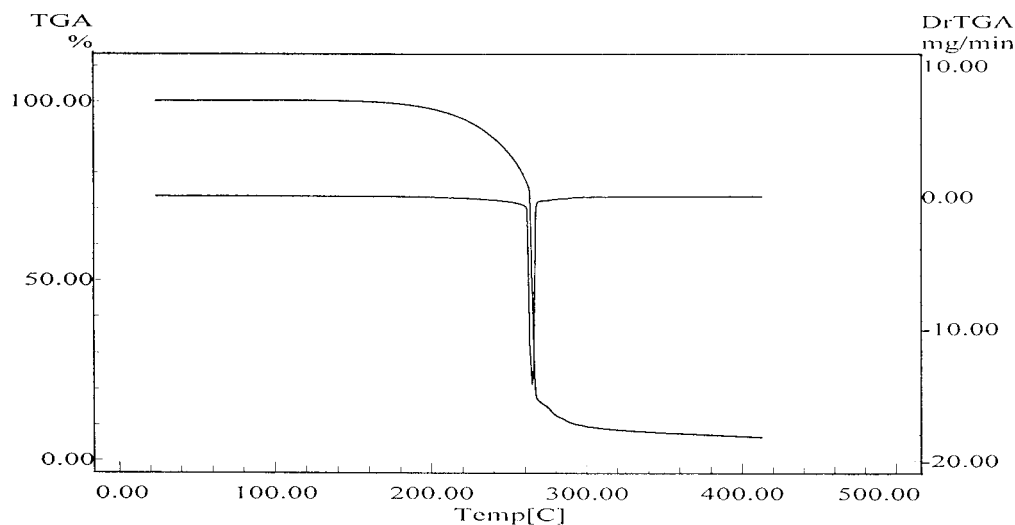

Figure 7 Nonisothermal TGA thermogram of the nitrocellulose sample containing centralite 1 (C1).
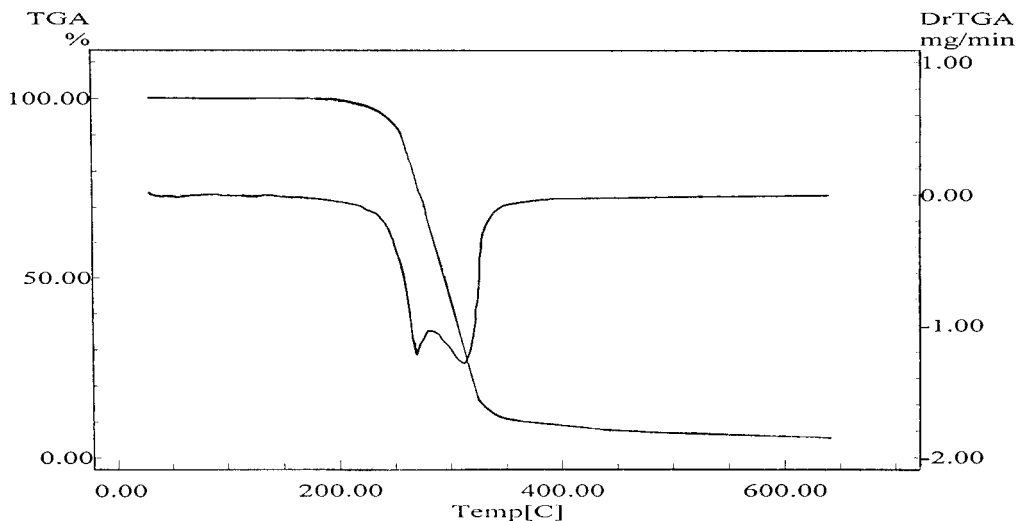
Figure 8 Nonisothermal TGA thermogram of the nitrocellulose sample containing poly(4-NPA).

