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# Structural Aspects of Novel Unsaturated Polyesters

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# STRUCTURAL ASPECTS OF NOVEL UNSATURATED POLYESTERS

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## ABSTRACT

Novel unsaturated polyesters designated NUP-I, NUP-II, and NUP-III have been synthesized by 1-step, 2-step, and 3-step polyesterification processes, respectively, and their possible structures have been assigned with the help of IR and NMR. Trends in the properties of uncured novel unsaturated polyesters (gel time and exotherm peak temperature) as well as cured novel unsaturated polyesters [tensile strength, elongation, bond strength with composite modified double-base (CMBD) propellants, Shore hardness, nitroglycerine (NG) absorption, thermal conductivity, and heat resistance] support these assigned structures.

## INTRODUCTION

The inhibition of rocket propellants demands higher elongation and lower explosive/nonexplosive plasticizer absorption in addition to other requirements [1–3]. It has been established that if elongation is higher, explosive/nonexplosive plasticizer absorption is also higher [4-8]. Novel unsaturated polyester-7 (III), designated NUP-7 (III), is based on MEXDIOL and three acids [i.e., isophthalic acid (IPA), adipic acid (AA), and maleic anhydride (MAn)] and is synthesized by a 3-step polyesterification process recently patented [9]. This NUP-7 (III) possesses higher elongation and lower nitroglycerine (NG) absorption—a combination of two contradictory properties reported for the first time [10] and is a potential candidate for inhibition of composite modified double-base (CMBD) propellants. These NUPs have been extensively characterized for various properties, but their structures have not been established chiefly because of MEXDIOL which is based on mixed glycols.

The objective of this study was to synthesize NUPs by different polyesterification processes using diethylene glycol (DEG), isophthalic acid (IPA), adipic acid (AA), and maleic anhydride (MAn) and to establish their structures. These NUPs have also been characterized for various properties which have been correlated with their assigned structures. This also indirectly provides evidence in support of these structures.

## EXPERIMENTAL

### Materials

The materials required for the synthesis are diethylene glycol (BDH, LR), isophthalic acid (LR), adipic acid (LR), maleic anhydride (technical), styrene monomer (LR), and hydroquinone (AR). These chemicals were procured from commercial sources and used as received. The curing agents, i.e., methyl ethyl ketone (MEK) peroxide (catalyst in dimethyl phthalate) and cobalt naphthenate (accelerator in methylene chloride), were of technical grade.

### Methods

#### Synthesis

These NUPs were prepared by 1-step, 2-step, and 3-step polyesterification processes as described earlier [10] and stabilized with 0.02% hydroquinone based on the weight of resin. The resulting polyesters were mixed with styrene monomer in the molar proportion of 65:35 and cured using MEK peroxide and cobalt naphthenate. The composition and acid values are given in Table 1.

#### Characterization

The IR spectra were recorded with a Perkin-Elmer Spectrophotometer, Model 457, by the Smear method.

The $^1$H-NMR spectra were recorded with a Brucker Apparatus AM-300 (frequency 300, 13 MHz) using $CDCl_3$ as solvent with tetramethyl silane (TMS) as internal standard.

The gel time and exotherm peak temperature of these NUPs containing styrene monomer were determined as described earlier [10]. The specimens for tensile strength and elongation [11], bond strength with CMDB propellants [3], Shore hardness [12], NG absorption [3], heat resistance [13], Oxygen Index [14], and

TABLE 1. Compositions and Acid Values of Novel Unsaturated Polyesters

| | Molar compositions | | | | | Acid values | | |
|---|---|---|---|---|---|---|---|---|
| Novel unsaturated polyesters | Diethylene glycol[a] (DEG) | Isophthalic acid (IPA) | Adipic acid (AA) | Maleic anhydride (MAn) | Polyesterification process | After adding IPA | After adding AA | After adding MAn |
| NUP-I | 12.0 | 2.0 | 5.0 | 5.0 | 1-Step | – | – | 40.0 |
| NUP-II | 12.0 | 2.0 | 5.0 | 5.0 | 2-Step | 40.0 | – | 40.0 |
| NUP-III | 12.0 | 2.0 | 5.0 | 5.0 | 3-Step | 40.0 | 40.0 | 40.0 |

[a] DEG was taken 0.10 mol in excess in order to compensate for glycol losses.

thermal conductivity [15] were cast and cured at ambient temperature (+27°C). These properties were determined by methods reported in the literature [3, 10–15].

## RESULTS AND DISCUSSION

### Structural Aspects

A comparison of the IR spectra of NUP-I, NUP-II, and NUP-III suggests that there is practically no difference among them. Most of the bands observed are common in all three products, suggesting they all contain the same functional groups.

The preparation of NUP-III consists of 3 steps as follows.

