# Polynitroalcohols Obtained Through Nitro Aldol Reaction Between Nitro Oligomers and $C_1$-$C_2$-Aldehydes

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**ABSTRACT:** Polynitroalcohols (PNA) were obtained by $A_N$-reaction of nitro oligomers from ground waste rubbers (NO-GWR) with $C_1$-$C_2$-aldehydes in presence of organic bases triethanolamine, triethylamine and cyclopropylamine. The $A_N$-reaction was studied at temperatures from 30 to 50°C, time 4 h, and NO-GWR : aldehyde = 1 : 0.5/2.0 mass ratios in the solution. PNA were characterized by elemental analyses, such as ^{1}H NMR spectra, IR spectroscopy—baseline method with internal standard and thermal analyses. The quantitative functional composition of PNA (%$NO_2$, %C=O, and %OH groups) was proved to be similar to the composition of PNA obtained from model butadiene–styrene nitro oligomer (BSNO). It was concluded that NO-GWR could replace NO based on elastomers in nitro aldol reaction with formaldehyde and acetaldehyde. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3241–3250, 2006

**Key words:** nitro oligomer; polynitroalcohol; $A_N$-reaction; rubber; organic base

## INTRODUCTION

The annual consumption of rubber products in the world is about 30 million tons, and after a year 1/3rd of them are depleted. They are resistant to atmospheric and biological processes, and so the development of effective methods for their utilization is an important task from environmental and economical point of view.

One of the methods for chemical transformation of elastomers is the polymer-analogous reaction nitration, which is used for nitro oligomers (NO) production.[1] The reaction can successfully be used for utilization of waste tires and other rubber articles.

Waste vulcanizates were nitrated with nitric acid to obtain nitro–oxygen-containing products and carbon black, but the NO were obtained at very low yields.[2,3] A method for nitration of waste tires with nitric acid was also developed, and the NO from ground waste rubbers (NO-GWR) were obtained at high yields.[4] NO-GWR are of practical interest as additives to rubber compositions, as components in lacquer coating materials, etc.

The polyfunctional composition of NO-GWR makes them suitable for use as reagents for preparation of oligo-derivatives, such as polynitroalcohols (PNA), *N*-sulfonic acids, etc.

Numerous studies on the chemistry of aliphatic nitrocompounds in nitro aldol reaction ($A_N$-reaction) with carbonyl compounds have been published in reviews and monographs.[5–8] Researcher's interest in the synthesis of nitroalcohols (NA) and their derivatives had increased. The methods for their preparation have been improved, and the range of catalysts and solvents used have widened.

Nitroalcohols were obtained by reaction of nitroethane with aromatic aldehydes containing PhCH=CH— and PhCH₂—CH₂— radicals in a solution of dichloroethane or tetrahydrofuran.[9] By reaction of 1,3,5-trialkylhexahydro-1,3,5-triazine with 1-nitroethanetriol through a oxazine derivative, a 3-alkylamino-2-hydroxymethyl-2-nitro-1-propanol salt was obtained.[10]

Through stereoselective reduction of nitroketones in the presence of yeast, (S)-nitroalcohols were obtained.[11] NA and some of their derivatives were prepared by nitration with nitrogen dioxide of substituted alkenes like 4-phenyl-1-butene in benzene or dichloroethane solution.[12,13] Secondary nitroalkanes and ketones were used as initial reagents for the synthesis of NA, which were then converted to alicyclic $\alpha$-nitroketones by treatment with oxidizers.[14] Besides inorganic bases, other catalysts have also been used for the $A_N$-reaction. For instance, the 2-fluoro-2,2-dinitroethanol was prepared from fluorochlorodinitromethane and formaldehyde in the presence of potassium iodide.[8] The nitro aldol reaction was carried out in heterogeneous medium with ionite Amberlist A-21 to obtain NA and nitrodiols.[15,16] Henry reaction

**TABLE I**
**Yields[a] of Polynitroalcohols (PNA-1) Obtained from NO-GWR and $C_1$-$C_2$-Aldehydes**

| No | Polynitroalcohol | Temperature (°C) | Reacion time (h) | NO-GWR : Aldehyde (mass ratio) | Base (g) | $K_B$ $10^{-4}$ at 25°C in $H_2O$ | Yields (%) |
|---|---|---|---|---|---|---|---|
| 1 | PNA-1-$C_1$ | 30 | 4.0 | 1 : 1.0 | TrEthA (1.0) | ~5.0 | 72 |
| 2 | PNA-1-$C_1$ | 40 | 3.5 | 1 : 0.5 | $Et_3N$ (1.0) | 5.7 | 75 |
| 3 | PNA-1-$C_1$ | 40 | 4.0 | 1 : 2.0 | CyPrA (1.2) | ~4.4 | 48 |
| 4[b] | PNA-1-$C_1$ | 50 | 4.0 | 1 : 0.5 | KOH (0.03) | — | 44 |
| 5[b] | PNA-1-$C_1$ | 40 | 4.0 | 1 : 0.5 | $Na_2CO_3$ (0.5) | — | 60 |
| 1' | PNA-1-$C_2$ | 50 | 4.0 | 1 : 1.0 | TrEthA (0.9) | ~5.0 | 64 |
| 2' | PNA-1-$C_2$ | 60 | 4.0 | 1 : 1.0 | $Et_3N$ (0.7) | 5.7 | 50 |
| 3' | PNA-1-$C_2$ | 50 | 5.0 | 1 : 0.5 | CyPrA (0.8) | ~4.4 | 75 |
| 4'[b] | PNA-1-$C_2$ | 60 | 4.0 | 1 : 0.5 | KOH (0.03) | — | 40 |

[a] The second reaction products PNA-2-$C_1$ and PNA-2-$C_2$ were obtained with yields 20–30% with TrEthA or $Et_3N$, and 35–45% with CyPrA.
[b] In solution of 1,4-dioxane-methanol.

was performed in a 0.025$N$ basic solution and acetyl-trimethylammonium chloride, and nitroalcohols with phenyl, 4-nitrophenyl, cyclohexyl and other radicals were obtained.[17] The reaction of nitromethane with 4-chloropentanal,[18] nitroethane with formaldehyde[19] and substituted, conjugated nitroalkenes with formaldehyde[20] were performed in the presence of triethyl-amine.

The preparation of PNA both from NO obtained from isoprene and butadiene rubbers with formaldehyde[21,22] and butadiene–styrene nitro oligomer

(BSNO) with $C_1$-$C_2$-aldehydes,[23,24] using alkaline bases or alkaline carbonates as catalysts, was reported.

