

# Bis(diisopropyl)thiophosphoryl Sulfides in Vulcanization Reactions

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## Synopsis

A synergistic combination of bis(diisopropyl)thiophosphoryl disulfide, dimorpholyl disulfide, and sulfur is used to produce an efficient vulcanizing system for a range of rubbers. This produces vulcanizates with the exceptional thermal and thermal-oxidative stability characteristic of sulfur donor vulcanizates and the rapid and extensive crosslinking reaction normally associated with a conventional sulfur-accelerator combination. A pronounced induction period is noted. The crosslinks initially produced in *cis*-1,4-polyisoprene rubbers are predominantly polysulfide but reduce to mono- and disulfides at optimum and extended cures. The crosslinks of the ethylene-propylene terpolymer and the styrene-butadiene vulcanizates are initially mainly disulfide but are rapidly reduced to monosulfides at the high curing temperatures (180°C) used. A comparison with vulcanization systems based on tetramethylthiuram disulfide and bis(diisopropyl)thiophosphoryl tri- and tetrasulfides as sulfur donors and with a conventional cyclohexylbenthiazol-2-sulfenamide-sulfur combination, respectively, shows it to have distinct advantages.

## INTRODUCTION

Bis(diisopropyl)thiophosphoryl disulfide (DIPDIS), when used as a sulfur donor for the vulcanization of *cis*-1,4-polyisoprene, has been shown to produce a simple network structure that exhibits high thermal and thermal-oxidative stability due to the formation of zinc diisopropyldithiophosphate *in situ*.<sup>1</sup> The level of physical properties, however, is low and the time required to reach optimum modulus is longer than that for conventional systems. The incorporation of dimorpholyl disulfide (DMDS) produces a synergistic combination with the DIPDIS which results in a considerable improvement in both the rate of vulcanization and the quality of the vulcanizate.<sup>2</sup> The decomposition products produced when DMDS is used to vulcanize *cis*-1,4-polyisoprene have been shown to include sulfur and secondary alkylamine,<sup>3-5</sup> and it is suggested that the synergism exhibited by the combined DMDS, DIPDIS, and sulfur donors is due to the two effects of the cleavage of the thiophosphoryl disulfide bond promoted by the base and the use of the free sulfur for additional crosslinking.

This paper describes the exploitation of the DMDS-DIPDIS combination by the addition of elemental sulfur, thus converting it from a sulfur donor to an accelerated sulfur vulcanization process. Its evaluation involves the characterization of the vulcanization reaction and of the network structure produced. These are then compared with those of conventional and allied systems.

## EXPERIMENTAL

### Synthesis of Bis(diisopropyl)thiophosphoryl Trisulfide (DIPTRI)<sup>5-7</sup>

A solution of sodium diisopropyldithiophosphate (236 g) in distilled water (472 g) was cooled in ice to 5°C, and sulfur dichloride (31.4 ml) was added to the stirred solution at such a rate that the temperature remained below 10°C. The resulting yellow oil was dissolved in ether, separated from the aqueous layer, dried, and the ether removed by rotary film evaporation. Two hundred grams of a light green oil remained, yield 87% theory.

ANAL. Carbon found 31.6% (calculated 31.44%); hydrogen found 6.3% (calculated 6.11%); sulfur found 37.1% (calculated 34.9%). Infrared spectra, CsI disk, maxima ( $\text{cm}^{-1}$ ) at 2990s, 2918s (C—H stretching), isopropyl group, 1465m, 1450m, doublet 1385s–1375s (C—H bending), 1180m, 1141m, 1100m, 1000s–970s (P—O—C stretching, mainly O—C); 890m, 800s, 780s (P—O—C stretching, mainly O—P), 645s (P=S stretching), doublet 530m, 510s (P—S stretching), 468m. Refractive index  $n_{25} = 1.542$ .

### Synthesis of Bis(diisopropyl)thiophosphoryl Tetrasulfide (DIPTET)<sup>5,6,8,9</sup>

A solution of sodium diisopropyldithiophosphate (236 g) in distilled water (472 ml) was cooled to 5°C, and sulfur monochloride was added slowly to keep the solution below 10°C. The resulting yellow oil was extracted with ether, dried, and the ether removed by rotary film evaporation. A yellow viscous oil (202 g) remained, yield 80% theory.

