

Preparation of Sodium Salts of *N*-Sulfonic Acids by Sulfomethylation of Nitro Oligomers Obtained from Waste Rubbers

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ABSTRACT: The sulfomethylation of nitro oligomers obtained from waste rubbers (NO-GWR) with sodium hydroxymethane sulfonate was studied in aqueous-alkali solutions from 50 to 80°C for reaction times of 3.5–5.5 h with weight ratios of 1.0:0.3–0.6. The initial NO-GWR was produced by the oxidation/destructive nitration of waste rubbers with nitric acid in a heterogeneous medium. The influence of the reaction conditions on the yields and functional compositions of the sodium salts of two types of *N*-sulfonic acids was investigated. Some of the nitro groups transformed into sulfamate groups at 80°C or lower. One type of *N*-sulfonic acid was isolated from its sodium salt by ion exchange. The oligosulfo derivatives were characterized by elemental and thermal analyses, IR and ¹H-NMR spectroscopy,

and the number-average molecular weight. The sodium salts of the *N*-sulfonic acids obtained from NO-GWR possessed functional compositions similar to those of sodium salts from butadiene–styrene nitro oligomers prepared from butadiene–styrene latexes. Therefore, NO-GWR obtained from available raw materials can be used as the initial derivative for the preparation of salts of *N*-sulfonic acids instead of the nitro oligomers used now from elastomers. The salts can be used in galvanic coating techniques as brighteners. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 1002–1013, 2005

Key words: oligomers; rubber; waste

INTRODUCTION

About 10 million tons of waste rubber products are disposed annually. They are resistant to atmospheric and biological processes. Refuse tires and other rubber articles contain elastomers with slightly changed structures, textile materials, metals, and so forth. A number of methods for their utilization have been proposed, but none of them is considered to be a general solution to the problem.¹

One of the methods for the utilization of refuse tires and other rubber articles is their transformation into nitro oligomer derivatives by oxidation/destructive nitration. An effective method for the preparation of nitro oligomers from waste rubbers (NO-GWR) with high yields has been suggested.² NO-GWR has a functional composition similar to that of nitro oligomers prepared from butadiene–styrene rubber and butadiene–styrene latexes (Bulex). Therefore, NO-GWR can successfully be used instead of nitro oligomers obtained from fresh elastomers as the initial oligomer for the production of new oligo derivatives.

The reaction of sulfoalkylation belongs to indirect sulfonation methods³ and is very suitable for nitro compounds unstable in acidic media. One sulfoalkylating agent is sodium hydroxymethane sulfonate [also called bisulfite compound of formaldehyde (BCF)], which is cheap and available. Sulfomethylation is also used for the addition of sulfomethyl groups to phenols, amines, amides, ketones, acetacetic, and malonic esters.

The sulfomethylation of butadiene–styrene nitro oligomers (BSNOs) from Bulex with sodium hydroxymethane sulfonate has been studied, and the obtained sodium salts of *N*-sulfonic acids (*N*-SAs) have been used as brighteners in zinc electrolytes.^{4–6}

The reaction of primary nitroalkanes such as nitroethane and 1-nitropropane with BCF produces sodium salts of nitrosulfonic acids.⁷

Recent publications have reported the use of bisulfite derivatives of aldehydes and 1,3- and 1,4-alkane-sultones as sulfoalkylating agents for low-molecular-weight compounds and some polymers.

Through the sulfomethylation of phenols or novolac resins based on phenols, synthetic tanning agents⁸ and sulfo derivatives have been obtained that reduce the viscosity of clay solutions used for oil and gas drilling.⁹

The sulfoalkylation of poly(styryllithium) and poly(styrene-*block-α*-methylstyrene) lithium with 1,3-pro-

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pane sultone and 1,4-butane sultone has been studied.¹⁰ Sodium salts of sulfonic acids containing sulfo-methylol groups have been synthesized from phenol, formaldehyde, and sodium sulfite.¹¹ 1,3-Dicarbonyl compounds have been sulfoalkylated with 1,3-propane sultone.¹² The sulfopropylation of substituted acridines with 1,3-propane sultone has been investigated, and the obtained salts have been used as chemiluminescent indicators.¹³ It has been reported that the reaction of substituted pyridines, chinolines, and acridines with 1,3-propane sultone takes place at the nitrogen atom in the heterocycle.¹⁴ Modified copolymers of acrylamide and acrylonitrile have been prepared by sulfomethylation^{15,16} and have been used as additives in mineral dispersions. Sulfomethylated polymers have been obtained from polyfunctional water-soluble polymers based on hydrolyzed waste polyacrylonitrile fibers.¹⁷ Both the initial and sulfomethylated polymers have been investigated as structure-forming additives (2–5 mass %) in soil.¹⁸

The objectives of this work were to prepare sodium salts of *N*-SAs from NO-GWR by sulfomethylation with sodium hydroxymethane sulfonate and to establish that those sodium salts had functional compositions similar to those of sodium salts obtained from BSNOs based on Bulex. In this way, potential applications as brighteners in cyanide-less electrolytes were expected to be revealed.

EXPERIMENTAL

The initial nitro oligomer (NO-GWR) was obtained by the oxidation/destructive nitration of ground waste rubber (diameter = 0.25–0.63 mm) with nitric acid in a heterogeneous medium in the presence of nonylphenolpolyglycoether (Veranol H-10, Vilnius, Litva) with heating from 40 to 60°C for 4–5 h with a nitrating factor of 5.²

Sulfomethylation of NO-GWR with BCF

The initial reagents were NO-GWR (3.0 g), Na₂SO₃ · 7H₂O (chemically pure; 1.6 g), 38% formaline (chemically pure; 0.65 mL), and NaOH (chemically pure; 0.20 g). The solution of the aci-form of NO-GWR, obtained by the dissolution of 3 g of the nitro oligomer in 25 mL of an aqueous-alkali solution (0.2 g of NaOH in 25 mL of water) was placed in a 250-mL, three-necked flask equipped with a stirrer, a reflux condenser, and a separating funnel. BCF was prepared through the dissolution of 1.6 g of Na₂SO₃ · 7H₂O in 25 mL of water and the addition of 0.65 mL of formalin (NO-GWR/BCF 1:0.3 mass ratio). The BCF solution was dropped into the solution of the aci-form of NO-GWR for 60 min at 60°C under continuous stirring. The reaction continued for another 3.5 h under the same conditions.

The reaction mixture was acidified with 25% hydrochloric acid until pH 2, and the sodium salt of *N*-SA SA-1 was obtained as a red-brown precipitate. After a certain period, the precipitate was filtered, and the filtrate was concentrated *in vacuo* (0.011 MPa) to about 20 mL. Then, 20 mL of ethyl alcohol was added, and the mixture was cooled to isolate the inorganic salts. The sodium salt of *N*-SA SA-2 was isolated by the evaporation of the filtrate as a brown hygroscopic precipitate. The yields were 1.2 g (40%) of the sodium salt of SA-1 and 1.5 g (50%) of the sodium salt of SA-2.