1. Reaction of IPA (2.0 mol) with DEG (12.0 mol) is the first step. The reaction product consists of an —OH terminated prepolymer, $-\mathrm{DEG}(\mathrm{IPA}-\mathrm{DEG})_x$ (designated A) and an excess of DEG. The NMR spectra of A (Fig. 1) suggests [16] the presence of

DEG: $HOCH_2.CH_2O.CH_2.CH_2OH$
3.7 ppm (21.75) $\underline{CH_2}OH$ of DEG
3.5 ppm (19.8) $O.\underline{CH_2}.CH_2OH$ of DEG

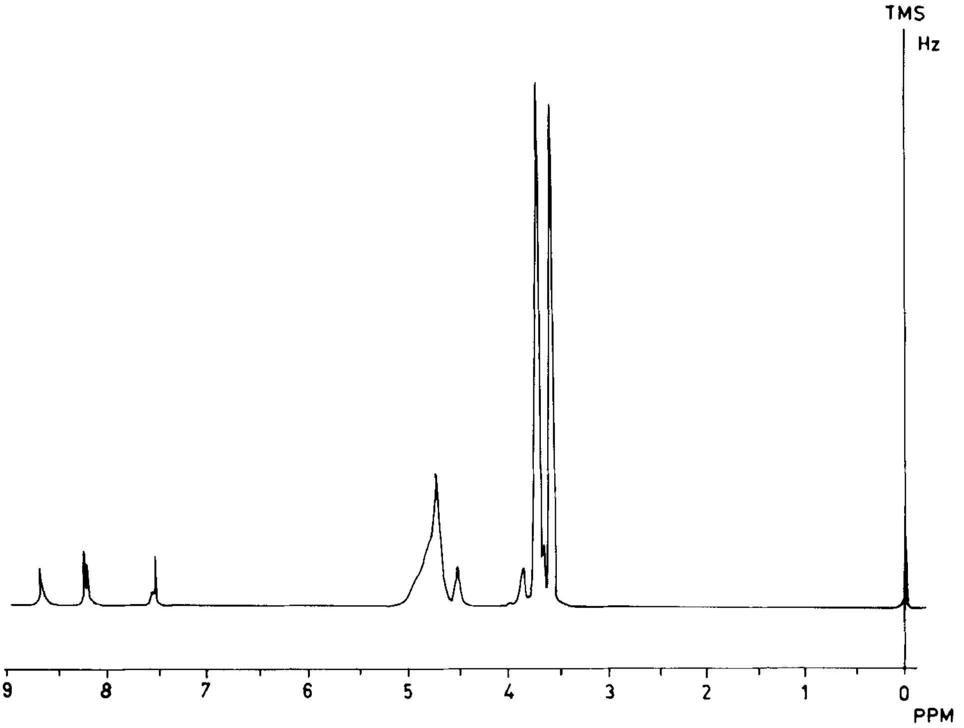
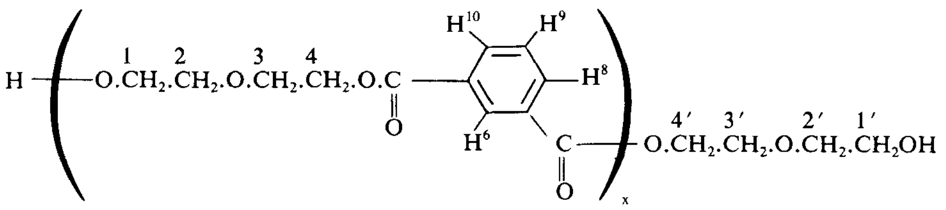
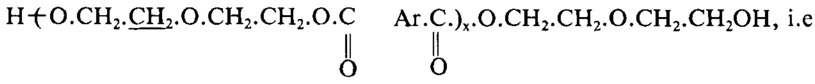


FIG. 1. $^1H$ spectra of A.

A: $DEG\text{-}(IPA-DEG)_x$, i.e.,



3.5 ppm (19.8)



$$H\text{-}(O.CH_2.\underline{CH_2}.O.CH_2.CH_2.O.\underset{\overset{\|}{O}}{C}\quad Ar.\underset{\overset{\|}{O}}{C}.)_x.O.CH_2.CH_2.O.CH_2.CH_2OH$$

i.e., $H^2$

3.6 ppm (0.27 $-\underline{CH_2}OH$, i.e., $H^1$

3.8 ppm (1.42) $O.\underline{CH_2}.CH_2.O.CO.-$, i.e., $H^3$

4.5 ppm (1.44) $\underline{CH_2}.O.CO.-$ i.e., $H^4$

4.8 ppm (5.23) Water as an impurity and/or terminal OH of DEG or prepolymer (oligoester) A

7.5 ppm (0.39) $H^9$

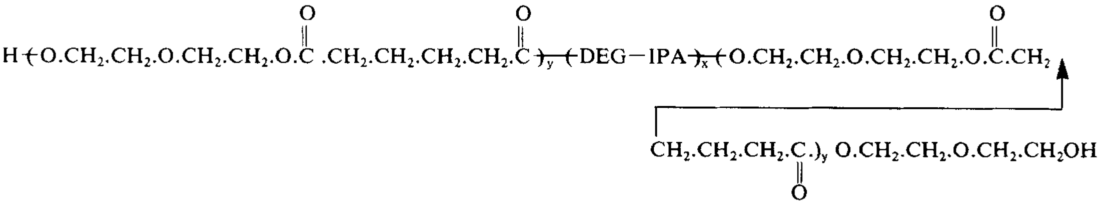
8.25 ppm (0.82) $H^8 + H^{10}$

8.65 ppm (0.44) $H^6$

2. Reaction of A (obtained in the first step) and an excess of DEG with AA (5.0 mol) in the second step, again giving a different —OH terminated prepolymer (designated B because DEG is still in excess) and consisting of

(a) reaction product of —OH terminated prepolymer A with AA and has the following structure supported by NMR spectra (Fig. 2):