ANAL. Carbon found 29.1% (calculated 29.38%), hydrogen found 5.7% (calculated 5.71%), sulfur found 41.6% (calculated 39.2%). Infrared spectra CsI disk, maxima ( $\text{cm}^{-1}$ ) at 2990s, 2918s (C—H stretching), isopropyl group, 1465m, 1450m, doublet 1385s–1373s (C—H bending), isopropyl group, 1350m (C—H bending), 1180m, 1143m, 1100m, 1010s–965s (P—O—C stretching, mainly O—C), 890m, 800s (P—O—C stretching, mainly O—P), 645s (P=S stretching), doublet 535s 510s (P—S stretching), 470m. Refractive index  $n_{25} = 1.56$ –1.57.

### Other Sulfur Donors and Accelerators

Bis(diisopropyl)thiophosphoryl disulfide was synthesized as previously described.<sup>1</sup> Tetramethylthiuram disulfide (TMTD); cyclohexylbenzthiazyl sulfenamide (CBS), and dimorpholyl disulfide (DMDS) were supplied by Monsanto Ltd. and used without further purification.

### Preparation of Vulcanizates

The formulations shown in Tables I–IV were prepared on a water-cooled, two-roll mill. The *cis*-1,4-polyisoprene (Natsyn-2200) was first extracted with acetone under nitrogen for 48 hr, but the other elastomers were used without prior treatment. All compounded stocks were tested on a Monsanto rheometer. The maximum modulus ( $R_{\text{max}}$ ) was taken directly from the rheograph; the induction period ( $t_i$ ) and the first-order rate constant were obtained from rheometer data by plotting  $\log_{10} (R_{\text{max}} - R_t)$  against cure time<sup>10,11</sup> where  $R_t$  = modulus at time  $t$ . Vulcanized sheets, nominally  $4 \times 5 \times 0.1$  in. were prepared for network analysis using the temperatures and cure times shown in the tables. They were continuously extracted, in the dark, under nitrogen with an azeotropic boiling mixture

TABLE I  
Rheometer Data (160°C) for Various DIPDIS:DMDS Formulations<sup>a</sup>

DIPDIS	6.0	5.5	3.0	0.5	0
DMDS	0	0.27	1.63	2.9	3.2
$R_{\max}$ , in. lb	15	21	30	26	12
$t_i$ , min	22	18	17	26	—
$K$ , min <sup>-1</sup>	0.15	0.25	0.92	0.20	0.15

<sup>a</sup> Optimum codonor ratio of DIPDIS:DMDS. Natsyn, 100; zinc oxide, 5; stearic acid, 1.0.

TABLE II  
Formulation Used for Comparison of Different Vulcanization Systems<sup>a</sup>

	Formulation					
	a	b	c	d	e	f
DIPDIS	3	—	—	6	—	—
DMDS	1.63	—	—	—	—	—
Sulfur	0.5	—	2.5	—	—	—
TMTD	—	4	—	—	—	—
CBS	—	—	0.5	—	—	—
DIPTRI	—	—	—	—	6	—
DIPTET	—	—	—	—	—	6
Rheometer data						
$R_{\max}$ , in. lb	50	40	44	15	40	40
$t_i$ , min	6.3	0.5	5	17.5	—	0.5
$K$ , min <sup>-1</sup>	0.47	0.3	0.78	0.75	—	0.3

<sup>a</sup> Natsyn, 100; zinc oxide, 5.0; stearic acid, 1.0.

TABLE III  
Synthetic Rubbers Used in Activated DIPDIS Formulations<sup>a</sup>

Formulation	Polymer
g	Nordel 1040: EPDM du Pont Ltd.
h	Enjay 3509: EPDM Esso Ltd.
i	Intol 1500: SBR ISR Ltd.
j	Butaclor MC31: CR Distigul Ltd.
k	Krynac 801: BNR Polysar Ltd.
l	Butyl 100: IIR Polysar Ltd.

<sup>a</sup> Polymer, 100; zinc oxide, 5.0; stearic acid, 1.0; DIPDIS, 3.0; DMDS, 1.63; sulfur, 0.5.