Preparation of *N*-SAs from their sodium salts

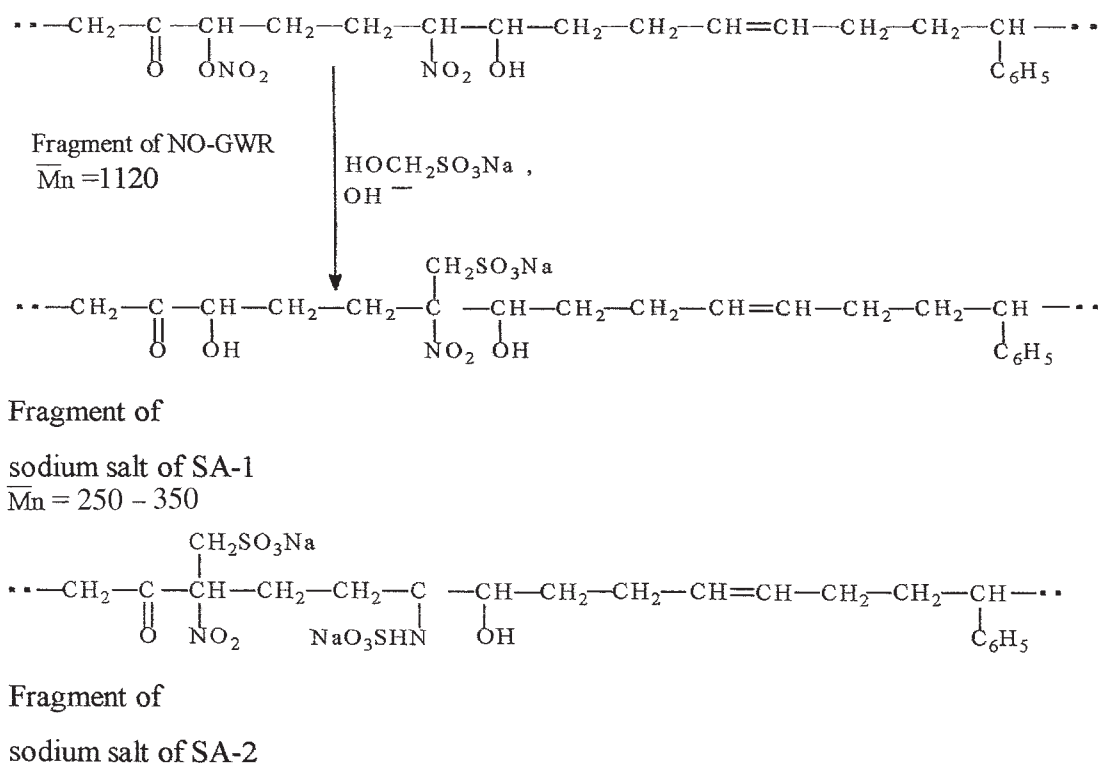
A glass column with a volume of 150 cm³ was filled with 50 mL of Woffatit KPS. The latter was treated first with a 10% aqueous solution of NaCl and then with aqueous solutions of NaCl at concentrations of 5.0, 2.5, and 1.2%. The ionite was washed with distilled water until the absence of chlorine ions. The ionite was transformed into the hydrogen form with a flowing 8% solution of hydrochloric acid. SA-2 was isolated by a 0.7% solution (200 mL) of its sodium salt (1.4 g) flowing through the ionite in the hydrogen form. The eluted solution of SA-2 was distilled *in vacuo* (0.011 MPa) to about 20 mL to obtain SA-2 as a brown, hygroscopic precipitate (0.8 g).

Analyses

IR spectra were taken with a UR-20 spectrophotometer in a KBr pellet (3 mg/100 mg). Elemental analyses (carbon, hydrogen, and nitrogen) were taken with a Perkin Elmer instrument. ¹H-NMR spectra were taken with a Bruker 250-MHz spectrophotometer, Germany. The percentage of sulfur was determined with the Shoniger method. A thermal analysis was performed with an OD-2 derivatograph (Hungary) from 20 to 600°C at heating rate of 6 K/min. The samples were prepared as metaloceramic crucibles (9 mm in diameter, 100 mg) equipped with Pt and Pt/Rd thermocouples. The analyses were conducted in static air. The number-average molecular weights (\bar{M}_n 's) were determined by gel permeation chromatography in a column filled with Ultrastragel in a solution of tetrahydrofuran.

RESULTS AND DISCUSSION

The preparation of alkali salts of *N*-SAs from NO-GWR and their use as brighteners in galvanic processes constitute an effective way of using refuse tires and other rubber articles by their transformation into oligo derivatives. These salts are expected to be produced at a low cost because of the use of waste materials and widely available sulfoalkylating agents (e.g., BCF). Sodium salts of *N*-SA have been synthesized from nitro oligomers obtained through the nitration of



Scheme 1

elastomers^{4,5} and have been used without separation for galvanic coatings. Two types of sodium salts of *N*-SAs obtained from BSNOs have been isolated.⁶

The aim of this study was to prepare sodium salts of *N*-SAs based on NO-GWR and to establish the applicability of NO-GWR as an initial oligo derivative for sulfomethylation instead of nitro oligomers produced from elastomers.

Because of the specific characteristics of sulfoalkylation with BCF and the polyfunctional composition of NO-GWR, the amounts of BCF and alkaline base necessary for the preparation of the aci-form of the initial nitro oligomer were reduced, and the reaction was carried out at 50–60°C.

The sulfomethylation of NO-GWR took place according to Scheme 1 and yielded sodium salts of two *N*-SAs denoted SA-1 and SA-2. The reaction conditions were varied (temperature, time, and NO-GWR/BCF ratio) to obtain sodium salts with optimal contents of sulfomethylate groups.

The yield of the sodium salt of SA-1 increased from 38 to 43% as the temperature increased from 40 to 60°C, whereas the yield of the sodium salt of SA-2 increased from 45 to 55% (Fig. 1, curves 1 and 2). The yields of the salts of the oligosulfonic acids were higher at an NO-GWR/BCF mass ratio of 1:0.4–0.5 mass ratio and at a longer reaction time of 4.5–5.0 h (Figs. 2 and 3, curves 1 and 2).

Fully water-soluble salts with high yields could be obtained at 50–60°C for 4.5–5.5 h.

Highly alkali media are not preferred for sulfoalkylation because of side reactions that take place.¹⁹ Therefore, the amount of the sodium base necessary for the formation of the NO-GWR aci-form was reduced from 0.5 (for BSNO)⁶ to 0.2 g/3 g of NO-GWR (Table I, samples 2–11).