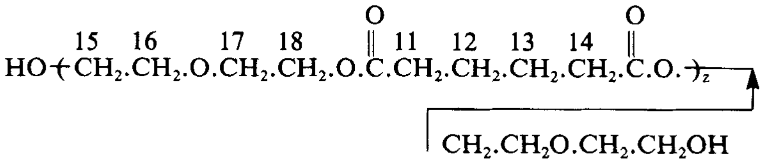
B:



$$H\text{-}(O.CH_2.CH_2.O.CH_2.CH_2.O.\overset{\overset{O}{\|}}{C}.CH_2.CH_2.CH_2.CH_2.\overset{\overset{O}{\|}}{C})_y\text{-}(DEG-IPA)_x\text{-}(O.CH_2.CH_2.O.CH_2.CH_2.O.\overset{\overset{O}{\|}}{C}.CH_2\; CH_2.CH_2.CH_2.\underset{\overset{\|}{O}}{C}.)_y\; O.CH_2.CH_2.O.CH_2.CH_2OH$$

i.e., $\text{-}(DEG-AA)_y(DEG-IPA)_x\text{-}(DEG-AA)_yDEG-$

(b) Reaction product of AA with DEG which is in excess and designated as B′:



$$HO\text{-}(CH_2.CH_2.O.CH_2.CH_2.O.\overset{\overset{O}{\|}}{C}.CH_2.CH_2.CH_2.CH_2.\overset{\overset{O}{\|}}{C}.O.)_z\; CH_2.CH_2O.CH_2.CH_2OH$$

i.e., $\text{-}(DEG-AA)_zDEG$

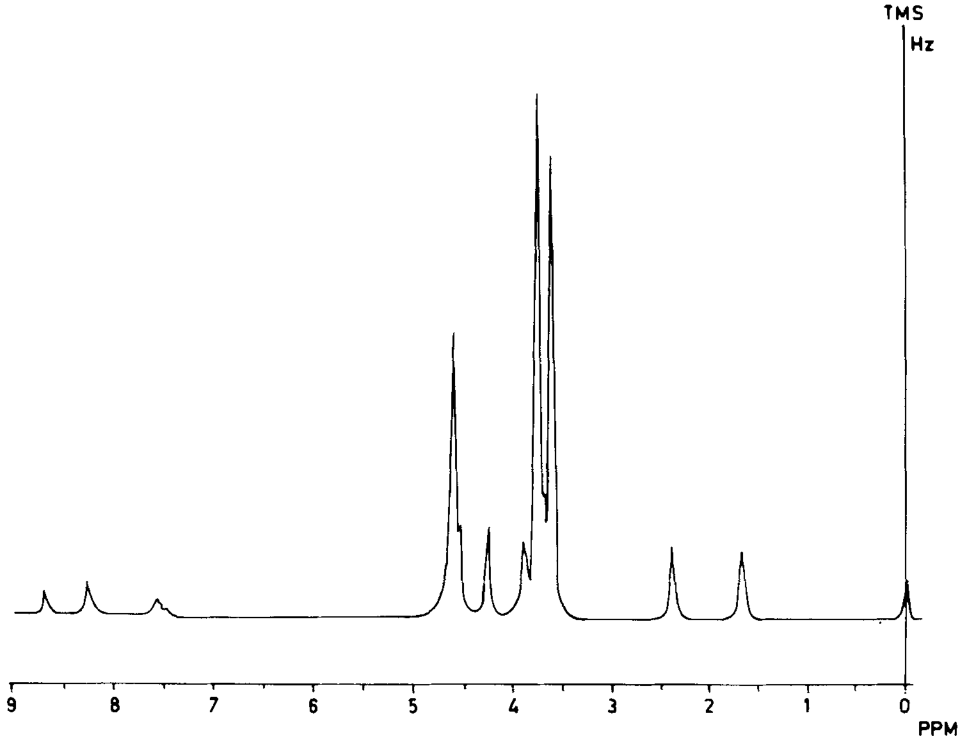


FIG. 2. $^1$H spectra of B.

2.3 ppm (2.62) $H^{11} + H^{14}$

1.6 ppm (5.20) $H^{12} + H^{13}$

4.3 ppm (3.38) $H^{15} + H^{18}$

3.8 ppm (3.15) $H^{16} + H^{17}$

3.7 ppm (20.2) $\mathrm{HO\underline{CH_2}.CH_2.O.}$of DEG

3.6 ppm (21.45) $\mathrm{HO\underline{CH_2}.CH_2.O.}$of prepolymers (oligoesters) of B and B′

4.6 ppm (12.0) $\mathrm{\underline{HO}CH_2.CH_2.O.}$of DEG

$\mathrm{\underline{HO}CH_2.CH_2.O.}$of prepolymers (oligoesters) of B and B′

3\. Reaction of B, B′ (obtained in the second step), and excess of DEG with MAn (5.0 mol) in the third step to give final product, i.e., NUP-III. This is likely to consist of

(a) the reaction product of B obtained in the second step with MAn in the third step to give a polyester designated as C of the following probable structure:

$$\left(\mathrm{DEG{-}MA/FA}\right)_a\left(\mathrm{DEG{-}AA}\right)_y\left(\mathrm{DEG{-}IPA}\right)_x\left(\mathrm{DEG{-}AA}\right)_y\left(\mathrm{DEG{-}MA/FA}\right)_a\mathrm{DEG}\quad \text{i.e. NUP-III}$$

(DEG, IPA, AA, and MA/FA represent moieties of the parent glycol and acids, respectively.)