The objectives of this work were to synthesize poly-nitroalcohols from NO obtained from waste vulcani-zates and the aliphatic aldehydes–formaldehyde and acetaldehyde in the presence of organic bases—trieth-anoamine (TrEthA), triethylamine ($Et_3N$), and cyclo-propylamine (CyPrA) and to compare the functional composition of the polynitroalcohols obtained with those of PNA prepared from model butadiene–styrene nitro oligomer, and to prove that NO produced from
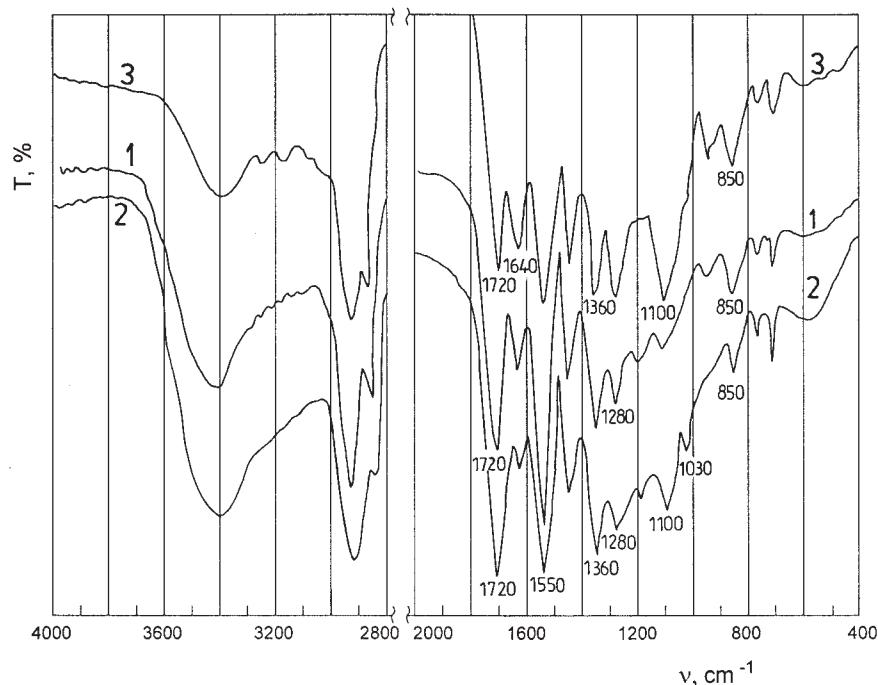


**Figure 1** IR spectra of polynitroalcohols, obtained from NO-GWR and $C_1$-$C_2$-aldehydes (1): Initial NO-GWR, (2) PNA-1-$C_1$ (40°C, 4 h, CyPrA), and (3) PNA-1-$C_2$ (60°C, 4 h, TrEthA).
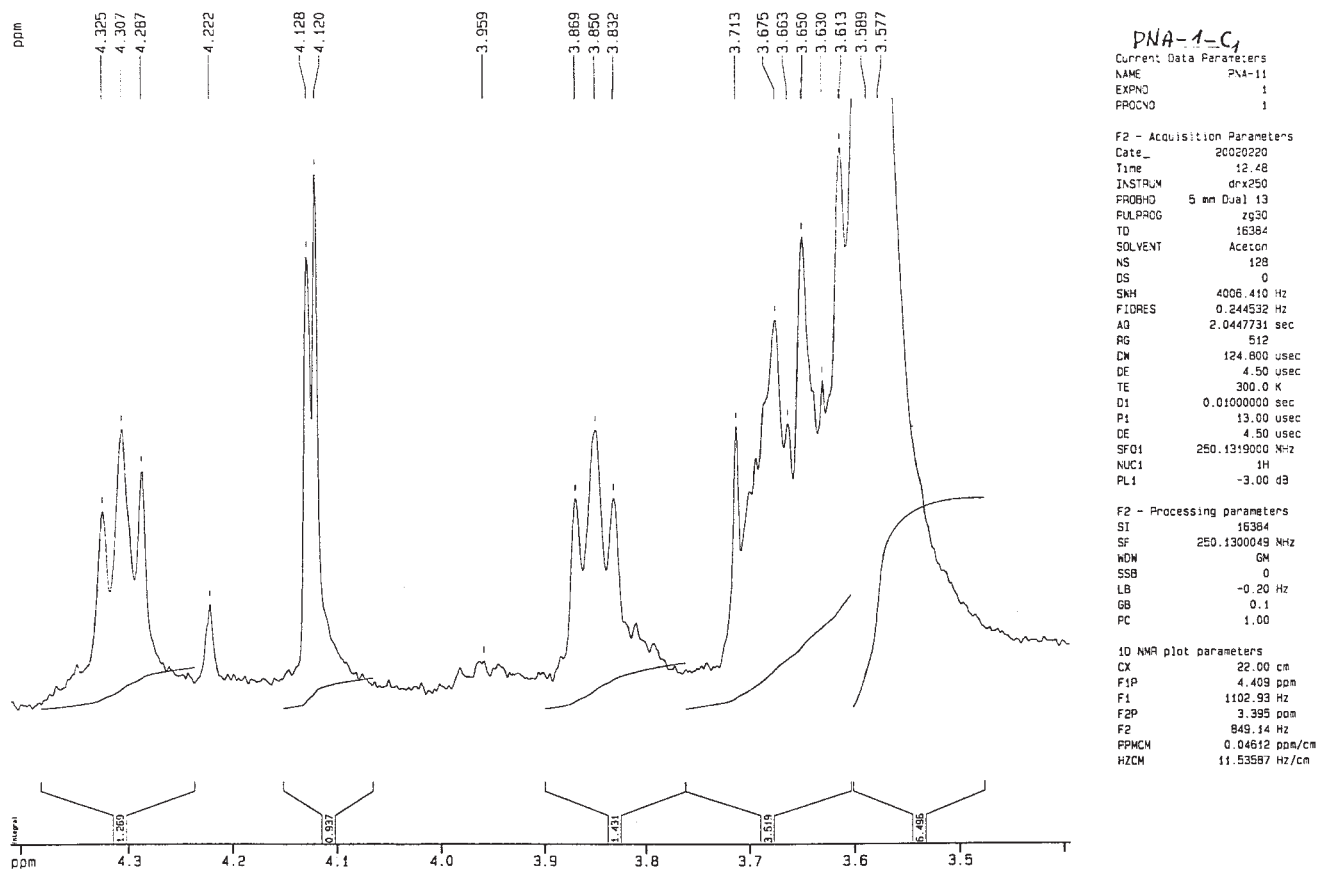
**Figure 2** $^{1}$H NMR spectrum (3,5–4,5 ppm) of a polynitroalcohol (PNA-1-C$_1$) obtained from NO-GWR and formaldehyde (40°C, 4 h, CyPrA).

waste rubber can be used as reagents for A$_N$-reaction with C$_1$-C$_2$-aldehydes.