The reaction was carried out with a deficiency of BCF toward the initial nitro oligomer at an NO-GWR/BCF mass ratio of 1.0:0.3–0.6 instead of 1.0:1.3 mass ratio.⁶ Thus, the process took place in solution, and the yields of the sodium salts of SA-1 were about 40%, and those of the sodium salts of SA-2 were approximately 55% (Table I).

For the salts obtained with BSNO, those of SA-1 were prepared in higher yields (~55%) than those of SA-2 (40%).⁶

The optimal conditions for the reaction were as follows: temperature = 50–60°C, NO-GWR/BCF mass ratio = 1.0:0.3–0.5, and reaction time = 4.5–5.5 h. The sodium salts of SA-1 were powdery substances, whereas those of SA-2 were dark-brown hygroscopic resins.

SA-2 was prepared from its sodium salt by ion exchange with ionite Woffatit KPS in the hydrogen form, and SA-2 was isolated as a pure substance through the removal of the inorganic salts.

The sodium salts of SA-1 and SA-2 were studied with IR and ¹H-NMR spectroscopy to determine their functional composition.

The following stretching vibrations were characteristic of the IR spectrum (Fig. 4, curve 2) of the SA-1 sodium

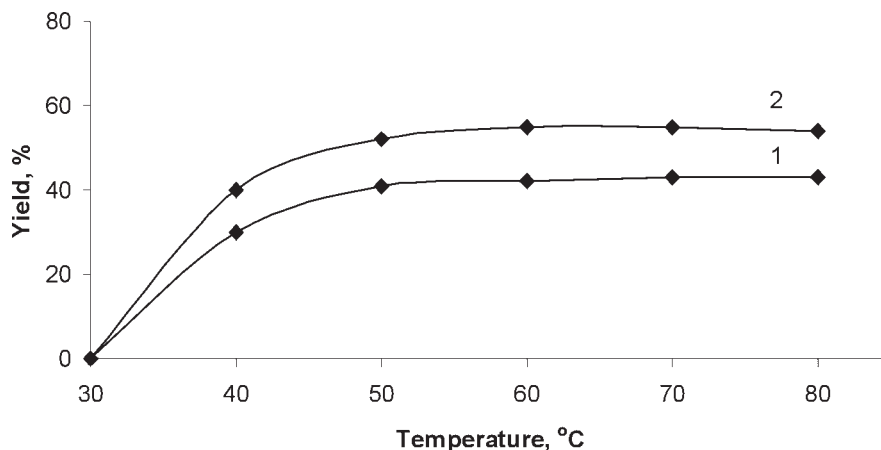


Figure 1 Yield of *N*-SA sodium salts versus the temperature (time = 4.5 h, NO-GWR/BCF = 1.0:0.6 mass ratio): (1) sodium salt of SA-1 and (2) sodium salt of SA-2.

salt ($\nu_{as,s} = 1540$ and 1360 cm^{-1} for the nitro group, $\nu_{as,s} = 1240$ and 1100 cm^{-1} for SO_2 , $\nu = 700\text{ cm}^{-1}$ for $\text{S}=\text{O}$, $\nu = 1620\text{ cm}^{-1}$ for $\text{C}=\text{C}$, and $\nu = 1720\text{ cm}^{-1}$ for $\text{C}=\text{O}$). The increased absorption in the range of $3200\text{--}2500\text{ cm}^{-1}$ showed the presence of sulfonate groups in the sodium salt of SA-1.

The IR spectrum of initial NO-GWR (Fig. 4, curve 1) showed the presence of nitro groups ($\nu_{as,s} = 1550$ and 1360 cm^{-1}), nitrate ester groups ($\nu_{as} = 1280\text{ cm}^{-1}$), $\text{C}=\text{C}$ ($\nu = 1620\text{ cm}^{-1}$) at a low intensity, and $\text{C}=\text{O}$ ($\nu = 1720\text{ cm}^{-1}$).

The IR spectrum of SA-2 (Fig. 5, curve 1) was characterized by stretching vibrations for the nitro group ($\nu_{as,s} = 1550$ and 1380 cm^{-1}), $\text{C}=\text{O}$ ($\nu = 1720\text{ cm}^{-1}$), SO_2 ($\nu_{as,s} = 1200$ and 1030 cm^{-1}), and $\text{S}=\text{O}$ ($\nu = 600\text{ cm}^{-1}$). The wide band between 3200 and 2500 cm^{-1} was due to the stretching vibration of the dimer OH group (νOH) from the sulfonic group of associated *N*-SAs.²⁰ The IR spectrum of the sodium salt of SA-2 (Fig. 5, curve 2) was similar to that of SA-2.

The IR spectrum of the sodium salt of SA-1 obtained from BSNO⁶ (Fig. 4, curve 3) showed stretching vibrations ($\nu_{as,s} = 1550$ and 1380 cm^{-1}) of lower intensity because, under the reaction conditions (temperature = 80°C , BSNO/BCF mass ratio = 1.0:1.3), some of the nitro groups were transformed into sulfamate groups (NH at $\delta = 1600\text{ cm}^{-1}$).

Comparing the IR spectra of SA-2 from NO-GWR (prepared at 60°C) and its sodium salt (prepared at 80°C), we identified an intensive vibration at $\delta = 1620\text{ cm}^{-1}$ for NH in the second one (Fig. 5, curves 1 and 2). On the other hand, sulfamate groups were present not only in the SA-1 sodium salt but also in the SA-2 sodium salt (Fig. 5, curve 3) obtained at 80°C ⁶ from BSNO.

The IR spectra of the *N*-SAs proved their polyfunctional compositions. The presence of sulfamate groups in some of them was probably due to the influence of formaldehyde.

BCF is a product of the following equilibrium reaction:¹⁹

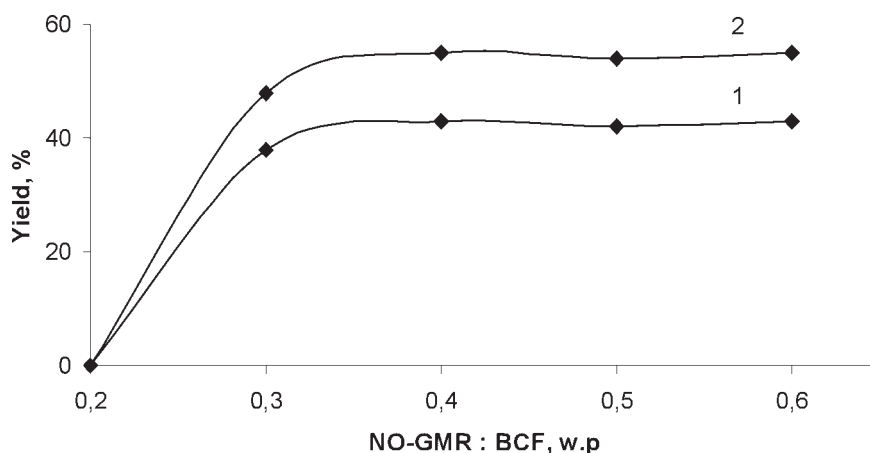


Figure 2 Yield of *N*-SA sodium salts versus the NO-GWR/BCF mass ratio (temperature = 60°C , time = 4.5 h): (1) sodium salt of SA-1 and (2) sodium salt of SA-2.