The NMR spectra of NUP-III (Fig. 3) is almost similar to Fig. 2. In addition, it shows the following chemical shifts

6.2 ppm (2.53) $-\mathrm{CH}=\mathrm{CH}-$ of maleic acid
6.8 ppm (4.06) $-\mathrm{CH}=\mathrm{CH}-$ of fumaric acid

$$3.4\ \text{ppm}\ (9.9)\ \begin{cases} \mathrm{MA.O.CH_2.\underline{CH_2}.O.\underline{CH_2}.CH_2.O.MA} \\ \text{or} \\ \mathrm{FA.O.CH_2.\underline{CH_2}.O.\underline{CH_2}.CH_2.O.FA} \end{cases}$$

The chemical shifts at 6.8 and 3.4 ppm are due to isomerization of maleic acid to fumaric acid. This is in accordance with the findings already reported in the literature [13, 17] on maleic to fumaric isomerization in unsaturated polyesters.

(b) Reaction product of B′ (obtained in the second step) with MAn in the third step to give a product of the following structure:

$$\left(\mathrm{DEG-MA/FA}\right)_b\left(\mathrm{DEG-AA}\right)_z\left(\mathrm{DEG-MA/FA}\right)_b\mathrm{DEG}$$

(c) Reaction product of MAn with an excess of DEG:

$$-\mathrm{DEG}\left(\mathrm{MA/FA-DEG}\right)_c$$

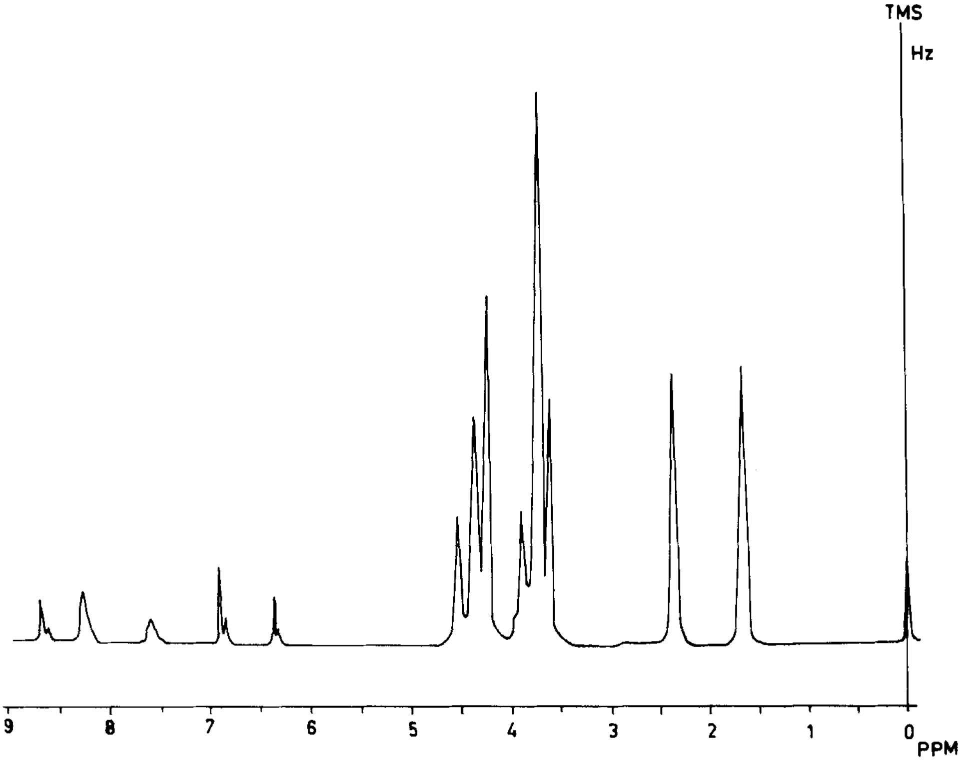
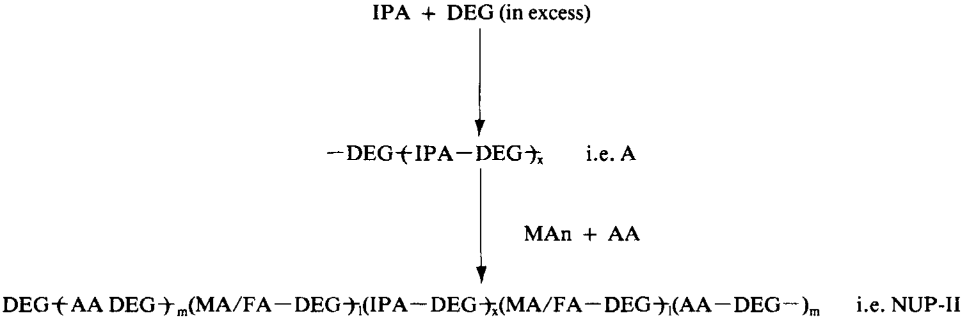


FIG. 3. $^1$H spectra of C.

Thus, the chain length built up in the first step is extended by the reaction of AA in the second step and further extended by the reaction of MAn in the third step. It may therefore be concluded that NUP-III consists mainly of molecules of higher chain lengths.

NUP-II is prepared by the (a) reaction of IPA (2.0 mol) with DEG (12.0 mol) to give a —OH terminated prepolymer A similar to the first step of NUP-III; (b) reaction of —OH terminated prepolymer A with AA (5.0 mol) and MAn (5.0 mol) together.