## EXPERIMENTAL

### Ground waste rubber

Initial ground waste rubber (GWR) was prepared from protective waste rubbers. The screening analysis was carried out through a set of screens with $\phi = 0.1$–0.80 mm and the fraction with particle size from 0.25 to 0.63 mm (~96% of the total amount) was used for the experiments.

### Preparation of nitro oligomers from ground waste rubber

The initial nitro oligomer (NO-GWR) with $\bar{M}_n = 1230$ and coefficient of polydispersity $D = 1.851$, was obtained by oxidation–destructive nitration of GWR with 65% nitric acid in a heterogeneous medium in presence of nonylphenolpolyglycolether, "Veranol H-10", at a temperature of 40–60°C, with a reaction time of 4–5 h, and nitration factor 4.[4]

### Preparation of polynitroalcohols from the NO-GWR and formaldehyde

The initial reagents were NO-GWR (sedimented from acetone), 2.5 g; formalin (chem. pure, 35%, $d = 1.09$), 7 mL (7.6 g); 1,2-dioxane (chem. pure, $t_k = 101.4°C$), 10 mL; ethyl alcohol (chem. pure, $t_k = 78°C$), 25 mL; triethanolamine (chem. pure $d = 1.12$), 1.8 mL (2.0 g). The solution of 2.5 g NO-GWR in 10 mL of 1,4-dioxane was placed in a three-necked flask equipped with stirrer, reflux condenser and dropping funnel. The solution was then diluted with 10 mL ethanol and 1 mL TrEthA was added to obtain pH 7–8. The reaction took place at about 40°C under continuous stirring and 7 mL formalin diluted with 15 mL ethanol (NO-GWR : CH$_2$O = 1 : 1 mass ratio) was dropped for 30 min. The pH of the medium was periodically measured and another ~0.8 mL TrEthA was added to obtain pH 7–8. The reaction was continued for another 3 h under stirring. The reaction mixture was then neutralized with 5 mL 5% hydrochloric acid to pH 6 and a precipitate of triethanolammonium chloride was obtained and filtered out. The first polynitroalcohol PNA-1-C$_1$ (1.8 g) was sedimented after 1 day storage (1.8 g). It was dissolved in 20 mL acetone and
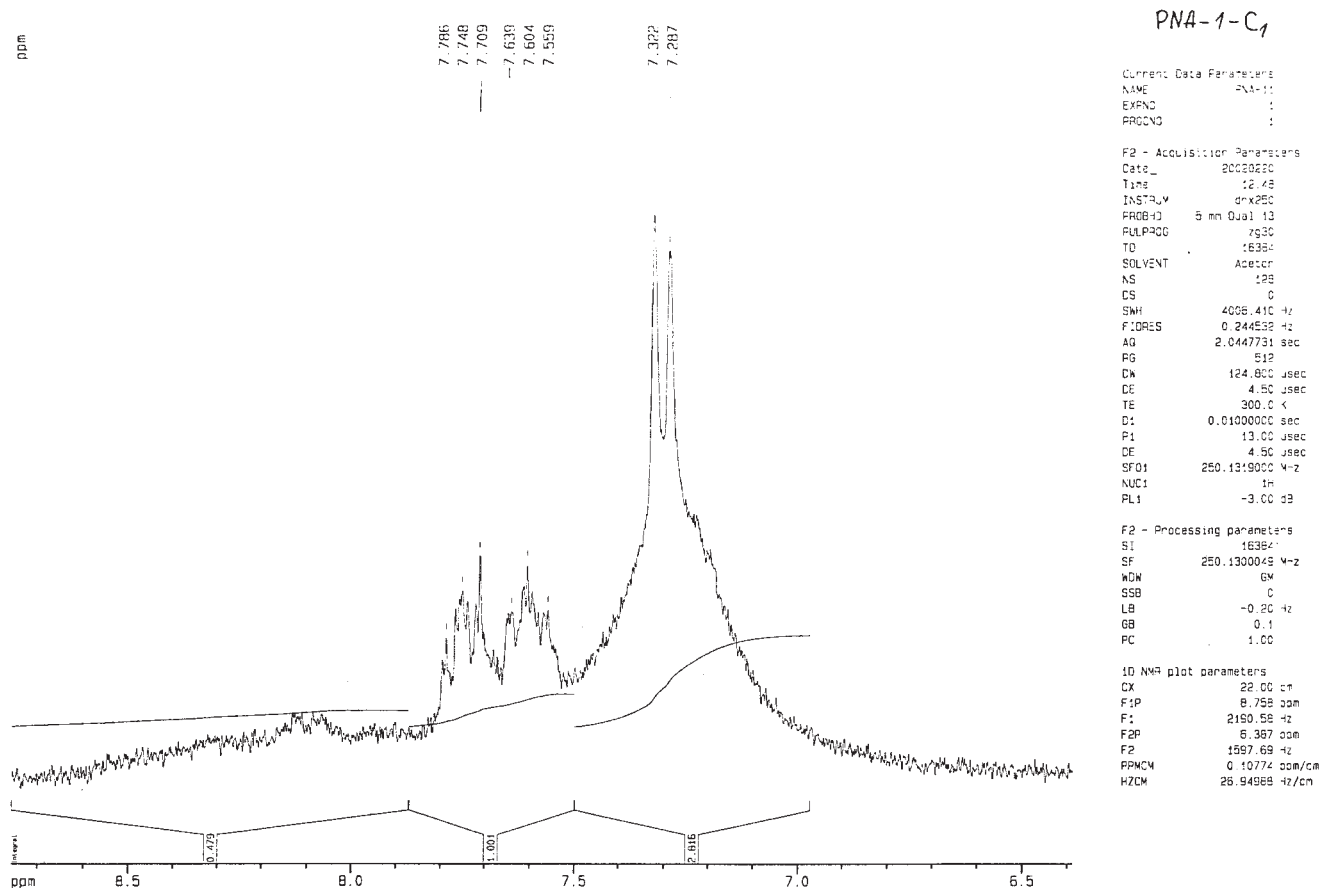
**Figure 3** $^1$H NMR spectrum (6,5–8,5 ppm) of a polynitroalcohol (PNA-1-C$_1$) obtained from NO-GWR and formaldehyde (40°C,4 h, CyPrA).

was precipitated in 200 mL of water acidified with 5 mL 10% hydrochloric acid. The other polynitroalcohol PNA-2-C$_1$ was obtained in vacuo (0.011 MPa) of the filtrate, followed by extraction with wet ethanol and separation by evaporation of the solvent. The yields were 1.8 g (72%) of PNA-1-C$_1$ and 0.5 g (15%) of PNA-2-C$_1$.