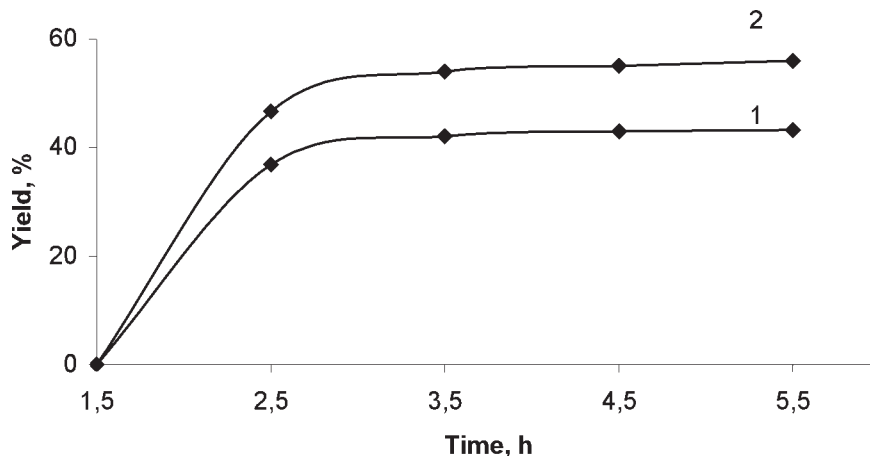
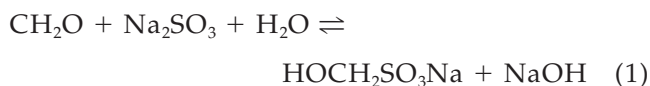


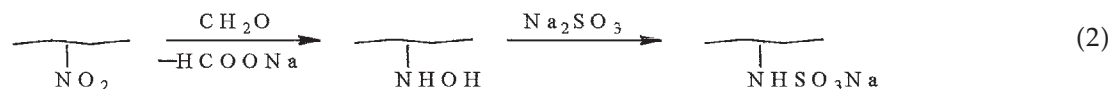
Figure 3 Yield of *N*-SA sodium salts versus the reaction time (temperature = 60°C, NO-GWR/BCF = 1.0:0.3 mass ratio): (1) sodium salt of SA-1 and (2) sodium salt of SA-2.



At temperatures below 80°C, the equilibrium shifts to the left side, and the unstable alkali media of

BCF decompose into formaldehyde and Na_2SO_3 [eq. (1)].

The results suggested that the formaldehyde reduced some of the nitro groups of NO-GWR and that they were transformed later into sulfamate groups²:



The other reactions taking place with sulfomethylation could also be explained with the generation of formaldehyde from BCF at higher temperatures. It is well known¹⁹ that at higher temperatures and in alkali media, formaldehyde transforms irreversibly

into methanol and formic acid (according to the Canizaro reaction) or aldol (through aldol condensation).

In light of these considerations, the sulfomethylation of NO-GWR was carried out under softer conditions,

TABLE I
Yields of the Sodium-Salts of SA-1 and SA-2 Obtained by Sulfomethylation of NO-GWR with BCF

No.	Temperature (°C)	Reaction time (h)	NO-GWR/BCF mass ratio	NaOH for 3 g, of NO-GWR	Sodium salt yield (%)	
					SA-1	SA-2
1 ^a	40	4.5	1:0.6	0.5	32	42
2	40	4.5	1:0.6	0.2	30	40
3	50	4.5	1:0.6	0.5	41	52
4	50	4.5	1:0.6	0.2	42	52
5	60	4.5	1:0.6	0.2	43	55
6 ^a	60	4.5	1:0.4	0.2	43	54
7	60	2.5	1:0.3	0.2	40	52
8 ^a	60	3.5	1:0.3	0.2	42	54
9	60	4.5	1:0.3	0.2	43	55
10 ^a	60	5.5	1:0.3	0.2	39	56
11 ^a	80	4.5	1:0.6	0.2	43	54
N-SA ^b	80	4.5	1:1.3	0.5	55	40

^a Two parallel probes.

^b From BSNO.⁶

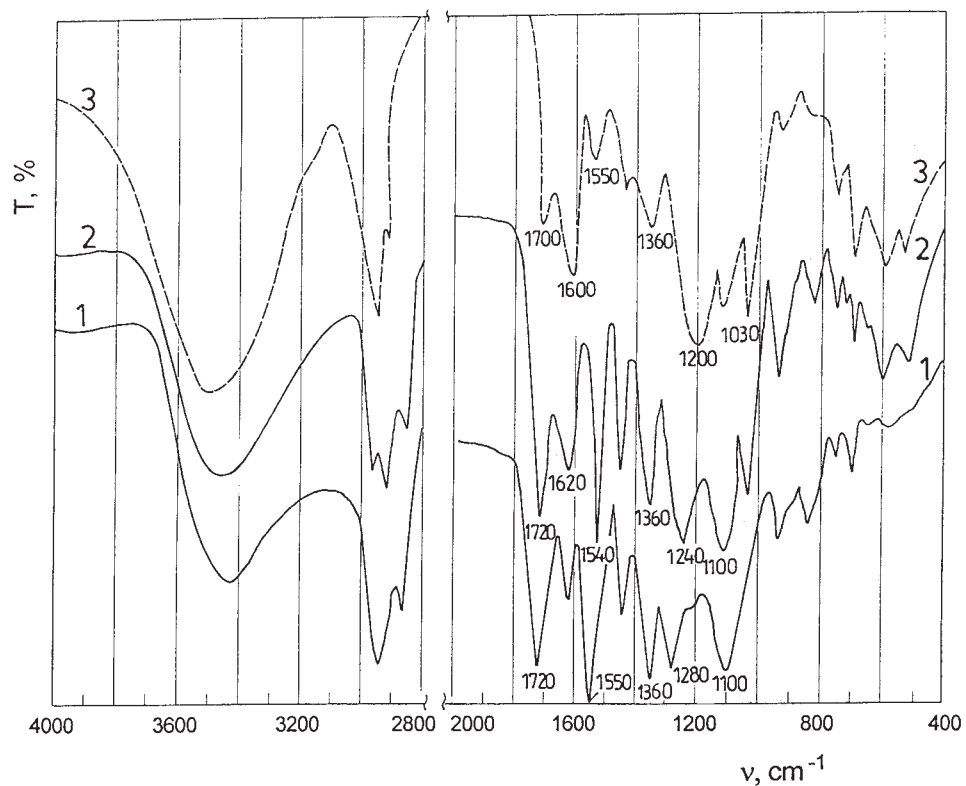


Figure 4 IR spectra of sodium salts of SA-1: (1) initial NO-GWR, (2) sodium salt of SA-1 (temperature = 80°C, mass ratio = 1.0:0.6), and (3) sodium salt of SA-1 from BSNO (temperature = 80°C, mass ratio = 1.0:1.3).