The prepolymer of the first step, i.e., A, has a certain chain length and it does not scramble on reaction with AA and MAn. As MAn is more reactive (as indicated by the dissociation constants of MA and AA [18, 19]), MAn reacts first with the prepolymer A followed by the reaction of AA. Therefore, NUP-II is likely to have structure



$$
\begin{tikzcd}
\text{IPA} + \text{DEG (in excess)} \arrow[d] \\
-\text{DEG}(\text{IPA}-\text{DEG})_x \quad \text{i.e. A} \arrow[d, "\text{MAn} + \text{AA}"] \\
\text{DEG}(\text{AA DEG})_m(\text{MA/FA}-\text{DEG})_l(\text{IPA}-\text{DEG})_x(\text{MA/FA}-\text{DEG})_l(\text{AA}-\text{DEG}-)_m \quad \text{i.e. NUP-II}
\end{tikzcd}
$$

The NMR spectra of NUP-II (Fig. 4) confirms the presence of ester linkages between DEG with each of the acids, i.e., IPA, AA, and MA. The chemical shifts of various protons in NUP-II (Fig. 4) are, however, almost the same as those recorded in NUP-III (Fig. 3).

In addition, there are minor proportions of —DEG—AA—DEG—, —DEG—MAn—DEG— (takes part in crosslinking because of —C=C— bonds), and $(\text{DEG}-\text{MA/FA})(\text{DEG}-\text{AA})\text{DEG}$ (also takes part in the crosslinking because of the presence of unsaturation in MA). The exact proportions cannot be estimated from the NMR spectra (Fig. 4) because the chemical shifts due to them cannot be differentiated from those of NUP-II. However, the presence of minor proportions of these compounds is supported by the fact that no oozing of liquids is observed at the time of casting of specimens for the determination of various properties. In the case of significant proportions of these compounds in NUP-II, some liquid will ooze out at the time of casting of specimens because it does not take part in curing.

NUP-I is made by a 1-step polyesterification process, i.e., by reacting IPA (2.0 mol), AA (5.0 mol), and MAn (5.0 mol), all at one time, with DEG (12.0 mol). In the first phase of the condensation reaction, all the acids react independently with DEG and give

$$(\text{DEG}-\text{MA})_n\text{DEG}$$
$$(\text{DEG}-\text{IPA})_o\text{DEG}$$
$$(\text{DEG}-\text{AA})_p\text{DEG}$$

When the condensation reaction is continued to achieve an acid value (AV) of ~40, there is a reaction among these prepolymers, resulting in a polyester having a random order of these blocks along the polyester backbone.

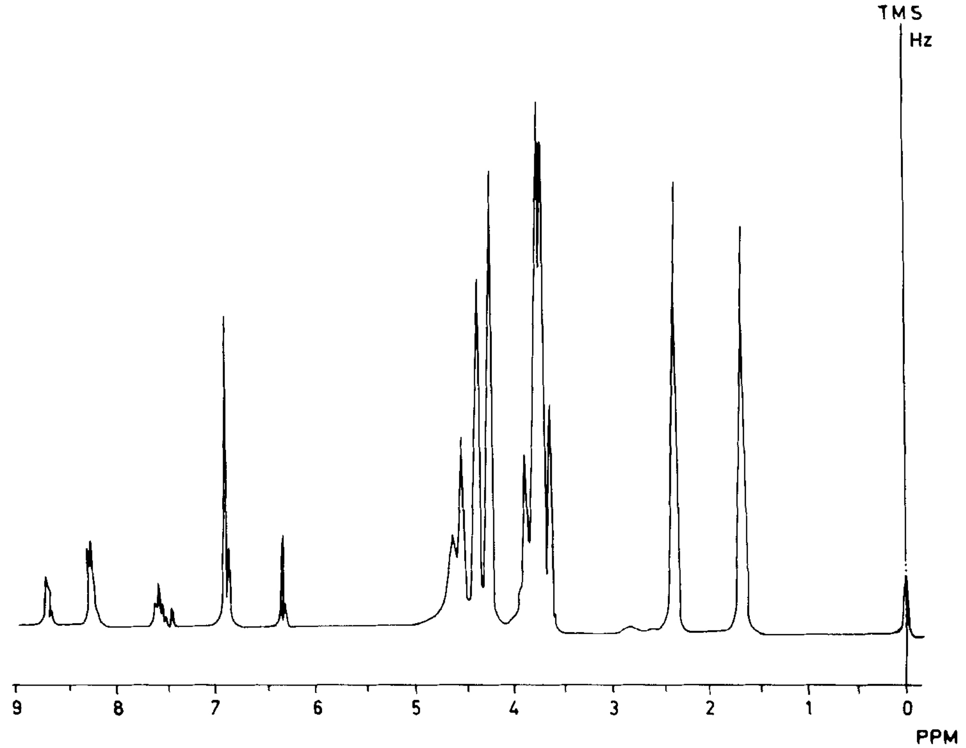


FIG. 4. $^1$H spectra of D.

