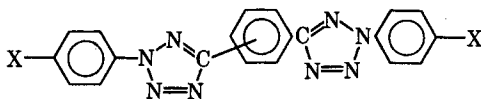


**Ditetrazoles as Crosslinking Agents****INTRODUCTION**

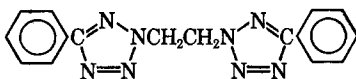
Several examples of the use of 1,3-dipolar cycloaddition reactions for crosslinking unsaturated elastomers have been reported recently.<sup>1-6</sup> The thermal elimination of nitrogen from ditetrazoles to form dinitriline 1,3-dipoles for curing unsaturated elastomers was claimed in a patent,<sup>1</sup> but since no examples of the use of these materials were given, we have synthesized and evaluated several ditetrazoles some of which have not been reported before.

**EXPERIMENTAL****Materials**

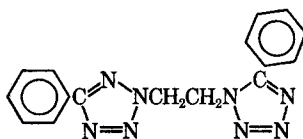
The method of Stille and Gotter<sup>7</sup> was used for the preparation of the ditetrazoles 1 to 4. The ditetrazole 5, along with its isomer 6, was prepared by coupling the potassium salt of 5-phenyl tetrazole<sup>8</sup> with 1,2-dibromoethane:



1-4



5



6

where compounds 1 and 2 are *p*-phenylene, with X = H and Cl, respectively; and compounds 3 and 4 are *m*-phenylene, with X = H and Cl, respectively.

The ditetrazoles 5 and 6 were distinguished by their NMR spectra. The compound assigned structure 5 has a singlet at  $\delta$  5.44 due to the ethylene protons, while the compound assigned structure 6 has a multiplet at  $\delta$  5.25 due to the ethylene protons. It has been shown that 2-alkyl substituents in tetrazoles resonate further downfield than 1-alkyl substituents.<sup>9</sup>

Table I gives the yields and melting points obtained for compounds 1 to 6. Satisfactory elemental analyses were obtained for all new compounds.

Polymers used were Solprene 300 (solution SBR), Taktene 1220 (solution BR) and Ameripol SN (solution IR).

**Compounding and Testing**

Black was added to the polymers in a 220-g laboratory internal mixer. Curing ingredients were added on a 3 in.  $\times$  6 in. laboratory mill.

The stress-strain properties were measured on size C ASTM dumbbells in an Instron tensile tester at a cross-head speed of 20 in./min at 25°C. Strain was measured by observing the separation of 1-in. bench marks.

TABLE I

Ditetrazole	Yield, %	Melting point, °C
1	70	220–222 (decomp) <sup>a</sup>
2	85	250–252 (decomp)
3	37	160–168 (decomp) <sup>b</sup>
4	31	212–213 (decomp)
5	29	202–203 (decomp) <sup>c</sup>
6	8.5	112–113 <sup>d</sup>

<sup>a</sup> Lit. mp 220–225° (decomp).<sup>9</sup>

<sup>b</sup> Lit. mp 162–165° (decomp).<sup>9</sup>

<sup>c</sup> HR-220 NMR (DMSO-d<sub>6</sub>)  $\delta$  5.44 (s, 2);  $\delta$  7.53 (m, 3);  $\delta$  7.98 (m, 2).

<sup>d</sup> HR-220 NMR (DMSO-d<sub>6</sub>)  $\delta$  5.25 (m, 2);  $\delta$  7.63 (m, 5).

The rheometer curves were obtained from a Monsanto oscillating disc rheometer with  $\pm 3^\circ$  arc.