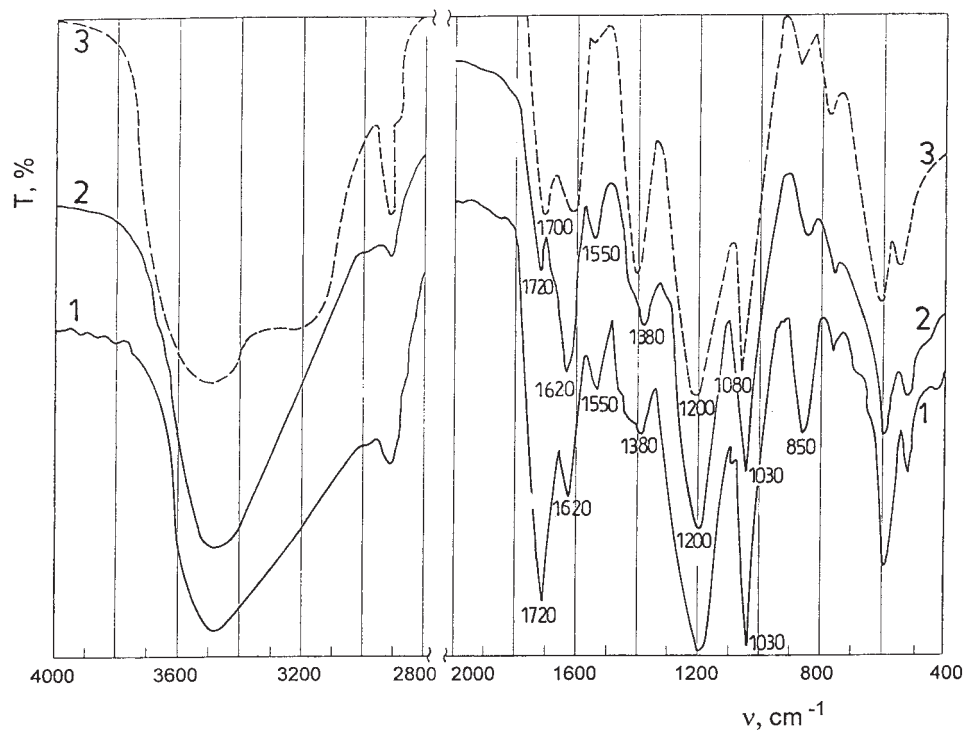


Figure 5 IR spectra of SA-2 and its sodium salts: (1) SA-2 (temperature = 60°C, mass ratio = 1.0:0.3), (2) sodium salt of SA-2 (temperature = 80°C, mass ratio = 1.0:0.6), and (3) sodium salt of SA-2 from BSNO (temperature = 80°C, mass ratio = 1.0:1.3).

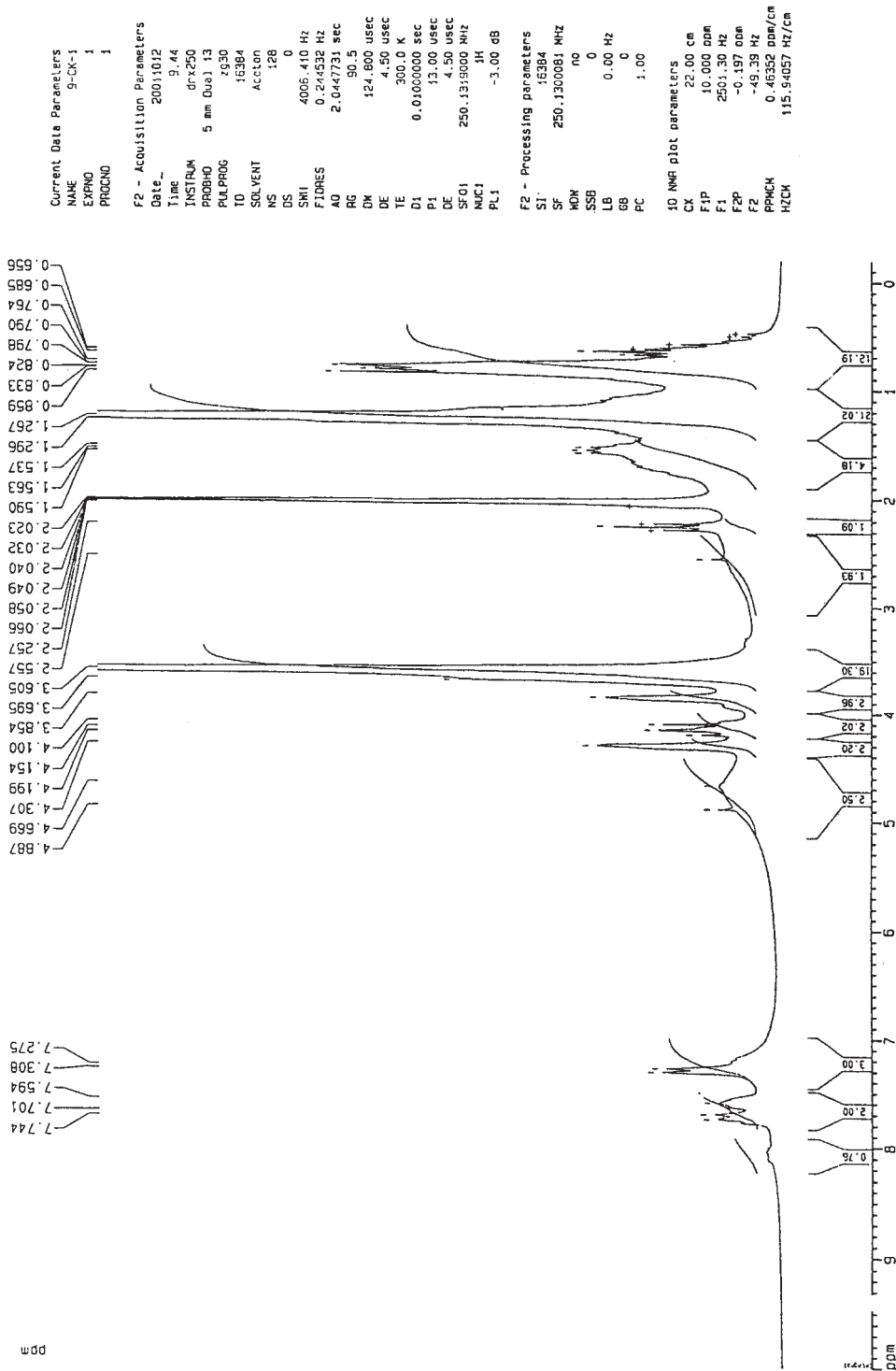


Figure 6 ¹H-NMR spectrum of the sodium salt of SA-1 (temperature = 80°C, NO-GWR/BCF = 1.0:0.6 mass ratio).