$-\!\!(AA-DEG)_p(IPA-DEG)_o(MA/FA-DEG)_n(IPA-DEG)_o(AA-DEG)_p$ i.e. NUP-I

The NMR spectra of NUP-I is shown in Fig. 5 and shows chemical shifts at

| | | |
|---|---|---|
| 1.3 ppm (15.3) | $-CO.CH_2.\underline{CH_2}.\underline{CH_2}.CH_2.CO-$ | AA |
| 2.6 ppm (15.13) | $-CO.\underline{CH_2}.CH_2.CH_2.\underline{CH_2}.CO-$ | AA |
| 3.8 ppm (42.4) | $-CH_2.-\underline{CH_2}.O.CH_2.CH_2.$ | $-DEG-AA-$<br>$-DEG-IPA-$<br>$-DEG-MA/FA-$ |
| 4.5 ppm (8.18) | $-\underline{CH_2}.O.CO.$ | $-DEG-IPA-$<br>$-DEG-AA-$<br>$-DEG-MA/FA-$ |
| 6.2 ppm (2.30) | $-CH{=}CH-$Maleic acid | |
| 6.8 ppm (22.10) | $-CH{=}CH-$Fumaric acid | |
| 7.5 ppm (0.39)<br>8.65 ppm (0.44) | Aromatic protons | |

The NMR spectra (Fig. 5) confirms the presence of ester linkages between DEG with all three acids in the polyester backbone but cannot be used to substantiate the probable sequence of the acids in NUP-I. However, the sequence of reaction of

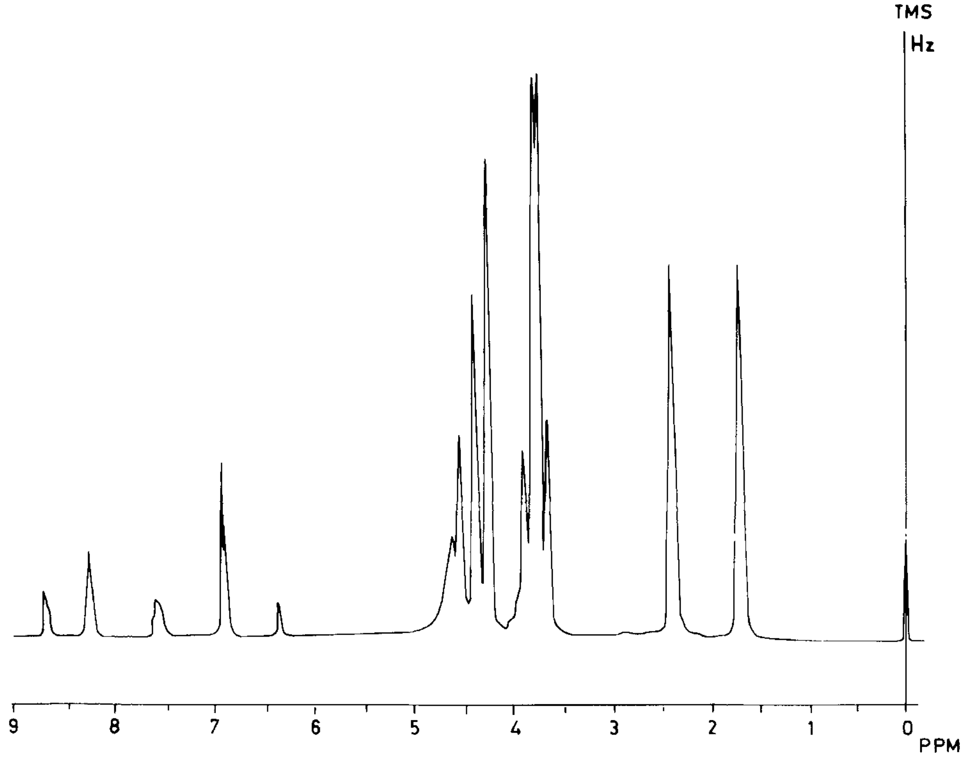


FIG. 5. $^1H$ spectra of E.

various acids with DEG as shown above is supported by the dissociation constants of IPA, AA, and MA.

The reaction products of IPA with DEG, i.e., $-(\text{DEG}-\text{IPA}-\text{DEG})-$, and AA with DEG, i.e., $-(\text{DEG}-\text{AA}-\text{DEG})-$, which are likely to act as plasticizers, may exist in minor proportions otherwise they will ooze out at the time of curing while casting specimens for determination of various properties (oozing of liquid is not observed). (Note: x, y, z, a, b, c, l, m, n, o, and p denote the degree of oligomerization.)

## Gel Time ($G_t$) and Exotherm Peak Temperature ($E_{PT}$)

The data are given in Table 2. They show that $G_t$ increases from NUP-I to NUP-III. The study of structural aspects clearly shows that there is a progressive increase in chain length from NUP-I to NUP-III, i.e., the distance between the crosslinking sites along the polyester backbones increases from NUP-I to NUP-III. Because long chain molecules are less reactive than short chain molecules, it is expected that $G_t$ will increase in this order. NUP-I, NUP-II, and NUP-III have the same quantity of MAn, and as the curing of unsaturated polyesters is reported to be exothermic by virtue of the conversion of —C=C— bonds to —C—C— bonds, all NUPs are theoretically expected to have the same $E_{PT}$. The data show that NUP-I

TABLE 2. Viscosity, Gel Time, and Exotherm Peak Temperature of Uncured Novel Unsaturated Polyesters

| Novel unsaturated polyesters | Viscosity without styrene (at 30°C), cP | Gel time[a] ($G_t$), min | Exotherm peak temperature[a] ($E_{PT}$), °C |
|---|---|---|---|
| NUP-I | 14,100 | 11.0 | 64.0 |
| NUP-II | 12,500 | 12.5 | 63.0 |
| NUP-III | 3,000 | 23.3 | 49.0 |