TABLE IV  
SBR Formulations Used to Assess Probe Reaction Times<sup>a</sup>

Formulation	m	n	o
Sulfur	2.5	0.5	0
CBS	1	2.5	—
TMTD	—	—	4
Cure time (160°C), min	25	30	15
Predominant crosslinks	— $S_x$ —	$S_1 + S_2$	$S_1$

<sup>a</sup> SBR (Intol 1500) 100; zinc oxide, 5; stearic acid 1.

of acetone (352 ml), chloroform (291 ml), and methanol (274 ml) for 96 hr and then deswollen under vacuum to constant weight and stored at  $-20^\circ\text{C}$ . The use of this extraction solvent mixture has now been discontinued owing to the re-

ported base-catalyzed explosion hazard<sup>12</sup> and replaced by acetone (110 ml), methanol (42 ml), and 1,1,1-trichloroethylene (60 ml).

In the case of the *cis*-1,4-polyisoprene formulations, the number-average molecular weight ( $\bar{M}_n$ ) of the compounded rubber was determined from viscosity measurements immediately before vulcanization.<sup>1</sup>

### Chemical Analysis of Vulcanizates

The relative amounts of mono-, di-, and polysulfide crosslinks in *cis*-1,4-polyisoprene (IR) vulcanizates are shown in Table V and for the ethylene-propylene terpolymers (EPDM) and styrene-butadiene (SBR) vulcanizates in Table VI. They were determined by comparing their crosslink densities before and after treatment with the chemical probes propan-2-thiol and *n*-hexanethiol as previously described.<sup>1,15</sup> The crosslink densities were obtained from compression modulus measurements on swollen specimens. Before the analysis of styrene-butadiene rubber (SBR) vulcanizates could be attempted, the appropriate conditions for probe treatment were established as follows. The three formulations shown in Table IV were used to prepare vulcanizates having high concentrations of  $S_x$ ,  $S_2 + S_1$ , and  $S_1$  crosslinks, respectively. Two sets of samples of each of these vulcanizates were separately treated with solutions of propan-2-thiol and *n*-hexanethiol in *n*-hexane for a range of reaction times. The concentration of these solutions were the same as those used for natural rubber vulcanizates.<sup>13,14</sup> A range of reaction times were tried. They were then ex-

TABLE V  
Crosslink Composition of IR Vulcanizates from DIPDIS-DMDS-Sulfur (Formulation a)

Cure time, min	Crosslinks, %		
	— $S_x$ —	— $S_2$ —	— $S_1$ —
140°C			
23	100	—	—
60	43	34	23
100	35	25	40
160°C			
12	34	37	29
80	2	18	80

TABLE VI  
Crosslink Compositions of EPDM and SBR Vulcanizates (DIPDIS-DMDS-S)  
(Formulations g, h, i)

Polymer	Formulation	Cure time (180°C), min	Crosslinks, %		
			— $S_x$ —	— $S_2$ —	— $S_1$ —
EPDM (Nordel 1040)	g	10	13	88	0
		20	20	42	38
		40	0	4	96
EPDM (Enjay 3509)	h	10	22	78	4
		20	0	0	100
		60	0	6	100
SBR (Intol 1500)	i	3	17	80	3
		6	13	15	72
		40	4	1	95

tracted with acetone, swollen to equilibrium in benzene at 25°C, and the volume fraction of rubber in the swollen gel ( $\nu_r$ ) determined. It was shown that the probe reaction times required for  $\nu_r$  to become constant, i.e., when the complete cleavage of the appropriate crosslinks has been achieved, are 6 hr for propan-2-thiol and 30 hr for *n*-hexanethiol.

In the case of the EPT and SBR networks, no attempt was made to convert the value of  $M_{c,phys}$  (the physically manifested number-average molecular weight between crosslinks as determined from compression modulus data) to  $M_{c,chem}$ , the actual number-average molecular weight between crosslinks.