## Preparation of polynitroalcohols from NO-GWR and acetaldehyde

The initial reagents were NO-GWR (sedimented from acetone) 2.5 g; acetaldehyde (chem. pure $d = 0.78$, $t_k = 21.3°C$, distilled), 7 mL (7.6 g); 1,4-dioxane (chem. pure $t_k = 101.4°C$), 10 mL; methyl alcohol (chem. pure $t_k = 67°C$) 25 mL; triethylamine (chem. pure $d = 0.73$) 1.8 mL. The reaction was carried out by the technique described earlier. The reaction conditions were as follows: 60°C, NO-GWR : CH$_3$CHO = 1 : 1 mass ratio, pH = 7–8 maintained by addition of ~1.8 mL Et$_3$N. The first reaction product PNA-1-C$_2$ (1.9 g) was separated after acidification of the reaction mixture and precipitation. The second product PNA-2-C$_2$ (0.4 g) was obtained in vacuo (0.011 MPa) and extraction

with solution of acetone : water = 5 : 1 volume parts. The yields were 1.9 g (76%) of PNA-1-C2 and 0.4 g (15%) of PNA-2-C$_2$.

## Analyses of PNA

Elemental analyses were carried out by using Perkin-Elmer instrument. The thermal analyses were performed on derivatograph OD-102 (Hungary) within the temperature range of 20–600°C at a heating rate of 6 K/min. The sample weight was 10–100 mg and the analyses were conducted in an air static atmosphere. A metaloceramic crucible of 9 mm diameter with Pt and Pt/Rh thermocouples was employed for the samples.

$^1$H NMR spectra were obtained by using a 250 MHz spectrometer Bruker (Germany) in a solution of (CD$_3$)$_2$CO or water. The IR spectra were recorded for samples prepared as potassium bromide pellets (1 mg/300 mg) with potassium hexacyanoferrat (II) as an internal standard on a Specord M 80 instrument. The content of nitro-, carbonyl-, and hydroxyl groups in the polynitroalcohols was determined from the corre-

sponding IR spectra by using the baseline and internal standard technique with respect to 2-bromo-2-nitro-1,3-propanediol and 10-nonadecanone standards under the same condition. The absorption $A$ and, subsequently, the ratio $R = Ax/Ast$ were calculated, where Ast and Ax were the absorption for the $\gamma C{\equiv}N$ band at 2116 cm$^{-1}$ and the absorption for the corresponding functional group, respectively. The content of the functional groups was determined by comparing their $R$-values to the corresponding value of the internal standard. $\overline{Mn}$ were determinated by gel-permeation chromatography in a column filled with Ultrastiragel in a solution of tetrahydrofuran.

## RESULTS AND DISCUSSION

In this investigation, NO obtained from waste vulcanizates by oxidation–destructive nitration were used for the first time for the $A_N$-reaction with $C_1$-$C_2$-aldehydes. NO-GWR were found to be polyfunctional and possessed the same functional groups as butadiene–styrene NO prepared from elastomers and latexes.[4] Hence, NO-GWR are potential reagents for preparation of PNA.

Until now, oligomeric PNA[21–24] have been synthesized from NO obtained from conventional elastomers in the presence of bases or alkaline carbonates. Use of
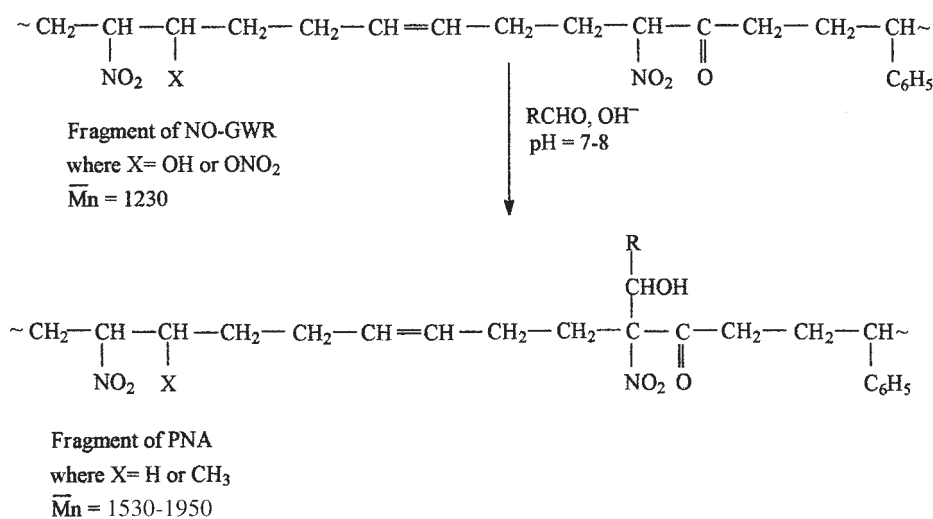
organic bases as catalysts for the $A_N$-reaction nitro oligomer-aldehyde has not been reported.

The reaction conditions for the nitro aldol reaction of NO-GWR with $C_1$-$C_2$-aldehydes were selected according to the results from previous studies[23,24] and taking into account the presence of aromatic rings in the main carbon chain (UV spectrum $\lambda_{max} = 250$ nm).

The $A_N$-reaction of NO-GWR with the aliphatic aldehydes formaldhyde and acetaldehyde (Table I), was carried out in a solution of 1,4-dioxane-ethanol in the temperature range from 30 to 60°C, at mass ratios 1 : 0.5/2.0, time 3–5 h and pH 7–8. The organic bases triethanolamine, triethylamine, and cyclopropylamine were used to maintain pH of the reaction medium.

The reaction centers of NO-GWR are the $\alpha$-H atoms at the carbon atoms bounded to the secondary nitro groups. In the presence of the organic base, the initial NO-GWR was transformed into aci-form, which reacted with the aldehyde until two types of polynitroalcohols were obtained (Table I). The first one, PNA-1, was the basic product (yield ~60–76%), and the second one, PNA-2, was water-soluble (yield ~15–35%). In this work, only the basic products of the $A_N$-reaction PNA-1-$C_1$ and PNA-1-$C_2$ were studied.

The reaction between NO-GWR and $C_1$-$C_2$-aldehydes takes place according to the Scheme 1:



Fragment of NO-GWR
where X= OH or ONO$_2$
$\overline{Mn}$ = 1230

Fragment of PNA
where X= H or CH$_3$
$\overline{Mn}$ = 1530-1950

The reaction of NO-GWR with formaldehyde was proceeded normally at 30–40°C and NO-GWR : CH$_2$O = 1.0 : 0.5 mass ratio to obtain PNA-1-$C_1$ at yields of 60–72%. It was found that the increase of the mass ratios NO-GWR : CH$_2$O from 1 : 0.5 to 1 : 1.0–2.0 gives a slight increase of the PNA-1-$C_1$ yield. The excess of aldehyde, however, leads to aldol condensation, therefore, it should be deficient.