[a] Catalyst (MEK peroxide) = 1%. Accelerator (cobalt naphthenate) = 1%. Temperature = 40°C.

and NUP-II have almost the same $E_{PT}$, i.e., 63 and 64°C, respectively. However, $E_{PT}$ for NUP-III is only 49°C. This is most likely because of the longer gel time ($G_t$) because $E_{PT}$ is related to $G_t$. It has already been established that if $G_t$ is larger, then $E_{PT}$ will be smaller and vice versa [20]. If $G_t$ is larger, some heat is dissipated and lost during gelling/curing, resulting, in smaller $E_{PT}$. This is also supported by the fact that NUP-I and NUP-II have almost the same $G_t$, resulting in almost the same $E_{PT}$ for these resins.

## Tensile Strength, Elongation, Bond Strength, and Shore Hardness

The data of these properties are given in Table 3. It is seen that the tensile strength (TS) decreases from NUP-I to NUP-III whereas elongation increases. It has been proved above that the chain length progressively increases from NUP-I to NUP-III. It has also been reported that the increase in chain length is reflected in terms of elongation of cured products. As elongation depends mainly on the chain length of molecular chains in a polymer, it is expected that the elongation will increase from NUP-I to NUP-III. It is well established that elongation and TS are interrelated in most thermosets, and if elongation increases, TS decreases and vice versa [21, 22]. As elongation increases from NUP-I to NUP-III, TS decreases in this order. TS is also indicative of crosslink density and infers a decrease in crosslink density from NUP-I to NUP-III and, accordingly, Shore hardness also has a similar trend.

TABLE 3. Tensile Strength, Elongation, Shore Hardness, and Bond Strength of Cured Novel Unsaturated Polyesters

| Novel unsaturated polyesters | Tensile strength, kg/cm$^2$ | Elongation, % | Shore hardness (A scale) | Bond strength with CMDB propellant, kg/cm$^2$ |
|---|---|---|---|---|
| NUP-I | 41.0 | 26.0 | 81.0 | 10.0 |
| NUP-II | 30.0 | 30.0 | 79.0 | 9.15 |
| NUP-III | 5.1 | 32.0 | 42.0 | 7.0 |

The bond strength (BS) of NUPs with CMDB propellants is also given in Table 3. The reason is not well understood, but one practical observation is that flexible and slow curing resins have weak bonds with DB and CMDB propellants whereas rigid and fast curing resins have strong bonds. This can perhaps be attributed to the migration of NG/nitro bodies from propellant toward inhibitor (resin), leading to incomplete curing and resulting in weak bonds [23, 24]. As the gel time increases from NUP-I to NUP-III (Table 2), the extent of interference due to migration of NG/nitro bodies also increases, resulting in a decrease in BS in this direction, as seen experimentally.

## Nitroglycerine Absorption

Nitroglycerine (NG) absorption was measured at different time intervals and the results are presented in Table 4. The variation of NG absorption against time is graphically shown in Fig. 6. The data show that NG absorption increases from NUP-I to NUP-II, and that NG absorption also increases as the time of immersion increases.

Tensile strength (indicative of crosslink density) decreases from NUP-I to NUP-III, which suggests a decrease in the tightness of molecular structures in this direction. This decrease in the tightness of molecular structures facilitates seeping of NG molecules into the cured 3-dimensional structures, resulting in higher NG absorption from NUP-I to NUP-II. Further, the double bonds in the polyester backbones of NUP-III are terminal and provide crosslinking sites for styrene monomer. This 3-dimensional network, because of crosslinking of terminal double bonds with styrene, offers more hindrance/resistance to the seepage of NG molecules through it, and the net result is a decrease in NG absorption in the case of NUP-III.

## Thermal Conductivity, Heat Resistance, and Oxygen Index

The data on thermal conductivity (λ), heat resistance (in terms of volatile losses at 150°C), and the Oxygen Index (*n*) are given in Table 5. Thermal conductivity increases from NUP-I to NUP-III, suggesting an increase in the orderliness of the structures with an increase in the chain length in this order [25, 26]. The elongation increases from NUP-I to NUP-III due to an increase in chain length (Table 2). The increase in chain length facilitates transmission of heat through the chains,

TABLE 4. Effect of Time on Nitroglycerine Absorption of Cured Novel Unsaturated Polyesters

| Novel unsaturated polyesters | Nitroglycerine absorption, %, with time in days | | | | |
|---|---|---|---|---|---|
| | 1 | 2 | 4 | 6 | 8 |
| NUP-I | 8.36 | 13.06 | 18.95 | 22.95 | 23.98 |
| NUP-II | 10.71 | 16.41 | 24.95 | 27.91 | 32.05 |
| NUP-III | 9.08 | 14.83 | 21.25 | 24.99 | 26.93 |