### Stress Relaxation

The thermal-oxidative ageing behavior of vulcanizates from formulations (a) through (f) at various cure times and temperatures were assessed by determining the degree of continuous stress relaxation in air at 120°C using the Wallace age tester.<sup>16</sup>

## RESULTS AND DISCUSSION

The rheometer data recorded in Table I show that the fastest rate of cure and the maximum crosslink density are obtained when an equimolar ratio of DIPDIS and DMDS is used. It was therefore decided that this should be the basis for the DIPDIS-DMDS-sulfur accelerator system. To maintain the monosulfide structure and give the good aging characteristics exhibited when DIPDIS is used as a sulfur donor,<sup>1</sup> the minimum amount of sulfur (0.5 phr) concomitant with the required increase in cure rate and crosslink density was used. The rheometer data obtained when vulcanizing this formulation are shown in Table II where they are compared with those obtained using TMTD, DIPTRI, or DIPTET as sulfur donors and with a conventional high-sulfur accelerator (S, 2.5; CBS, 0.5) formulation. The DIPDIS-DMDS-sulfur mixture is shown to produce the highest crosslink density, a cure rate that is only exceeded by the CBS-S formulation and a very substantial induction period that places it well within the "delayed action" accelerator category. This is further illustrated by the rheograph shown in Figure 1 which also shows that it has the outstanding thermal stability characteristic of a TMTD vulcanizate without its disadvantages of short induction period and low crosslink density. A comparison of the curing characteristics of the thiophosphoryl di-, tri-, and tetrasulfides, when used as sulfur donors for *cis*-1,4-polyisoprene, is shown in Figure 2 and once again demonstrates the crosslink stability of the vulcanizate. The increasing number of sulfur atoms in the thiophosphoryl compounds produces much faster rates and higher levels of cure. Analyses of the DIPTRI and DIPTET show a higher sulfur content than required for the tri- and tetrasulfide structures, respectively, and there may be some free sulfur present which would explain their higher reactivity. DIPTET is obviously a more effective and safer sulfur donor than TMTD. Examination of the crosslink composition of *cis*-1,4-polyisoprene cured with various sulfur donors shown in Table VII explains their high thermal stabilities as they are all predominantly monosulfide. The thermal stability of the DIPDIS-DMDS-S-IR vulcanizates, however, is not so apparent as there is a significant amount of polysulfide crosslinks (Table V) even at an advanced stage of cure. The presence

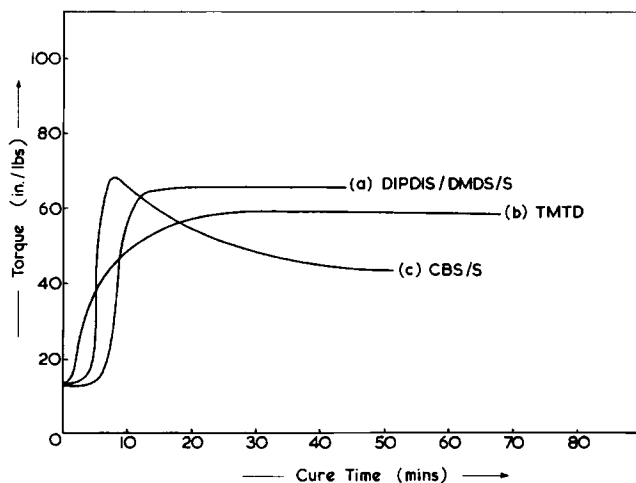


Fig. 1. Monsanto rheographs for formulations a, b, and c cured at 160°C.

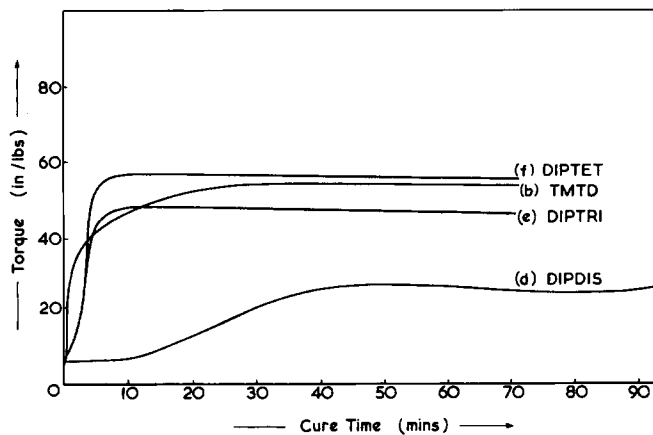


Fig. 2. Monsanto rheographs for formulations b, d, e, and f cured at 160°C.

