

Syntheses, spectroscopic characterization, crystal structure and natural rubber vulcanization activity of new disulfides derived from sulfonyldithiocarbimates



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HIGHLIGHTS

- Five novel sulfonyldithiocarbamate disulfides were synthesized and fully characterized.
- The disulfides were active as vulcanization accelerators for natural rubber.
- They provide mechanical properties similar or superior to those given by commercial accelerators.

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ABSTRACT

The compounds $(\text{Bu}_4\text{N})_2[(4\text{-R-C}_6\text{H}_4\text{SO}_2\text{N}=\text{CS}_2)_2]$ [Bu_4N = tetrabutylammonium cation; R = H (**1**), F (**2**), Cl (**3**) and Br (**4**)] and $(\text{Ph}_4\text{P})_2[(4\text{-R-C}_6\text{H}_4\text{SO}_2\text{N}=\text{CS}_2)_2]\cdot\text{H}_2\text{O}$ [Ph_4P = tetraphenylphosphonium cation and R = I (**5**)] were synthesized by the reaction of the potassium dithiocarbimates $(4\text{-R-C}_6\text{H}_4\text{SO}_2\text{N}=\text{CS}_2\text{K}_2\cdot 2\text{H}_2\text{O})$ with I_2 and Bu_4NBr or Ph_4PCl . The IR data were consistent with the formation of the dithiocarbimato-disulfides anions. The NMR spectra showed the expected signals for the cations and anions in a 2:1 proportion. The structures of compounds **1–5** were determined by the single crystal X-ray diffraction. The compounds **2**, **3** and **4** are isostructural and crystallise in the centrosymmetric space group C2/c of the monoclinic system. Compound **1** crystallises in the monoclinic system in the space group of P2₁/n and the compound **5** crystallises in the centrosymmetric space group P-1 of the triclinic system. The complex anions of compounds **2**, **3** and **4** exhibit similar conformations having twofold symmetry, while in **1** and **5** the anions exhibit C₁ symmetry. The activity of the new compounds in the vulcanization of the natural rubber was evaluated and compared to the commercial accelerators ZDMC, TBBS and TMTD. These studies confirm that the sulfonyldithiocarbimato disulfides anions are new vulcanization accelerators, being slower than the commercial accelerators, but producing a greater degree of crosslinking, and scorch time values compatible with good processing safety for industrial applications. The mechanical properties, stress and tear resistances were determined and compared to those obtained with the commercial accelerators.

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1. Introduction

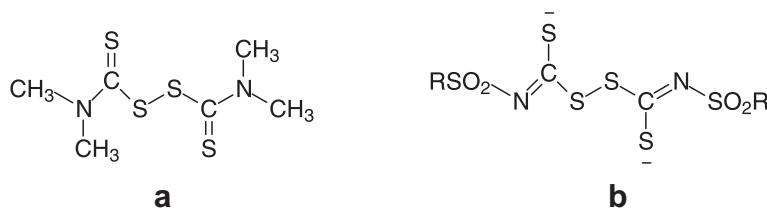
Global rubber demand is expected to rise 4.3% per year through 2015, strongly stimulated by the increase in tyre output, accelerated by the vehicle industry growth [1]. In 2012 the world rubber consumption achieved 25,869 thousand tons, from which 10,942 thousand tons consisted of natural rubber (Source: Malaysian

Rubber Board, Natural Rubber Statistics, International Rubber Study Group – IRSG), produced mainly by Thailand, Indonesia and Malaysia.

Epidemiologic studies have reported excess of cancers of different types among rubber products workers. This segment makes use of a wide variety of substances (vulcanizing agents, accelerators, colorants, solvents, etc.) from different chemical classes [2,3] some of which are potentially carcinogenic. Among these substances the vulcanization accelerators are notable for being frequently used in such production process. Accelerators are

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Scheme 1. Tetramethylthiuran disulfide (TMTD) (a) and sulfonyldithiocarbamate disulfide dianion (b).

responsible for controlling the time of crosslinks formation in the elastomer and to provide certain properties. Some of these substances are secondary amines or amines precursors and, as such, are potential producers of N-nitrosamines, compounds formed by the reaction of secondary amines with NO_x to give substances with carcinogenic effects [4–7]. In recent years the nitrosamines forming substances found in rubber products have received increasing attention because of the threat they present to human health and their ability to induce the formation of tumors at different sites in the body, even at low concentrations.

Tetramethylthiuran disulfide (TMTD) (Scheme 1) is known as an ultra-accelerator due to the promotion of a high vulcanization rate [8]. However, the use of this accelerator can result in the formation of nitrosamines during the vulcanization process [9]. In addition, during manipulation of this compound one must avoid skin contact, breathing and inhalation, as it causes nose and throat irritation.

We have previously described that zinc complexes with dithiocarbamate ligands are active as vulcanization accelerators [10,11]. We became interested in the syntheses and characterization of other dithiocarbamate derivatives such as the sulfonyldithiocarbamate disulfides due to their similarities with tetramethylthiuran disulfide. However, in this case the formation of nitrosamines can be avoided, as the sulfonyldithiocarbamate disulfides are derived from sulfonamides and therefore secondary amines will not be released during the vulcanization process.