than using C1, which started decomposition at 172°C. Another important factor that judges the efficiency of propellant stabilizers is the DTG peak temperature. The higher the peak temperature, the more efficient the stabilizer. The results in Table III show that the highest DTG peak temperature (312°C) is recorded for the sample containing poly(4-NPA), followed by the peak of the sample containing the copolymer at 293°C. Meanwhile, the sample containing the homopolymer poly(4-DMA) did not show any significant difference compared with that containing C1. This order indicates the efficiency of the copolymer and poly(4-NPA) as stabilizers. The TGA and DTG thermograms of poly(4-NPA) as an example of the prepared polymers compared with C1 are shown in Figures 7 and 8. On the other hand, the time difference between starting the decomposition and reaching the DTG peak is also an indication of the extent of stability that the stabilizer could impart to the propellant sample. The greater the time difference, the more efficient the

stabilizers. From Table III, it can be seen that the time difference descends in the order: poly(4-NPA), 13.97 min > copolymer, 10.6 min > C1, 8.8 min > poly(4-DMA), 8.2 min. These results show that the greatest time difference was recorded for poly(4-NPA) and ensures its efficiency. Thermogravimetric analysis was also carried out at isothermal conditions, 150, 160, and 170°C. The percentage weight losses for all samples are shown in Table IV.

It is generally clear that nitrocellulose samples stabilized by the prepared polymers showed lower percentage weight loss than that of the sample stabilized by C1. The nitrocellulose sample stabilized by poly(4-NPA) showed the lowest weight loss at all temperatures. These results are in good agreement with the results obtained earlier from studies at nonisothermal conditions and obviously indicate that this polymer is strongly capable of stabilizing propellant samples and prolonging their storage time. The results of the other polymers were in the descending order, copolymer

Table IV   Isothermal TGA of Nitrocellulose Samples Containing Different Stabilizers

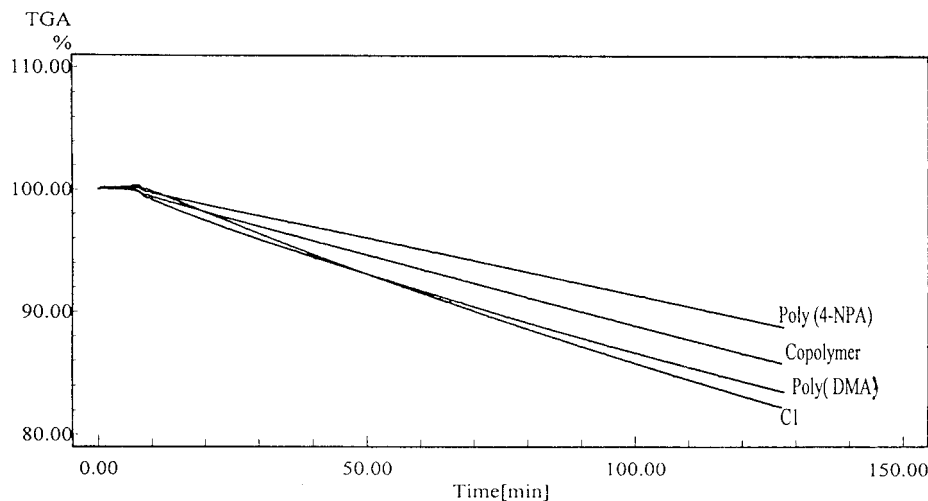|	Weight Loss (%) at Isothermal Temperatures (°C)		
Stabilizer	150	160	170
Poly(4-NPA)	2.966	5.083	7.101
Copolymer	5.929	8.672	13.468
Poly(4-DMA)	7.330	9.342	16.504
Centralite 1	8.888	10.483	17.735

Figure 9 Collective isothermal TGA thermogram of nitrocellulose samples stabilized by the prepared polymers compared with C1, at 170°C.

> poly(4-DMA) > C1, which also confirms the better efficiency of the prepared polymers to stabilize nitrocellulose samples. Figure 9 shows a collective thermogram for all samples at 170°C as an example supporting the above discussions.

The study of TGA and DSC thermograms together also provides another effective technique for the evaluation of the efficiency of propellant stabilizers. If TGA shows a lower percentage weight loss within the range of thermal decomposition shown by DSC, this gives an indication on the efficiency of the stabilizer and the potential long storage time of the propellant sample.

Table V shows the results of the percentage weight loss and the DSC range of decomposition (start: T_i; maximum, T_m; end: T_f).