TABLE VII  
Crosslink Composition of *cis*-1,4-Polyisoprene Vulcanizates Prepared From DIPTRI and DIPTET (IR)

S Donor	Cure time (160°C), min	Crosslinks, %		
		—S <sub>x</sub> —	—S <sub>2</sub> —	—S <sub>1</sub> —
DIPTRI (e)	6	16	19	65
	80	0	17	83
DIPTET (f)	8	0	21	79
	80	0	37	63

of zinc diisopropyldithiophosphate (ZDP) known to be formed *in situ* during vulcanization reactions involving DIPDIS<sup>1</sup> confers thermal-oxidative stability, but its contribution to the thermal stability is uncertain. The preponderance of the combined thermally stable mono- and disulfidic crosslinks is probably responsible.

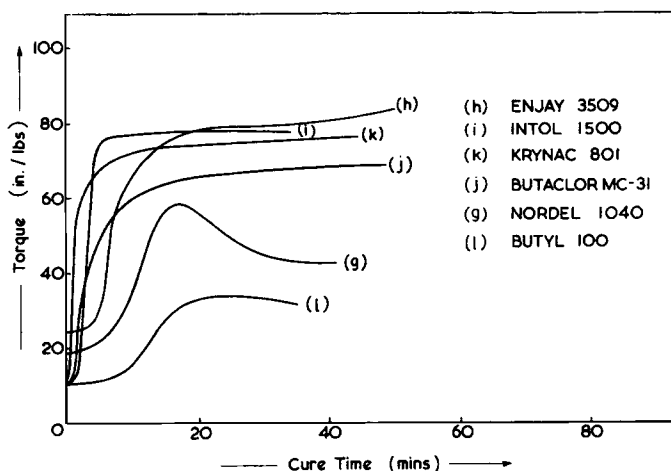


Fig. 3. Monsanto rheographs for formulations g, h, i, j, k, and l cured at 180°C.

The applicability of the DIPDIS-DMDS-S vulcanizing systems to the range of synthetic rubbers shown in Table III is demonstrated by the rheograph in Figure 3. A common formulation has been used for all the synthetic rubbers, and no attempt has been made to find the most effective ratio of DIPDIS-DMDS-S or the most effective concentration of this mixture in each case. Despite this, it can be seen that even at the very high vulcanizing temperature used (180°C), the elastomers based on the ethylene-propylene-norbornene (Enjay-3509), styrene-butadiene (Intol 1500), butadiene-acrylonitrile (Krynac 801), and chloroprene (Butachlor MC-31) showed satisfactory rates and levels of crosslinking and very high resistance to reversion. Both the isobutylene-iso-

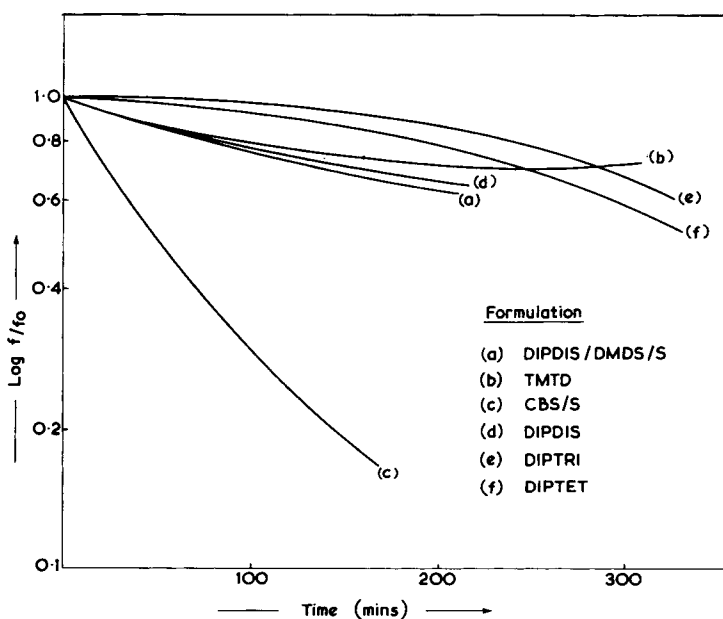


Fig. 4. Continuous stress relaxation of *cis*-1,4-polyisoprene vulcanizates in air at 120°C.