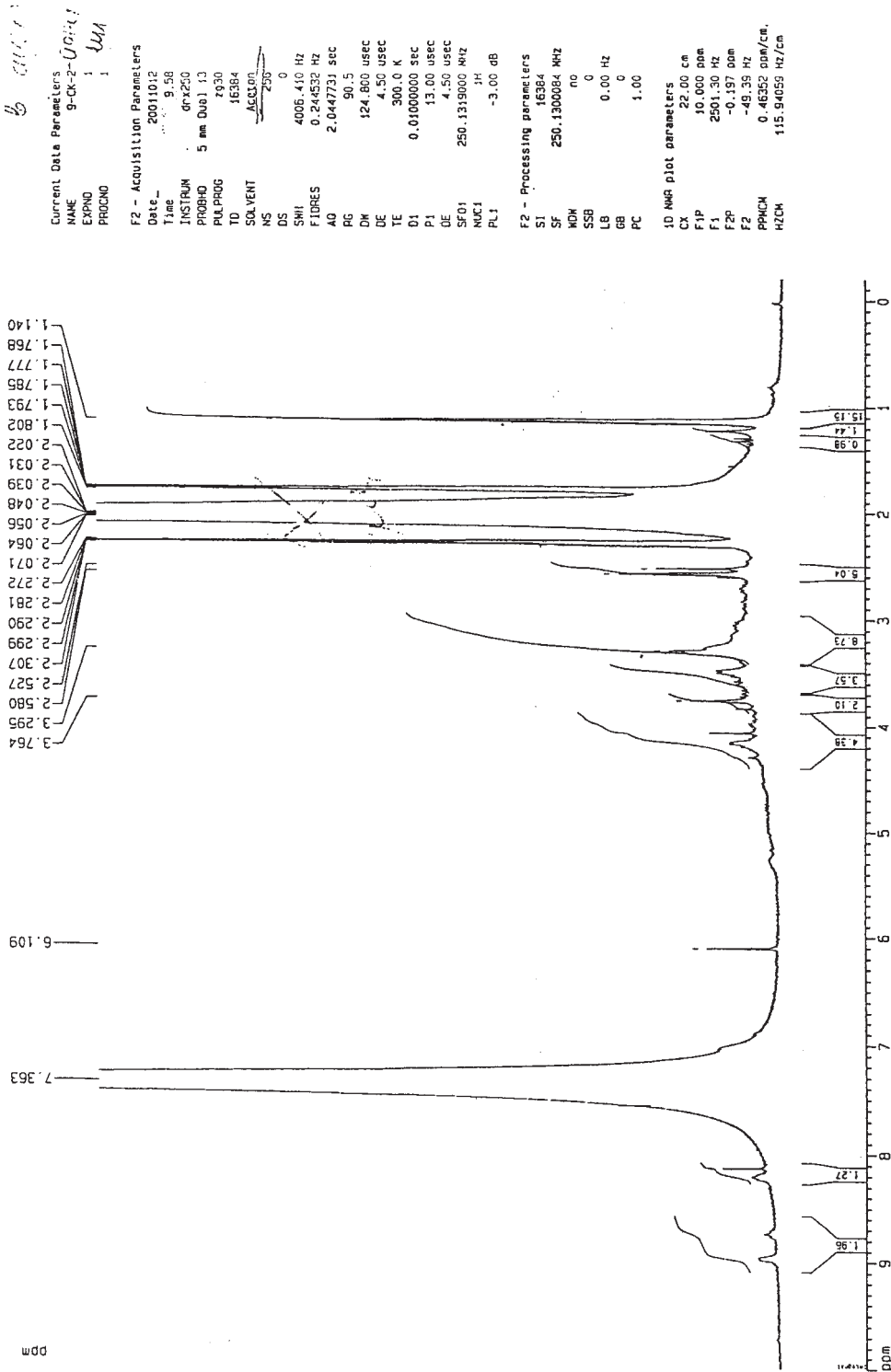


Figure 7 ¹H-NMR spectrum of the sodium salt of SA-2 (temperature = 80°C, NO-GWR/BCF = 1.0:0.6 mass ratio).

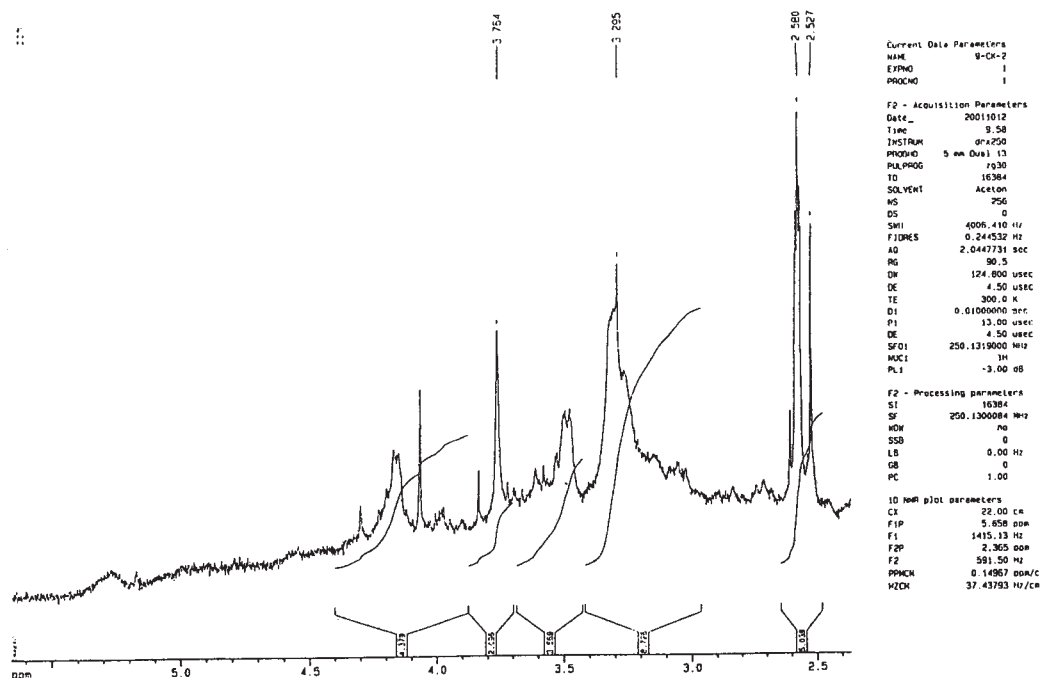


Figure 8 $^1\text{H-NMR}$ spectrum of SA-2 (temperature = 80°C , NO-GWR/BCF = 1.0:0.6 mass ratio).

at temperatures of $40\text{--}60^\circ\text{C}$ and with a deficiency of BCF toward NO-GWR (NO-GWR/BCF = 1.0:0.3 mass ratio). Thus, the sodium salts of SA-2 were water-soluble, and their yields were 50–55%. When a higher quantity of BCF was used (NO-GWR/BCF = 1.0:0.5–0.6 mass ratio) and the reaction was carried out at $70\text{--}80^\circ\text{C}$, the *N*-SA sodium salts were found to contain some sulfamate groups along with sulfonate groups.