The $A_N$-reaction of NO-GWR with acetaldehyde took place at temperatures 50–60°C and mass ratios

from 1 : 0.5 to 1 : 2.0 to obtain PNA-1-$C_2$ at yields of 64–76%. It should be noted that when the reaction was carried out in methanol with catalysis using KOH or Na$_2$CO$_3$, the PNA-1-$C_2$ yields were lower owing to the partial solubility of the NO-GWR aci-form in the reaction medium.

The organic base triethanolamine can easily be separated as ammonium salt by slight acidification of the reaction medium. PNA-1 were powdery substances with golden to brown color, soluble in polar solvents,
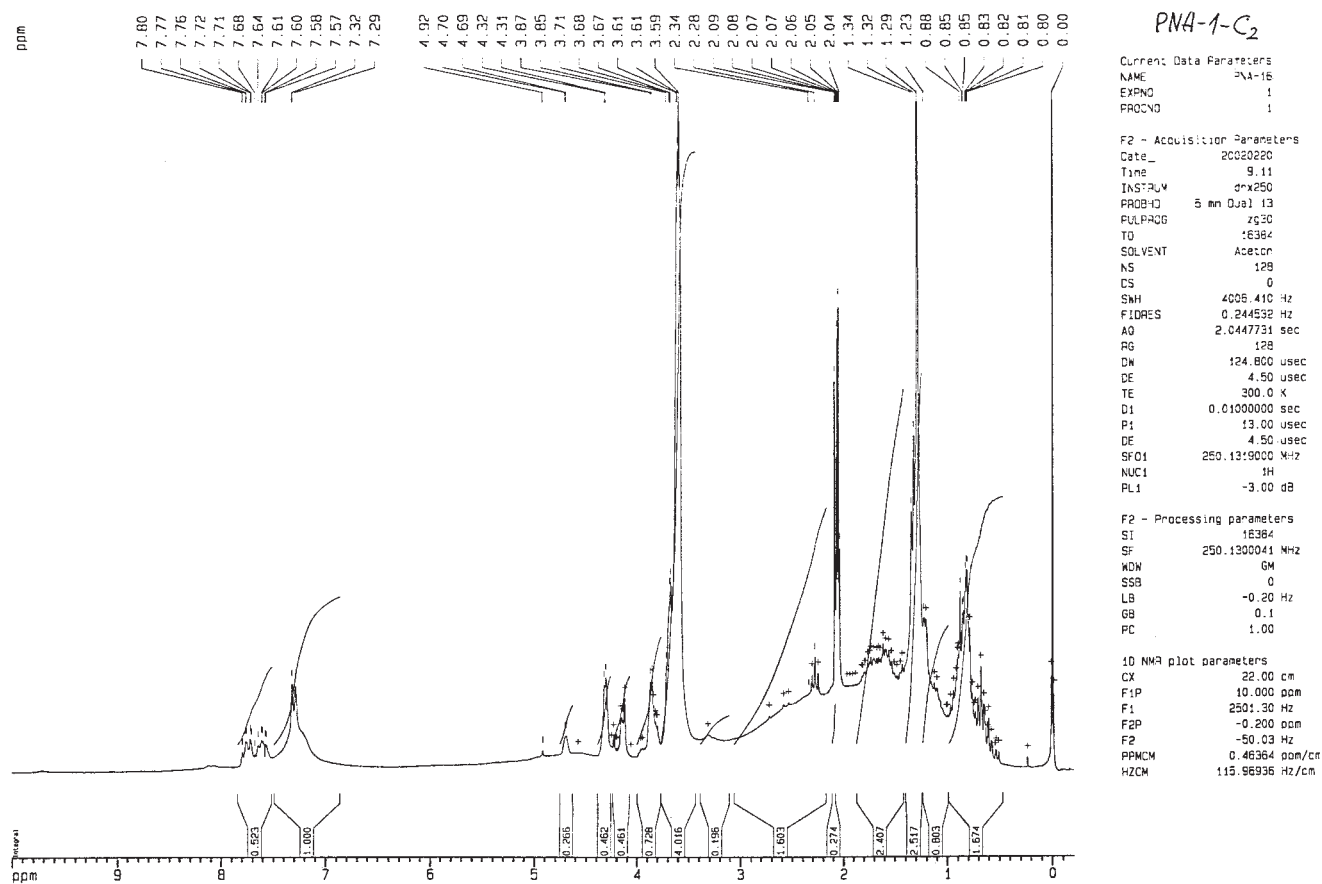
**Figure 4** $^1$H NMR spectrum of polynitroalcohol (PNA-1-C$_2$) obtained from NO-GWR and acetaldehyde (50°C, 5 h, CyPrA).

while PNA-2 were hydroscopic beige–brown resins soluble in water.

The IR spectra of the PNA-1-C$_1$ and PNA-1-C$_2$ obtained revealed their polyfunctional composition. The IR spectrum of PNA-1-C$_1$ (Fig. 1, curve 2) showed the following characteristic vibrations: $\gamma_{as,s}$ = 1550 and 1360 cm$^{-1}$ for the nitro group, $\gamma$ = 1720 cm$^{-1}$ for CAO with intensity close to that at 1550 cm$^{-1}$, $\gamma_{as}$ = 1280 cm$^{-1}$ for the nitratestergroup and $\gamma$ = 1640 cm$^{-1}$ for C=C. The stretching vibrations for methylene and methyl groups were in the interval of 2950–2800 cm$^{-1}$. The stretching vibration $\gamma_{COO(H)}$ for primary hydroxyl group of PNA-1-C$_1$ was registered at 1090 cm$^{-1}$ (with K$_2$CO$_3$), 1100 cm$^{-1}$ (with TrEthA) and two bands at 1030 and 1100 cm$^{-1}$ (with CyPrA). A wide absorption band was registered also in the range of 3600–3200 cm$^{-1}$, indicating hydroxyl groups in compounds with associated intramolecular hydrogen bonds.[25]

The IR spectra of PNA-1-C$_2$ (Fig. 1, curve 3) was similar to above interpreted one, but $\gamma$C—O—(H) for secondary hydroxyl group was registered at 1100 cm$^{-1}$ like the same group in cis–trans cyclohexanols.[25]

The IR spectra of polynitroalcohols obtained from model BSNO and C$_1$-C$_2$-aldehydes[23,24] clearly showed the presence of the functional groups described ear-

lier. For PNA-1-C$_1$, $\gamma_{C—O—(H)}$ was at 1050 cm$^{-1}$ and for PNA-1-C$_2$ at 1100 and 1120 cm$^{-1}$.