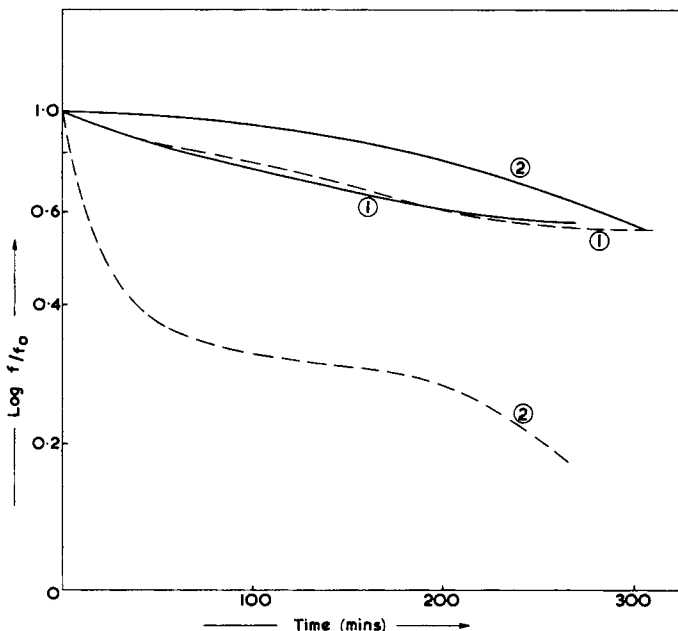


Fig. 5. Continuous stress relaxation behavior of *cis*-1,4-polyisoprene vulcanizates in air at 120°C before and after acetone extraction: (1) DIPDIS/DMDS/S; (2) DIPTET; (—) unextracted; (---) extracted.

prene (Butyl 100) and ethylene-propylene-hexadiene-1,4(Nordel 1040) rubbers were however quite unsatisfactory. The crosslink composition of Nordel, Intol, and Enjay vulcanizates at various stages of cure at 180°C are shown in Table VI. The relative thermal-oxidative stabilities of the networks is shown in Figure 4 which depicts the continuous stress relaxation, in air, at 120°C of unextracted *cis*-1,4-polyisoprene vulcanizates prepared from the formulations of (a) through (f) given in Table II. The oxidation of TMTD, DIPDIS-DMDS-S, and DIPDIS vulcanizates is slightly autoinhibitive, while that of the DIPTRI and DIPTET sulfur donor vulcanizates is autocatalytic. They are all very superior to the conventional CBS-S vulcanizate (c). Extraction of the DIPDIS-DMDS-S vulcanizate has very little effect upon its rate of thermal-oxidative degradation (Fig. 5), but extraction of vulcanizates prepared from DIPTET obviously removes some protective material.

## CONCLUSIONS

A 1:1 molar ratio of DIPDIS:DMDS with a small addition of sulfur produces a very useful vulcanization system for *cis*-1,4-polyisoprene. It has a pronounced induction period, a fast rate of vulcanization, a high level of crosslinking, and good resistance to thermal and thermal-oxidative aging. The crosslink structure is predominantly monosulfide at high curing temperatures (160°C) but retains approximately equal amounts of mono-, di-, and polysulfide crosslinks at lower curing temperatures (140°C). As the physical properties are, to some extent, dependent upon the crosslink structure vulcanizates suitable for a wide range of service requirements can be produced. It has further been shown that the



DIPDIS-DMDS-S system can be used for a variety of synthetic rubbers including EPDM, SBR, CR, and BNR although it is unsuitable, at the concentration used, with IIR or with EPDM elastomers containing hexadiene-1,4 as the unsaturated termonomer. Because of their resistance to reversion and the delayed-action characteristics of this accelerator system, high vulcanization temperatures can be used ( $>180^{\circ}\text{C}$ ), and this increases the rate of cure to very acceptable levels.

Although the use of DIPDIS on its own as a sulfur donor is impracticable for vulcanizing *cis*-1,4-polyisoprene, the tri- and tetrasulfides (DIPTRI and DIP-TET) rapidly produce networks with a high density of monosulfide crosslinks giving vulcanizates of high thermal and thermal-oxidative stability.

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