Crosslink densities were obtained by the swelling method of Kraus.<sup>10</sup>

## RESULTS

### Types of Elastomers Cured by Ditetrazoles

It was found that ditetrazoles would not cure all unsaturated polymers. Of the types of polymers tried with ditetrazoles, only solution-polymerized polybutadiene, polyisoprene, and SBR were cured, and the levels of cure of the solution BR and IR were not very high (Fig. 1). The corresponding emulsion polymers and natural rubber did not cure with the ditetrazoles. It was determined that the presence of fatty acids or their salts inhibited the cure of SBR by ditetrazoles, thus no cure was obtained with solution

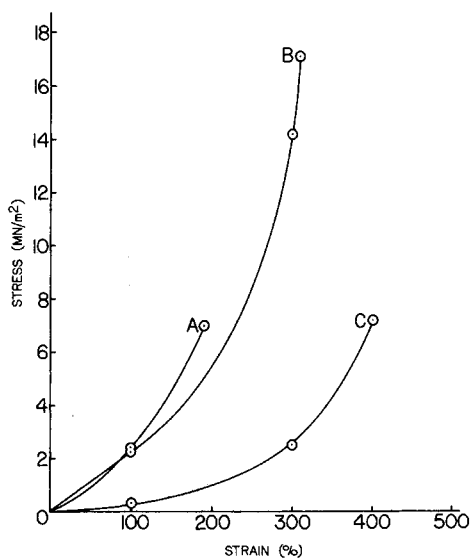


Fig. 1. Stress-strain curves for elastomers cured with ditetrazole 4 for 40 min at 180°C: (A) Taktene 1220; (B) Solprene 300; (C) Ameripol SN. Elastomer, 100; HAF, 50; 4, 2.

SBR when stearic acid or zinc stearate was added to the compound. Cures were not obtained with the low-unsaturation rubbers Butyl 101 and EPDM.

#### Effect of Structure of Ditetrazole on Cure Rate

The rates of cure of a solution SBR with the various ditetrazoles prepared were measured by means of the Monsanto rheometer. As can be seen from Figure 2, the two *m*-phenyleneditetrazoles, 2,2'-diphenyl-5,5'-*m*-phenyleneditetrazole (**3**) and 2,2'-bis(4-chlorophenyl)-5,5'-*m*-phenyleneditetrazole (**4**), give higher rates of cure and higher cure levels than the two *p*-phenyleneditetrazoles 2,2'-diphenyl-5,5'-*p*-phenyleneditetrazole (**1**) and 2,2'-bis(4-chlorophenyl)-5,5'-*p*-phenyleneditetrazole (**2**). Table II, which gives the stress-strain properties and crosslink densities of Solprene 300 cured with ditetrazoles **1** to **4**, shows the same effect.

The ditetrazole **4** gave both the highest rate and level of cure; 5,5'-diphenyl-2,2'-dimethyleneditetrazole (**5**) was ineffective in curing solution SBR at 180°C. Alkyl substitution in the 2-position of 2,5-disubstituted tetrazoles is known to raise the decomposition temperature of these compounds above that of the 2-aryl-substituted compounds,<sup>11</sup> and this may account for the failure of **5** to crosslink SBR.

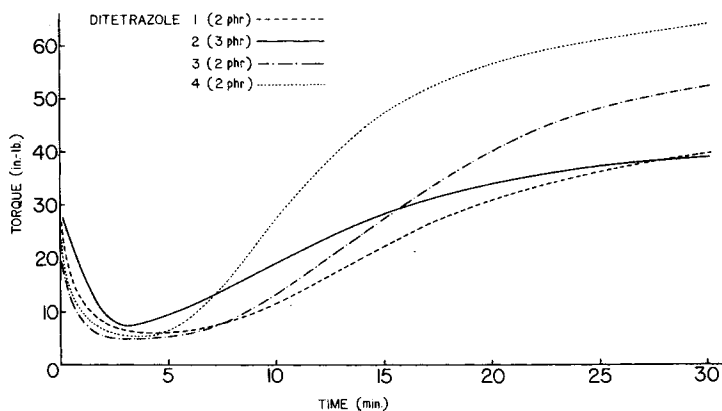


Fig. 2. Rheometer curves for Solprene 300 cured with various ditetrazoles at 180°C. Solprene 300, 100; FEF, 50; ditetrazole as indicated.