The $^1$H NMR spectrum of PNA-1-C$_1$ (Fig. 2) showed the following characteristic signals: 4.30 ppm for methyl proton at a carbon atom bounded with nitro group, 4.12 ppm for a proton from hydroxyl group, 3.85 ppm for methyl proton at a carbon atom bounded to hydroxyl group. The signals at 7.30 ppm for phenyl protons, 1.32 ppm for methylene protons from —(CH$_2$)$n$— and 0.82 ppm for methyl protons were also observed. A multiplet at 7.6–7.7 ppm for a proton from hydroxyl group was characteristic for the $^1$H NMR spectrum of PNA-1-C$_1$ (Fig. 3). It was not observed in the spectrum of the initial NO-GWR. The characteristic signals of PNA-1-C$_2$ $^1$H NMR spectrum (Fig. 4) were 4.30, 4.14, and 3.87 ppm interpreted for $^1$H NMR spectrum of PNA-1-C$_1$. The signals at 2.03 and 3.63 ppm represented the solvent–deuterized acetone and deuterized water, respectively.

The $^1$H NMR spectrum of the initial NO-GWR (Fig. 5) registered in deuterized acetone (2.06 ppm) contained all the characteristic signals described earlier: 4.29 ppm for methyl proton at a carbon atom carrying nitro group, 3.57 ppm for methyl proton at a carbon
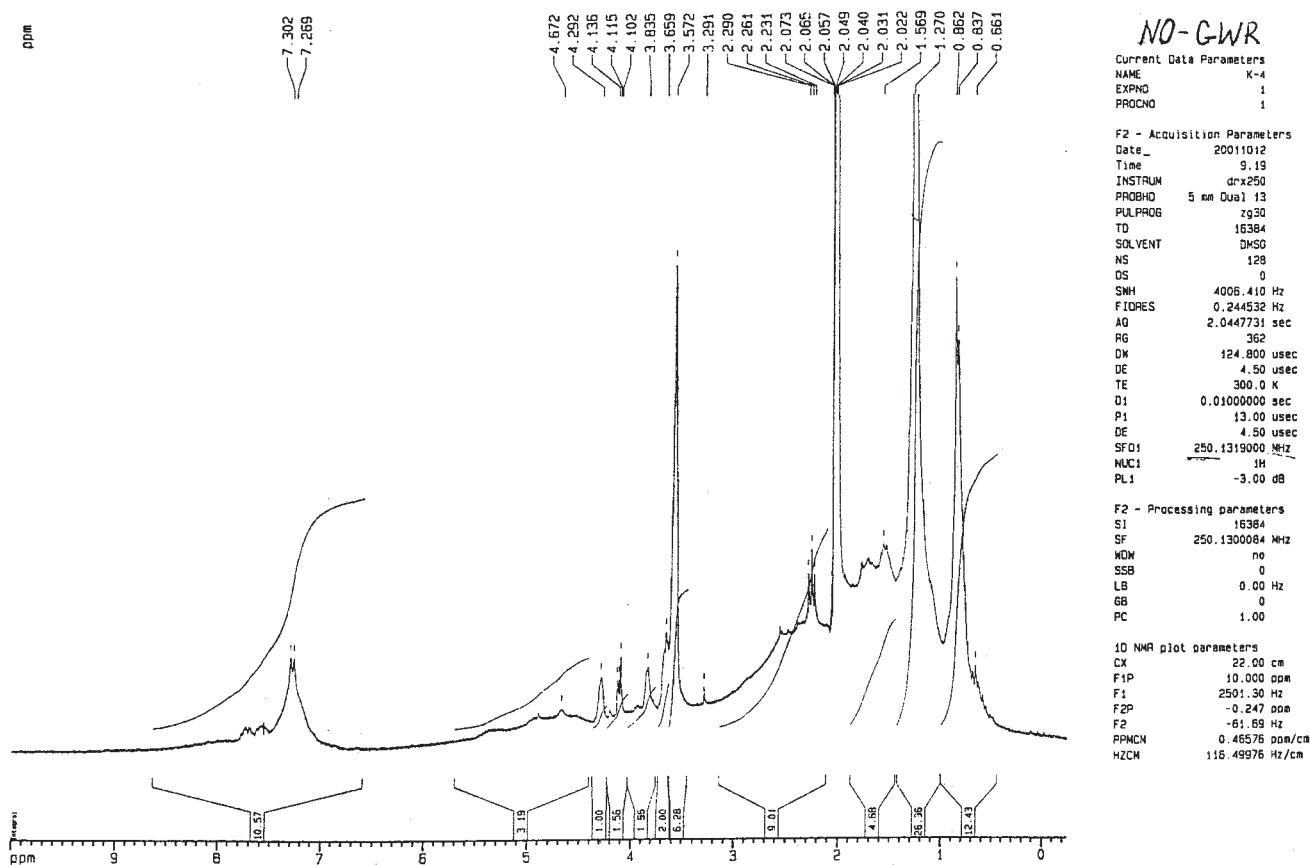
**Figure 5** $^1$H-NMR spectrum of initial NO-GWR.

atom bounded to hydroxyl group, and 3.83 ppm for a proton from hydroxyl group.

The $^1$H NMR spectra clearly showed that the $A_N$-reaction between the aci-form of NO-GWR and $C_1$-$C_2$-aldehydes was not fully accomplished and, hence, there are still unreacted $\alpha$-H atoms adjacent to the carbon atoms bounded to nitro groups. The presence of aromatic protons in the initial NO-GWR and polynitroalcohols obtained was proved by the corresponding signals at 7.30 ppm. In the UV spectra of the polynitroalcohols and NO-GWR studied, the aromatic system was registered at $\lambda_{max} = 250$ nm.

Through the $A_N$-reaction between NO-GWR and $C_1$-$C_2$-aldehydes, hydroxymethyl, and hydroxyethyl groups were introduced. As a result, the carbon content in PNA-1-$C_1$ increased by 3.5–5.5%, while that in PNA-1-$C_2$ by 1.0–3.7% (Tables II and III). PNA-1-$C_1$ and PNA-1-$C_2$ had ~1–6% lower content of nitro groups compared to that of the initial NO-GWR (Table IV) due to the introduction of hydroxyalkyl groups.

Comparing the functional composition of PNA obtained from NO-GWR with that of PNA prepared from model BSNO and $C_1$-$C_2$-aldehydes, it was found that the contents of nitro and ketone groups in the

**TABLE II**
**Elemental Analysis of Polynitroalcohols Obtained from NO-GWR and Formaldehyde in 1,4-Dioxan-ethanol**

| No | Polynitroalcohol | Temperature (°C) | Reaction time (h) | NO-GWR : CH$_2$O (mass ratio) | Base | C (%) | H (%) | N (%) |
|---|---|---|---|---|---|---|---|---|
| 1 | PNA-1-C$_1$ | 30 | 4.0 | 1 : 1.0 | TrEthA | 56.29 | 6.42 | 7.05 |
| 2 | PNA-1-C$_1$ | 40 | 3.5 | 1 : 0.5 | Et$_3$N | 58.91 | 6.82 | 6.73 |
| 3 | PNA-1-C$_1$ | 40 | 4.0 | 1 : 2.0 | CyPrA | 58.89 | 6.81 | 6.52 |
| 4[a] | PNA-1-C$_1$ | 50 | 4.0 | 1 : 0.5 | KOH | 56.89 | 6.29 | 7.11 |
| 5[a] | PNA-1-C$_1$ | 40 | 4.0 | 1 : 0.5 | Na$_2$CO$_3$ | 56.30 | 6.45 | 6.91 |
| NO-GWR | — | — | — | — | — | 53.36 | 7.91 | 6.91 |

[a] In solution of 1,4-dioxane-methanol.