From these results, it can be noticed that the percentage weight loss difference between samples containing the prepared polymers and that containing C1 is large. For example, the sample containing poly(4-NPA) showed only 6.71% weight loss within the decomposition range 166–246°C, whereas the sample containing C1 showed a 48% weight loss within the range 173–268°C. Furthermore, the efficiencies of nitrocellulose samples are arranged in the descending order: poly(4-NPA) > copolymer > poly(4-DMA) > C1. An explanation to that order of efficiency would be given on the basis that the presence of NO_2 groups of poly(4-NPA) in the p-position has activated phenyl rings toward receiving the nitric oxide gases that are produced from the decomposition process of propellant samples. On the other hand, phenyl rings of poly(4-DMA) are involved in the backbone chain of the polymer and each is bonded to an amide group from two sides. The lone pair of electrons available on the nitrogen atom is more involved in resonance within the amide group, thus contributing little to the acti-

Table V   DSC Results of Nitrocellulose Samples Containing Different Stabilizers in Correlation with TGA Percentage Weight Losses Within the Decomposition Range (T_i–T_f)

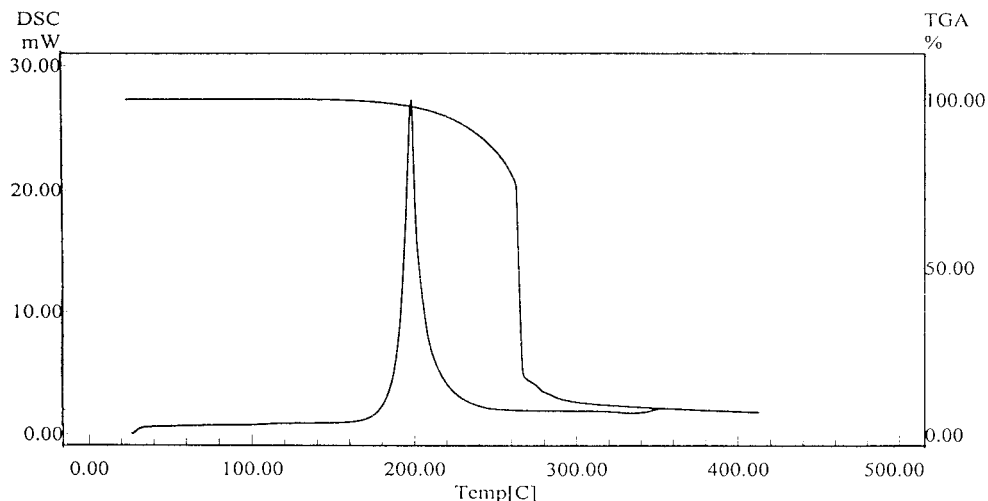| Stabilizer	T_i (°C)	T_m (°C)	T_f (°C)	Percentage Weight Loss
Poly(4-NPA)	166.00	195.00	246.00	6.71
Copolymer	175.00	194.50	241.00	7.71
Poly(4-DMA)	194.35	201.41	249.00	8.02
Centralite 1	173.81	187.99	268.00	48.00

Figure 10   The relation between DSC and TGA of the nitrocellulose sample containing C1.

vation of the phenyl rings. This may account for its lower activity to react with nitric oxide gases. Figures 10 and 11, which show TGA and DSC thermograms of nitrocellulose samples containing poly(4-NPA) and C1, respectively, at the decomposition temperatures, give an illustrative example to the results obtained.

The activation energy (E_a) required to start decomposition was calculated for each sample at 12% weight loss and 5, 10, and 15°C min^{-1} heating rates using the Ozawa method.[10] The results are given in Table VI. The higher the activation energy required, the more stable the propellant sample. From the table it can be noticed that the highest activation energy is recorded for the sam-

ple stabilized by poly(4-NPA), 136.34 kJ mol^{-1}, which is 26.34 kJ mol^{-1} greater than that of the sample stabilized by the common stabilizer C1. The activation energy of the sample stabilized by the copolymer, 126.94 kJ mol^{-1}, is also 16.94 kJ mol^{-1} greater than that of the sample containing C1. Meanwhile, the result of poly(4-DMA) is comparable to that of C1. These results confirm the better efficiency of poly(4-NPA) obtained earlier. Figure 12 shows the thermogram of poly(4-NPA) compared with that of C1 as an illustrative example.