TABLE II  
Properties of SBR Cured With Various Ditetrazoles<sup>a</sup>

	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
Amount of ditetrazole, phr	2	3	3	2
Cure time, min	30	30	30	20
Cure temperature, °C	190	190	190	190
Modulus, MN/m <sup>2</sup>				
100%	1.8	2.7	1.5	2.7
300%	8.5	13.0	5.0	14.0
500%	—	—	8.5	—
Tensile strength, MN/m <sup>2</sup>	13	14	9	16
Elongation at break, %	410	310	550	250
Crosslink density, (moles/cm <sup>-3</sup> ) × 10 <sup>4</sup>	1.0	1.7	0.5	1.9

<sup>a</sup> Solprene 300; 100; FEF, 50; ditetrazole, various.

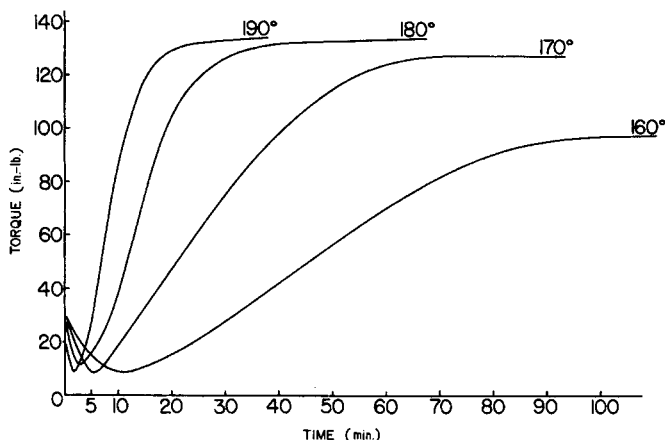


Fig. 3. Effect of temperature on rate of cure. Solprene 300, 100; FEF, 50; 4, 2. Cure temperature as indicated.

From Figure 3, which shows the rheometer curves for solution SBR cured with 4 at various temperatures, it can be seen that a reasonable rate of cure is achieved only at 180°C.

#### Effect of the Amount of Ditetrazole 4 on Cured Properties

Solprene 300 was compounded with 50 phr FEF black and various amounts of the ditetrazole 4 and cured at 180°C. From Figure 4 it can be seen that the highest strength is achieved with 2 to 2.5 phr of 4. With larger amounts of 4, the cured slab was quite porous and therefore had lower strength.

#### Effect of Blacks on Ditetrazole Cures

The stress-strain curves for solution SBR loaded with FEF, HAF, and ISAF blacks and cured with 2 phr of 4 are shown in Figure 5. The FEF-loaded material shows the

TABLE III  
Effect of Antioxidant

Composition	100		50		2	
Solprene 300	100	100	100	100	100	100
HAF	50	50	50	50	50	50
4	2	2	2	2	2	2
Flexzone 7-L	—	2	—	—	—	—
Santowhite Powder	—	—	—	—	2	2
Cure time/temp., min/°C	40/180	40/180	40/180	40/180	40/180	40/180
Properties						
Modulus, MN/m <sup>2</sup>						
100%	3.8	2.8*	2.8	2.5*	3.7	2.1*
300%	20	16*	13	7.3*	18	—
Tensile strength, MN/m <sup>2</sup>	28	21*	24	17*	25	5.7*
Elongation, %	400	350*	460	430*	400	190*

\* Aged 48 hr at 100°C.