The presence of sulfamate, sulfonate, and hydroxyl groups in the sodium salts and their pronounced surfactant properties ($\sigma = 45\text{--}50\text{ N/m}$) determined their complex-forming properties with Zn(II), Cd(II), and other metals and, therefore, their application as brighteners.

The $^1\text{H-NMR}$ spectrum of the sodium salt of SA-1 (Fig. 6) showed the following signals: a triplet for methylene protons at a carbon atom bonded to the electron-acceptor $\text{CH}_2\text{SO}_3\text{Na}$ group (7.07 ppm), C—H protons from phenyl (7.30 ppm), a methine proton from CHNO_2 (4.30 ppm), a methine proton from CHOH (3.85 ppm), and a proton of the hydroxyl group (4.15 ppm). Characteristic signals at 1.26–1.29 ppm for methylene protons from $\text{---}(\text{CH}_2)_n\text{---}$ and a multiplet at approximately 0.79 ppm for methyl protons were also recorded.

The $^1\text{H-NMR}$ spectrum of SA-2 (Figs. 7 and 8) was characterized by signals for a proton from the sulfonic group (7.7–7.9 ppm) at 7.36 ppm, a methine proton from CHNO_2 (4.05 ppm), a methine proton from CHOH (3.76 ppm), methylene protons from $\text{---}(\text{CH}_2)_n\text{---}$ (1.14 ppm), and methyl protons (~ 0.8 ppm). The $^1\text{H-NMR}$ spectrum of SA-2 was taken in

deuterated acetone (~ 2.2 ppm), and that of the sodium salt of SA-1 was taken in deuterated acetone and water (~ 3.6 ppm).

An analysis of the $^1\text{H-NMR}$ spectra showed that the sulfomethylation occurred as some of the α -H atoms with respect to the nitro groups were replaced by sulfomethylate ones. Therefore, some methine protons in CHNO_2 groups (4.1 ppm) were present in SA-1 and SA-2. The presence of phenyl protons from the aromatic ring was also proved (7.3 ppm). Aromatic rings existed in the initial NO-GWR (UV spectrum, $\lambda_{\text{max}} \sim 250\text{ nm}$) and in the butadiene–styrene rubber of the vulcanizate.

Through the sulfomethylation of NO-GWR ($\bar{M}_n = 1120$, D (coefficient of polydispersity) = 1.85), two types of sodium salts of *N*-SAs were obtained. The sodium salts of SA-1 ($\bar{M}_n = 260\text{--}350$, $D \sim 1.42$) contained 2.5–3.9% S, and those of SA-2 contained 7.5–10.5% S (Tables I–III).

The sulfur content of the sodium salts of SA-1 slightly increased as the temperature increased from 40 to 60°C . The suitable mass ratios were considered to be NO-GWR/BCF = 1.0:0.3–0.4 (mass ratio; Table I, samples 5–9). The nitrogen content in the sodium salts was lower (3.8–4.7% N) than that in NO-GWR (7.4% N) because of the introduction of sulfomethylate groups.

Comparing the data from the elemental analyses of the sodium salts of *N*-SA obtained from NO-GWR and those from BSNO,⁶ we determined the following:

- The sodium salts of SA-1 obtained at 60°C had similar sulfur contents and higher nitrogen con-

TABLE II
Elemental Analysis of the Sodium-Salts of SA-1 Obtained from NO-GWR and BSNO

No.	Temperature (°C)	Reaction time (h)	NO-GWR/BCF mass ratio	NaOH (g)	C (%)	H (%)	N (%)	S (%)
1 ^a	40	4.5	1:0.6	0.5	56.22	6.91	3.72	2.43
1-A ^a	40	4.5	1:0.6	0.5	55.4	7.08	4.17	2.49
2	50	4.5	1:0.6	0.2	57.66	7.61	4.48	2.85
3	60	4.5	1:0.6	0.2	55.11	6.56	3.83	2.90
5	60	2.5	1:0.3	0.2	53.03	5.77	4.05	3.25
6	60	3.5	1:0.3	0.2	55.54	7.19	4.70	3.92
7	60	4.5	1:0.4	0.2	53.59	7.10	4.26	3.41
8	60	4.5	1:0.3	0.2	53.86	6.86	4.20	3.72
9	60	5.5	1:0.3	0.2	51.49	6.43	3.37	3.00
9-A	60	5.5	1:0.3	0.2	52.20	5.91	4.36	3.58
4	80	4.5	1:0.6	0.2	54.34	7.12	2.90	2.64
NO-GWR	—	—	—	—	54.80	6.20	7.39	—
1	80	4.5	1:1.3	0.5	59.88	6.74	2.66	3.48
2 ^b	80	4.5	1:1.3	0.5	59.95	6.84	1.75	3.84
BSNO	—	—	—	—	55.83	6.19	8.16	—

^a Parallel probes.

^b Reactor 200 L.

tents (4.3–4.7%), in comparison with those based on BSNO (1.8–2.6% N). Obviously, partial denitration of the BSNO nitro groups had taken place at 80°C.

- The nitrogen content in SA-2 (3.0–3.7% N) prepared at 60°C was closed to that of the sodium salts of SA-2 prepared from BSNO (4.1%). This sodium salt, however, showed slightly higher sulfur contents (11.4–13.3% S) than SA-2 (8.5–10.4% S), and this was attributed to the higher temperature of the sulfomethylation.