This work describes the syntheses, characterization and the rubber vulcanization activity of dithiocarbamate disulfides derived from sulfonamides with the formulae (Bu₄N)₂[(4-R-C₆H₄SO₂N=CS₂)₂] [Bu₄N = tetrabutylammonium cation; R = H (1), F (2), Cl (3) and Br (4)] and (Ph₄P)₂[(4-I-C₆H₄SO₂N=CS₂)₂]·H₂O [Ph₄P = tetraphenylphosphonium cation] (5). The new compounds were characterized by high-resolution mass spectrometry (HRMS), IR, ¹H and ¹³C NMR spectroscopies. Additionally, the structures of the compounds 1–5 were determined by X-ray diffraction techniques.

Standard compositions of natural rubber (NR) with the compounds 1–5 were studied for their rheometric parameters, and the mechanical properties tensile strength, elongation at break and tear resistance of the vulcanized rubber were determined. These results were compared to those obtained with the commercial accelerators ZDMC (Zinc dimethyldithiocarbamate), TBBS (*N-tert*-butylbenzothiazolesulfenamide) and TMTD (tetramethylthiuran disulfide).

2. Experimental

2.1. Materials and methods

The solvents were purchased from Vetec and used without purification. 4-Fluorobenzenesulfonyl chloride, 4-iodobenzenesulfonyl chloride, benzenesulfonamide, 4-chlorobenzenesulfonamide, 4-bromobenzenesulfonamide, tetraphenylphosphonium chloride and tetrabutylammonium bromide were purchased from Sigma–Aldrich. Carbon disulfide, iodine and potassium hydroxide

were purchased from Vetec. Melting points (m.p.) were determined with a Microquímica MQAPF301 equipment, without correction. 4-Fluorobenzenesulfonamide and 4-iodobenzenesulfonamide were prepared from the parent sulfonyl chlorides by a previously described method [12]. The N-R-sulfonyldithiocarbamate potassium salts dihydrate (R-SO₂N=CS₂K₂·2H₂O) were prepared from the sulfonamides as described in the literature [13–16]. Mass spectra were recorded on a Shimadzu LCMS-IT-TOF mass spectrometer. The IR spectra were recorded with a Perkin–Elmer FT-IR 1000 infrared spectrometer using CsI or KBr pellets. The ¹H (300 MHz) and ¹³C (75 MHz) NMR spectra were recorded with a Varian Mercury 300 spectrophotometer with TMS as internal standard in CDCl₃, except for the spectra of 5 which were recorded in DMSO-*d*₆.

2.2. Syntheses

The disulfides were prepared by a variation of the methodology proposed in the literature for the synthesis of (Ph₄As)₂[(4-Cl-C₆H₄-SO₂N=CS₂)₂], where Ph₄As = tetraphenylarsonium cation [17].

A solution of iodine (5.0 mmol) in ethyl acetate (10 mL) was added to a suspension of the appropriate potassium N-R-sulfonyldithiocarbamate (10.0 mmol) in ethyl acetate (10 mL). The mixture was stirred at room temperature for 20 min. Tetrabutylammonium bromide (for 1–4) or tetraphenylphosphonium chloride (for 5) (10.5 mmol) was slowly added and the mixture was placed in an ice bath and stirred for further 20 min. The yellow solids obtained were filtered, washed with distilled water, ethanol, diethyl ether (5 × 10 mL) and dried under reduced pressure yielding the sulfonyldithiocarbamatodisulfides 1–5 (ca. 80%). Appropriate crystals for X-ray diffraction experiments were obtained by recrystallization in acetone:water 1:1 mixture. The synthetic route is shown in Scheme 2.

2.2.1. Tetrabutylammonium N-(phenylsulfonyl)-dithiocarbamatodisulfide (1)

IR (most important bands) (cm⁻¹): 1401 ν(C=N), 1281 ν_{as}(SO₂), 1146 ν_s(SO₂), 914 ν_{as}(CS₂). ¹H NMR (300 MHz, CDCl₃) (δ): 0.93 (t, ³J_{H4'-H3'} = 7.5 Hz, 24H, H4'), 1.39 (sext, ³J_{H3'-H4'} = ³J_{H3'-H2'} = 7.5 Hz, 16H, H3'), 1.55–1.73 (m, 16H, H2'), 3.20–3.35 (m, 16H, H1'), 7.28–7.40 (m, 6H, H3, H4, H5), 7.93–8.05 (m, 4H, H2, H6). ¹³C NMR (75 MHz, CDCl₃) (δ): 13.75 (C4'), 19.72 (C3'), 24.14 (C2'), 59.04 (C1'), 127.42 (C2, C6), 127.77 (C3, C5), 130.26 (C4), 143.63 (C1), 198.09 (C7). HRMS: Calcd for C₁₄H₁₀N₂O₄S₆²⁻: m/z = 230.9483; Found: m/z = 230.9458. HRMS: Calcd for C₁₆H₃₆N⁺: m/z = 242.2848; Found: m/z = 242.2822. M.p. 130.8–131.5 °C.

2.2.2. Tetrabutylammonium N-(4-fluorophenylsulfonyl)-dithiocarbamatodisulfide (2)

IR (most important bands) (cm⁻¹): 1398 ν(C=N), 1269 ν_{as}(SO₂), 1141 ν_s(SO₂), 915 ν_{as}(CS₂). ¹H NMR (300 MHz, CDCl₃) (δ): 0.96 (t, ³J_{H4'-H3'} = 7.5 Hz, 24H, H4'), 1.41 (sext, ³J_{H3'-H4'} = ³J_{H3'-H2'} = 7.5 Hz, 16H, H3'), 1.62–1.73 (m, 19H, H2' + H₂O), 3.22–3.37 (m, 16H, H1'), 6.95–7.07 (m, 4H, H3, H5), 7.93–8.07 (m, 4H, H2, H6). ¹³C

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