**TABLE III**
**Elemental Analysis of Polynitroalcohols Obtained from NO-GWR and Acetaldehyde**

| No | Polynitroalcohol | Temperature (°C) | Reaction time (h) | NO-GWR : CH$_3$CHO (mass ratio) | Base | C (%) | H (%) | N (%) |
|---|---|---|---|---|---|---|---|---|
| 1 | PNA-1-C$_2$ | 30 | 4.0 | 1 : 1.0 | TrEthA | 55.10 | 6.20 | 6.51 |
| 2 | PNA-1-C$_2$ | 40 | 4.0 | 1 : 1.0 | Et$_3$N | 55.79 | 5.88 | 6.50 |
| 3 | PNA-1-C$_2$ | 40 | 4.0 | 1 : 0.5 | CyPrA | 57.65 | 6.44 | 6.51 |
| 4[a] | PNA-1-C$_2$ | 50 | 4.0 | 1 : 0.5 | KOH | 58.47 | 6.73 | 6.80 |
| NO-GWR | — | — | — | — | — | 54.80 | 6.20 | 7.37 |

[a] In solution of 1,4-dioxane-methanol.

initial NO and resulting polynitroalcohols did not differ significantly (Table IV).

PNA-1-C$_1$ and PNA-1-C$_2$ studied contained higher amount of ketone groups (4.1–5.3%) compared to that of the polynitroalcohols prepared from BSNO (1.9–3.0%). This corresponded to the amount of ketone groups in the initial NO-GWR (4.3%). The ketone groups were introduced into NO-GWR by the oxidative–destruction nitration of waste vulcanizate. Model BSNO contained 1.9% ketone groups due to the "softer" conditions of the nitration carried out in solution.

On the other hand, the higher content of ketone groups in the two types of PNA obtained, compared to the initial NO-GWR, was probably a result from the partial transformation of nitro groups under the reaction conditions.

Another characteristic of PNA obtained from NO-GWR was their higher content of hydroxyl groups (5.4–8.7%) compared to that of the PNA prepared from model BSNO (3.3–5.8%). The hydroxyl groups were introduced in NO-GWR (4.0–5.7%) by oxidation–destructive nitration as substituents in the carbon chain. On the other hand, additional amount of hydroxyl groups take part of hydroxyalkyl ones obtained through the nitro aldol reaction.

The polynitroalcohols obtained from the model BSNO also possess hydroxyl groups (3.0–3.8%), but most of them belong to the hydroxyalkyl groups produced through the A$_N$-reaction.

The organic bases triethanolamine, triethylamine, and cyclopropylamine provided "softer" conditions for the process, thus, they limited the reactions of elimination and hydrolyzation. As a result, PNA-1-C$_1$, PNA-1-C$_2$, and initial NO-GWR had small differences in unsaturation values, determined as R=A$_{C=C}^{1632}$/A$_{CN}^{2116}$ (Table IV).

The nitrogen content in PNA obtained with organic bases was by ~1.5% lower than that of NO-GWR, while for PNA based on BSNO prepared with sodium carbonate base the difference was ~3.0%.[23]

The advantage of triethanolamine is that it can easily be isolated from the reaction mixture as an ammonium salt. The second reaction product PNA-2-C$_1$ (PNA-2-C$_2$) of A$_N$-reaction with catalyst cyclopropylamine was obtained with 35–45% yields. These polynitroalcohols were found to have surfactant properties ($\sigma$ = 40–45 N/m).

The thermal stability (DTA, DTG, and TG) of PNA-1-C$_1$ and PNA-1-C$_2$ was studied and compared to that of PNA obtained from model BSNO (Fig. 6). The starting temperature of decomposition of the initial NO-GWR was 100°C (Fig. 6, curve 1) while for both PNA it was 120°C (Fig. 6, curves 2,3). Their thermal destruction took place in two stages. The first one was in the temperature interval 120–250°C (~30% weight loss) and the second one from 250 to 450°C (~50% weight loss). Until 600°C, the sample burnt without coke residue. On DTA curves, an exothermal effect with maximum at ~220°C was observed, which represented the heterolytic breaking of the C—N bonds resulting in the decomposition of the nitro-groups (Fig. 6, curves 2,3). The second exothermal effect at 450°C, characteristic for the initial NO-GWR, was not registered on DTA curves of PNA. The thermal decomposition PNA-1-C$_2$ prepared from model BSNO (Fig. 6, curve 4) showed three exothermal effects at 215, 330, and 500°C.[24]

The similarity of the thermal characteristics of PNA obtained from NO-GWR and from model BSNO, was because of their similar functional compositions.

The slower rate of decomposition and the shift of the exothermal effects to higher temperatures showed that the PNA studied had slightly higher thermal stability than that of the initial NO-GWR.

The polyfunctional PNA can be used as reagents for synthesis of salts of N-sulfonic acids possessing fire retardant properties, bromine derivatives, etc.

Through sulfonation of the some polynitroalcohols, PNA-1-C$_1$, sulfonated groups were introduced into them and these oligo derivatives were used like fire retardant additives into first ground coats for protective–decorative coats on wooden articles[26] and for polymer coats on timber boards.[27]

The studies carried out prove that NO-GWR can successfully be used as reagents in the nitro aldol reaction instead of NO obtained from conventional methods. Besides, the present work emphasizes on the method of oxidation–destructive nitration of waste tires to produce nitro oligomers, which can further be