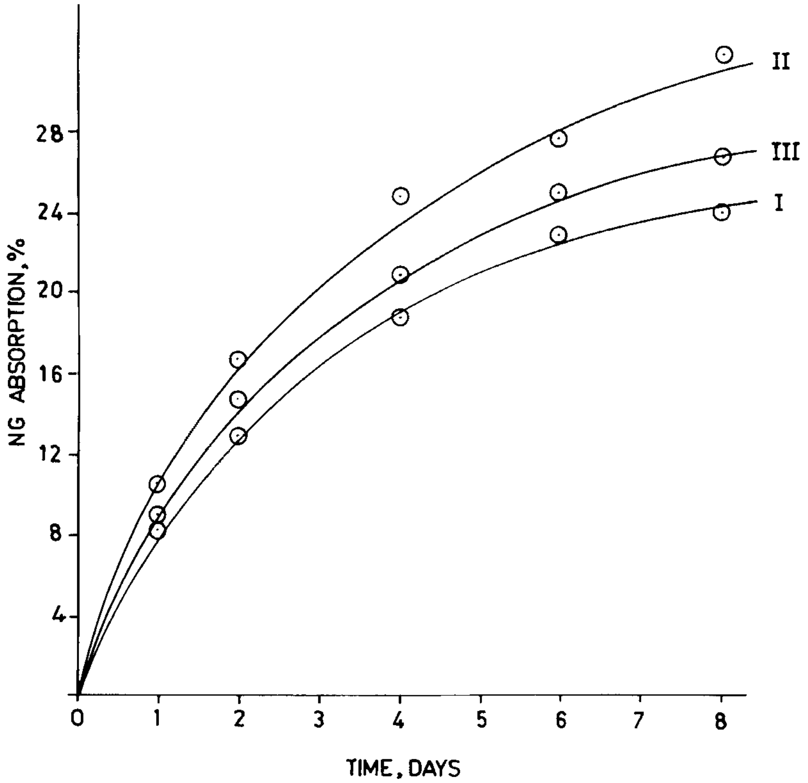


FIG. 6. Variation of nitroglycerine (NG) with time.
A, B, C, D and E are represented by

$$\underset{12.0\text{ M}}{\text{DEG}} + \underset{2.0\text{ M}}{\text{IPA}} \xrightarrow[\text{distilled until acid value comes to 40}]{\text{refluxed and water}} \text{A} \tag{1}$$

$$\text{A} + \underset{5.0\text{ M}}{\text{AA}} \xrightarrow[\text{distilled until acid value comes to 40}]{\text{refluxed and water}} \text{B} \tag{2}$$

$$\text{B} + \underset{5.0\text{ M}}{\text{MAn}} \xrightarrow[\text{distilled until acid value comes to 40}]{\text{refluxed and water}} \text{C} \tag{3}$$

$$\text{A} + \underbrace{\underset{5.0\text{ M}}{\text{AA}} + \underset{5.0\text{ M}}{\text{MAn}}}_{\text{(Added together)}} \xrightarrow[\text{distilled until acid value comes to 40}]{\text{refluxed and water}} \text{D} \tag{4}$$

$$\underset{12.0\text{ M}}{\text{DEG}} + \underset{2.0\text{ M}}{\text{IDA}} + \underbrace{\underset{5.0\text{ M}}{\text{AA}} + \underset{5.0\text{ M}}{\text{MAn}}}_{\text{(Added together)}} \xrightarrow[\text{distilled until acid value comes to 40}]{\text{refluxed and water}} \text{E} \tag{5}$$

TABLE 5. Thermal Conductivity, Oxygen Index, and Heat Resistance of Cured Novel Unsaturated Polyesters

| Novel unsaturated polyesters | Thermal conductivity (λ), w/mK | Oxygen Index (*n*), % | Heat resistance (volatile losses after 6 h at 150°C), % |
|---|---|---|---|
| NUP-1 | 0.0579 | 14.22 | 1.57 |
| NUP-II | 0.0720 | 14.53 | 1.64 |
| NUP-III | 0.0909 | 14.96 | 3.21 |

resulting in an increase in λ as observed experimentally. The loss of volatiles also increases from NUP-I to NUP-III, i.e. heat resistance decreases in this order, and this is attributed to a decrease in the tightness of molecular structures in this direction. The decrease in the tightness of molecular structures from NUP-I to NUP-III makes the escape of volatile matter easier. However, the Oxygen Index (*n*), which is a measure of flammability of polymers/plastics, is of almost the same order.

The trends of these properties of NUP-I, NUP-II, and NUP-III have been explained on the basis of their assigned structures and, therefore, also indirectly support these proposed structures.

The inhibition of rocket propellants demands lower NG absorption and higher elongation—a combination of two contradictory properties. The elongation and NG absorption data of NUP-III show that it possesses this unique combination of properties and makes it an ideal candidate for inhibition of CMDB propellants. At the same time, NUP-III possesses lower viscosity as compared to NUP-I and NUP-II (Table 3). This facilitates processing and higher loading of flame retardants, thus imparting better flame retardant characteristics to the system. However, NUP-III may not have practical application because of its 26.93% NG absorption, but its counterpart, designated NUP-7 (III), is being used for the inhibition of CMDB propellants.

## CONCLUSION

The novel unsaturated polyester-III (NUP-III), synthesized by a 3-step polyesterification process, possesses a unique combination of two contradictory properties: higher elongation and lower NG absorption (or higher chemical resistance). The chain length of polyester backbones increases on successive addition of acids, thereby leading to higher elongation, whereas NG absorption decreases (or chemical resistance increases) because of the location of terminal double bonds which give a 3-dimensional network on crosslinking with styrene monomer. The presence of bulky and voluminous styrene molecules on the terminal of the 3-dimensional network in cured product offers hindrance to the approach of NG molecules and leads to lower NG absorption or higher chemical resistance. The trends among various properties of NUP-I, NUP-II, and NUP-III (uncured as well as cured) have been explained on this basis.

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