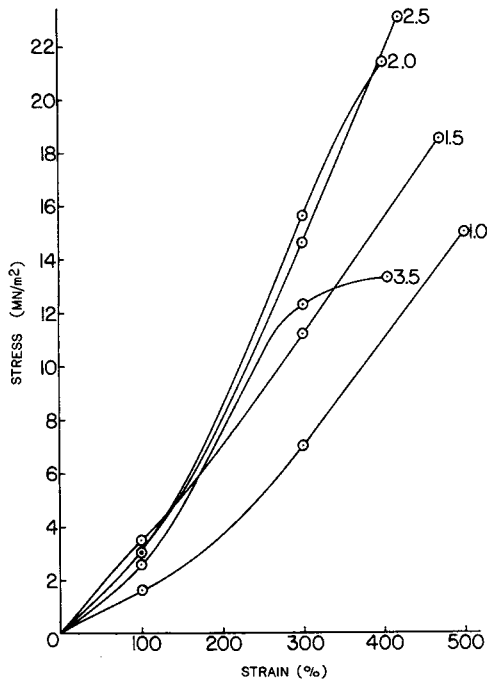


Fig. 4. Effect of the amount of 4 on stress-strain properties. Solprene 300, 100; FEF, 50; 4, as indicated. Cured 20 min at 180°C.

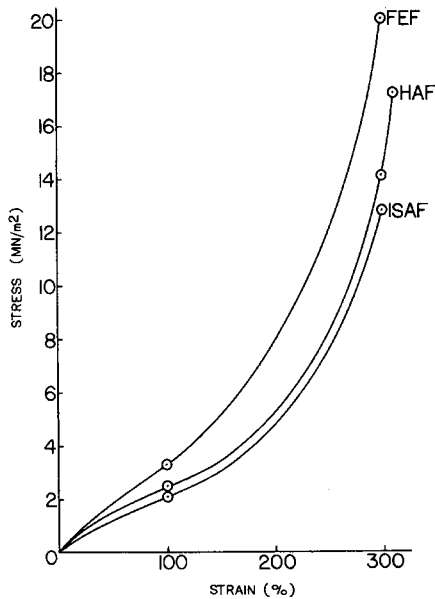


Fig. 5. Effect of various blacks on stress-strain properties. Solprene 300, 100; Black, 50; 4, 2. Cured 40 min at 180°C.

best properties and ISAF, the poorest. It was also observed that FEF-loaded stock showed a more rapid rate of cure on the rheometer than the HAF-loaded SBR.

#### Effect of Antioxidant

Addition of either a phenolic type of antioxidant, Santowhite Powder, or an aromatic amine type, Flexzone 7-L, had little effect on the initial physical properties of Solprene 300 cured with 4 compared with the control, which was an unextracted sample of Solprene 300 containing no further added antioxidant (Table III). On aging for 48 hr at 100°C, however, the properties of the specimen containing the phenolic type of antioxidant showed an unexpectedly large fall, while the properties of the specimen containing the amine antioxidant changed about the same extent as the control.

The author wishes to thank K. C. Edwards for technical assistance in preparing the ditetrazoles and D. R. Renton for supplying the physical testing results.

#### References

1. D. S. Breslow, Can. Pat. 813,931 (1969).
2. D. S. Breslow and M. Gardens, U.S. Pat. 3,390,204 (1968).
3. D. S. Breslow and M. Gardens, U.S. Pat. 3,504,017 (1970).
4. S. Nishita, J. Furukawa, and S. Yamashita, *Nippon Gomu Kyokaishi*, **43**, 307 (1970).
5. J. Hayashi, J. Furukawa, and S. Yamashita, *ibid.*, **43**, 313 (1970).
6. J. Hayashi, J. Furukawa, and S. Yamashita, *ibid.*, **43**, 358 (1970).
7. J. K. Stille and L. D. Gotter, *J. Polym. Sci. A-1*, **7**, 2493 (1969).
8. R. A. Henry, *J. Amer. Chem. Soc.*, **73**, 4470 (1951).
9. L. A. Lee and J. W. Wheeler, *J. Org. Chem.*, **37**, 348 (1972).
10. G. Kraus, *Rubber World*, **135**, 67 (1956).
11. R. Huisgen, *Angew. Chem. Int. Ed. English*, **2**, 570 (1963).

Norman V. Schwartz

Dunlop Research Centre  
Sheridan Park  
Ontario, Canada

Received May 18, 1972