## TABLE IV
### Quantitative Functional Composition[a] of PNA Obtained by AN-reaction of NO-GWR with C1-C2-aldehydes

| No | PNA Initial NO | Temperature (°C) | Reaction time (h) | NO : Aldehyde (mass ratio) | Base | $R = \dfrac{A^{1546}_{NO_2}}{A^{2116}_{CN}}$ | NO2 (%) | $R = \dfrac{A^{1728}_{C=O}}{A^{2116}_{CN}}$ | C=O (%) | $R = \dfrac{A^{1632}_{C=C}}{A^{2116}_{CN}}$ | $R = \dfrac{A^{10688}_{C=O-(H)}}{A^{2116}_{CN}}$ | OH (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | PNA-1-C$_1$ | 40 | 4.0 | 1.0 : 0.5 | Et$_3$N | 0.7956 | 21.6 | 0.7320 | 5.3 | 0.1541 | 0.2306 | 5.4 |
| 2 | PNA-1-C$_1$ | 40 | 4.0 | 1.0 : 1.0 | CyPrA | 0.8066 | 21.9 | 0.7070 | 5.1 | 0.1609 | 0.2562 | 6.0 |
| 3 | NO-GWR | — | — | — | — | 1.0011 | 27.2 | 0.5901 | 4.3 | 0.1752 | 0.1770 | 4.1 |
| 4[b] | PNA-1-C$_1$ | 40 | 4.0 | 2.0 : 1.0 | KOH | 0.5478 | 17.4 | 0.1242 | 1.8 | 0.1257 | 0.0682 | 3.1 |
| 5[b] | PNA-1-C$_1$ | 40 | 5.0 | 2.0 : 1.0 | KOH | 0.6323 | 20.1 | 0.1251 | 1.8 | 0.1265 | 0.0708 | 3.3 |
| 6[b] | BSNO | — | — | — | — | 0.7978 | 27.6 | 0.1308 | 1.9 | 0.1264 | — | — |
| 7 | PNA-1-C$_2$ | 50 | 4.0 | 1.0 : 1.0 | TrEthA | 0.7706 | 20.9 | 0.5880 | 4.3 | 0.1812 | 0.3733 | 8.7 |
| 8 | PNA-1-C$_2$ | 60 | 4.0 | 1.0 : 1.0 | Et$_3$N | 0.7814 | 21.2 | 0.6894 | 5.0 | 0.1665 | 0.3557 | 8.3 |
| 9 | NO-GWR | — | — | — | — | 0.8235 | 22.3 | 0.5921 | 4.3 | 0.1601 | 0.3251 | 7.5 |
| 10[c] | PNA-1-C$_2$ | 60 | 4.0 | 2.0 : 1.0 | KOH | 0.5129 | 17.8 | 0.2106 | 3.0 | 0.1548 | 0.0781 | 3.6 |
| 11[c] | PNA-1-C$_2$ | 50 | 4.0 | 2.0 : 1.0 | KOH | 0.3616 | 12.5 | 0.1796 | 2.6 | 0.1371 | 0.0820 | 3.8 |
| 12[c] | BSNO | — | — | — | — | 0.5859 | 20.0 | 0.1285 | 1.9 | 0.1286 | — | — |

[a] Standard compounds: 2-bromo-2-nitro-1,3-propandiol, $\nu$C—O—(H), 1094 cm$^{-1}$; $\nu_{as}$NO$_2$, 1552 cm$^{-1}$. 10-nonadecanone, $\nu$C═O 1698 cm$^{-1}$.
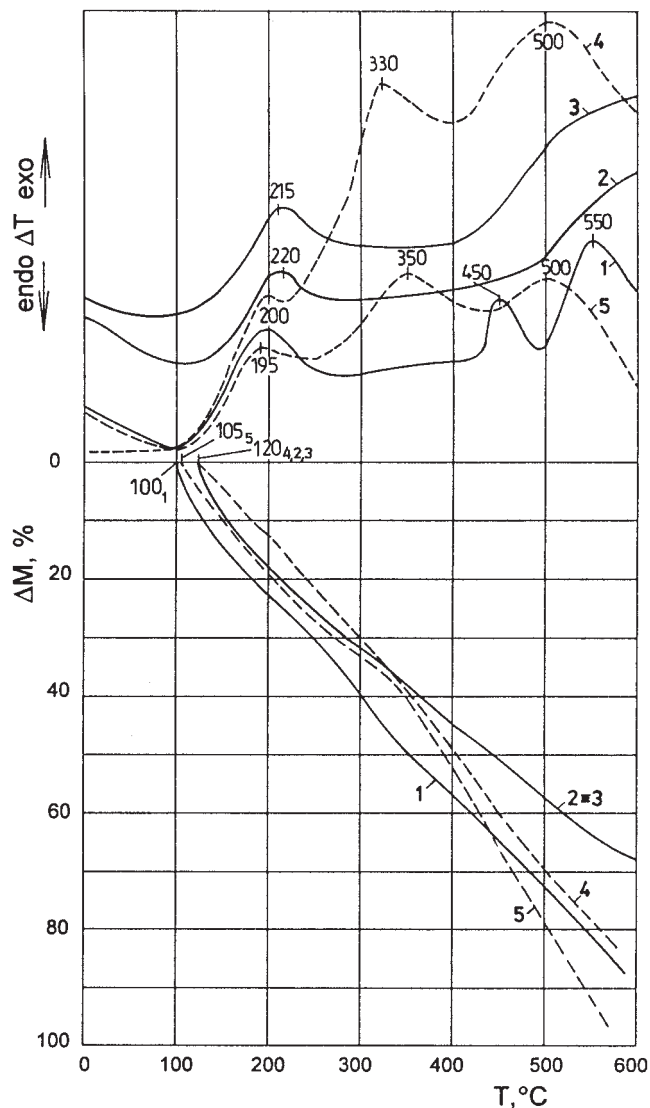[b] From ref. 23.
[c] From ref. 24.



**Figure 6** Thermal analysis of polynitroalcohols obtained from nitro oligomers and C$_1$-C$_2$-aldehydes (1) Initial NO-GWR, (2) PNA-1-C$_1$ from NO-GWR (40°C, 4 h, CyPrA), (3) PNA-1-C$_2$ from NO-GWR (60°C, 4 h, CyPrA), (4) PNA-1-C$_2$ from BSNO (40°C, 3 h, KOH) and (5) Initial BSNO.

used for the production of other important oligo derivatives.

## CONCLUSIONS

It was found that the A$_N$-reaction of NO prepared from waste vulcanizates with C$_1$-C$_2$-aldehydes carried out with catalyst, such as the organic bases—triethanolamine, triethylamine, and cyclopropylamine, takes place under "soft" conditions.

The quantitative functional composition (%NO$_2$, %C═O, %OH groups) of polynitroalcohols of PNA-1-C$_1$ and PNA-1-C$_2$ was found to be similar to that of polynitroalcohols prepared from model BSNO.

Using $^{1}$H NMR spectroscopy, it was found that the $A_N$-reaction was not accomplished and not all of the $\alpha$-H atoms bonded to the nitro groups were substituted by hydroxylalkyl groups.

Polynitroalcohols, based on NO from waste vulcanizates and $C_1$-$C_2$-aldehydes, have similar thermal characteristics (DTA, DTG, and TG) to those of polynitroalcohols obtained from model BSNO, which is connected with their similar functional composition.

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