The Bergmann–Junk test is also one of the most important and reliable techniques to judge the efficiency of propellant stabilizers. When the
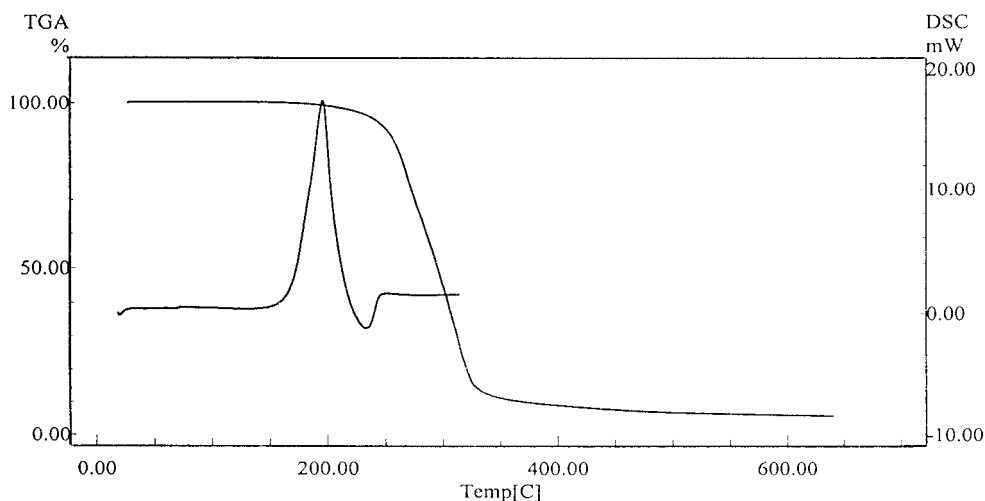

Figure 11   The relation between DSC and TGA of the nitrocellulose sample containing poly(4-NPA).

Table VI   Kinetic Parameters of the Thermal Decomposition of Nitrocellulose Samples Containing Different Stabilizers

Stabilizer	E_a (kJ/mol^{-1})
Poly(4-NPA)	136.34
Copolymer	126.94
Poly(4-DMA)	110.88
Centralite 1	110.00

Table VII   Bergmann–Junk Results of Nitrocellulose Samples Containing Different Stabilizers

Stabilizer	Milliliter Equivalent of NaOH (0.05N)
Poly(4-NPA)	0.3
Copolymer	0.7
Poly(4-DMA)	0.8
Centralite 1	0.8

number of milliequivalents of NaOH required to neutralize the nitric oxides dissolved in water is small, it indicates a highly efficient stabilizer. The
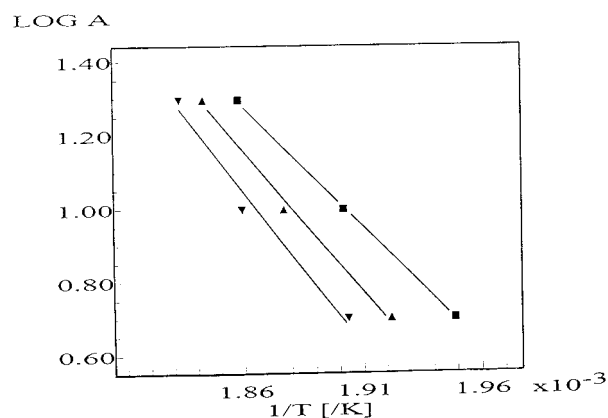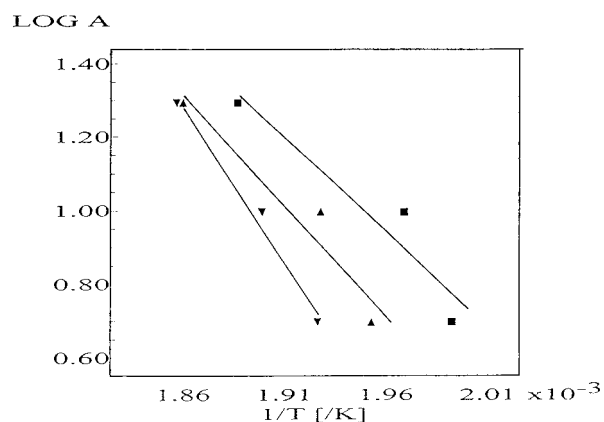
results obtained from B&J are shown in Table VII.

From this table, it can be seen that poly(4-NPA) is still the most efficient stabilizer compared with C1 and the other investigated polymers. These results are also in good agreement with the results obtained by thermal analysis in all cases discussed above.

CONCLUSIONS

1. The prepared poly(4-NPA) is a superior propellant stabilizer.
2. The prepared copolymer is a more efficient stabilizer than centralite 1 (C1).
3. The efficiency of the prepared poly(4-DMA) is comparable to that of C1.

Figure 12   Ozawa plot of nitrocellulose samples containing C1 and poly(4-NPA) at heating rates of 5, 10, and 15°C/min.

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