The thermal stability of the sodium salts of SA-1 and SA-2 was also studied [thermogravimetry (TG) and

dynamic thermal analysis (DTA)]. The starting temperature of the decomposition of the SA-1 sodium salt was 120°C (Fig. 9, curve 2). The DTA curve showed exothermal effects with maxima at 230, 310, 480, and 590°C. The weak effect registered at 230°C due to the decomposition of nitro groups was compensated by the endothermal effect at 115°C resulting from the release of hygroscopic moisture. The sodium salt of SA-1 based on BSNO decomposed with similar exothermal effects, which can be seen in the DTA curve (Fig. 9, curve 2'). However, an exothermal effect at 230°C was not observed, probably because the quantity of nitro groups was low. The exothermal effect at 200°C on the DTA curves of

TABLE III
Elemental Analysis of SA-2 (Based on NO-GWR) Obtained from Sodium Salts by Ion Exchange with Woffatit KPS and Sodium Salts SA-2 (Based on BSNO)

No.	Temperature (°C)	Reaction time (h)	NO-GWR/BCF mass ratio	NaOH for 3 g of NO	C (%)	H (%)	N (%)	S (%)
1	40	4.5	1:0.6	0.5	23.95	3.24	3.14	6.26
2	50	4.5	1:0.6	0.5	24.14	3.60	3.39	7.62
3	60	4.5	1:0.6	0.2	33.97	4.22	3.73	8.15
5	60	2.5	1:0.3	0.2	25.00	4.95	3.15	8.50
6	60	3.5	1:0.3	0.2	26.19	4.86	3.68	8.53
7	60	4.5	1:0.3	0.2	24.02	4.67	2.45	8.67
8	60	4.5	1:0.4	0.2	24.01	3.72	3.01	8.88
9	60	5.5	1:0.3	0.2	24.66	5.08	3.07	10.45
4 ^a	80	4.5	1:0.6	0.2	28.55	4.81	3.22	10.64
NO-GWR	—	—	—	—	54.80	6.20	7.39	—
1 ^b	80	4.5	1:1.3	0.5	23.08	2.55	4.15	13.3
2 ^b	80	4.5	1:1.3	0.5	23.17	2.90	3.97	11.4
BSNO	—	—	—	—	55.83	6.19	8.16	—

^a Three parallel probes.

^b SA-2 from BSNO.

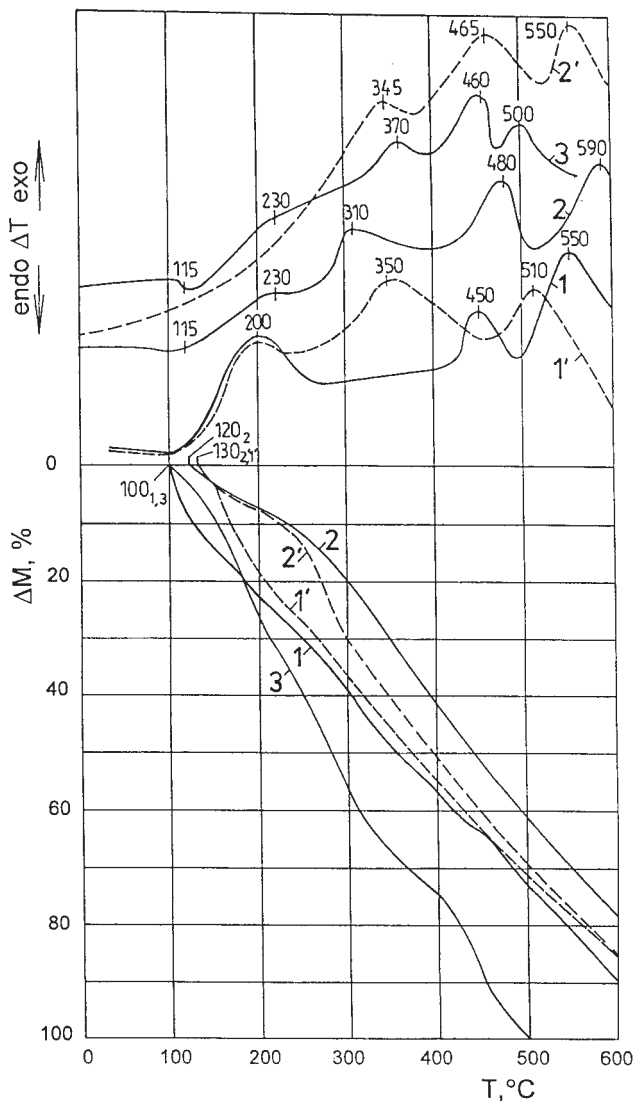


Figure 9 Thermal analysis of the sodium salt of SA-1, SA-2, and initial nitro oligomers: (1) NO-GWR, (1') BSNO, (2) sodium salt of SA-1 (temperature = 80°C, time = 4.5 h, NO-GWR/BCF = 1.0:0.6 mass ratio), (2') sodium salt of SA-1 (temperature = 80°C, time = 4.5 h, BSNO/BCF = 1.0:1.3 mass ratio), and (3) SA-2 (temperature = 80°C, time = 4.5 h, NO-GWR/BCF = 1.0:0.6 mass ratio).

initial NO-GWR and BSNO (Fig. 9, curves 1 and 1') was due to the decomposition of the nitro groups.

SA-2 (Fig. 9, curve 3) started to decompose at 100°C, and the rate of its thermal destruction, according to the TG curve (Fig. 9, curve 3), was rather high. In the temperature interval of 120–280°C, the weight of the SA-2 sample decreased by approximately 50%, whereas for the SA-1 sodium salt, the decrease was only 20% because of its saltlike nature. A weak endothermal effect was observed in the DTA curve at 115°C along with several exothermal effects at 370, 460, and 500°C.

On the basis of the thermal analyses, we concluded that the sodium salts of SA-1 and SA-2 had thermal

stability similar to that of the sodium salts of *N*-SAs obtained from model BSNO.

The sodium salts of *N*-SAs obtained from BSNO were used as brighteners in cyanide-less zinc electrolytes. Sodium salts were found to increase the scattering ability and widen the range of the current density of electrolytes²¹ like the salts of *N*-SAs obtained from NO-GWR.

The chemical transformation of waste rubber articles into nitro oligomers and salts of oligosulfonic acids, which are of practical interest, is an effective method for their utilization.

CONCLUSIONS

Sodium salts of SA-1 and SA-2 were prepared from NO-GWR by a treatment with sodium hydroxymethane sulfonate in an aqueous-alkali solution from 40 to 60°C for reaction times of 3.5–5.5 h with mass ratios of 1.0:0.3–0.4. SA-2 was isolated from its sodium salt by ion exchange.

The main reaction centers of NO-GWR, with respect to sodium hydroxymethane sulfonate, were α -H atoms at carbon atoms bonded to nitro groups, which were partially substituted by sulfomethylate groups. The partial transformation of the nitro groups into sulfaminato ones was observed at 80°C or lower.

The sodium salts of the obtained *N*-SAs were proved to be polyfunctional and to have functional compositions and thermal stabilities similar to those of sodium salts prepared from model BSNO based on Bulex. The similarity between the functional compositions of the new sodium salts and those based on nitro oligomers based on elastomers proved the applicability of NO-GWRs as initial oligo derivatives for sulfomethylation.

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