

Tetramethylthiuram Disulfide and 2-Mercaptobenzothiazole as Binary Accelerators in Sulfur Vulcanization. II. Exchange Reactions Between the Accelerators and Their Zinc Salts in the Absence of Rubber

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SYNOPSIS

Exchange reactions between tetramethylthiuram disulfide, 2-mercaptobenzothiazole, and sulfur in the presence of ZnO were studied by heating powdered mixes to vulcanization temperatures at a preprogrammed rate in a DSC. The reaction was stopped at points along the thermal curve and the mixture was analyzed. Sulfide exchange reactions between the accelerators leads to a mixed accelerator and dimethyldithiocarbamic acid that is trapped by ZnO to give the zinc accelerator complex bis(dimethyldithiocarbamato)zinc (II). Exchange also occurs between the accelerators and ligands on both the thiuram and benzothiazole zinc accelerator complexes. Zinc complexes containing ligands of both accelerators were synthesized. These showed little interaction on being heated with sulfur, but on dissolution yielded a spectrum of products similar to that obtained in the other system containing zinc. Reactions to account for changes in the spectrum of products on heating different mixes of these curatives to different temperatures are discussed. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Combinations of accelerators are commonly used in industry, and in the first article¹ in this series we showed that in mixtures of the binary accelerator system tetramethylthiuram disulfide/2-mercaptobenzothiazole (TMTD/MBT) and sulfur, exchange reactions lead to the ready formation of the unsymmetrical accelerator *N,N*-dimethylthiocarbamylbenzothiazole disulfide (P2). Polysulfides of TMTD and P2 are also formed. These exchange reactions occur not only on heating mixes of curatives to vulcanization temperatures, but also on dissolving curatives in a solvent. Dimethyldithiocarbamic acid (Hdtmc), formed in the exchange, affects the product spectrum that changes at higher temperatures when Hdtmc is lost from the system. We now consider exchange reactions that occur in the system in the presence of ZnO.

EXPERIMENTAL

Sulfur CP from Halpro, TMTD, and MBTS from Orchem (South Africa), MBT from Monsanto, TMTU from Fluka, and TMTM (Vulkacit MS), Zn(mbt)₂ (Vulkacit ZM) and Zn₂(dmtc)₄ (Vulkacit L) from Bayer and ZnO from BDH, were used. Two zinc-accelerator complexes were prepared as described below and were analyzed by the techniques detailed earlier.¹

Aqueous tetra-*n*-butylammonium hydroxide (45 mL, 40%) and MBT (11.4 g) were reacted according to McCleverty et al.² to give tetra-*n*-butylammonium-benzothiazole-2-thiolate, [NBu₄⁺][C₇H₄NS₂⁻] (18.9 g). Zn₂(dmtc)₄ (3.6892 g, 0.0012 mol) and [NBu₄⁺][C₇H₄NS₂⁻] (4.9313 g, 0.0012 mol) were then reacted to give tetra-*n*-butylammonium(benzothiazole-2-thiolato)bis(dimethyldithiocarbamato) zincate, [NBu₄⁺][Zn(S₂CNMe₂)₂(C₇H₄NS₂)⁻] (0.7324 g, 0.00103 mol, 85%). Found: C 45.78, H 7.15, N 7.60%. Calculated: C 48.75, H 7.34, N 7.84%.

Aqueous tetra-*n*-butylammonium hydroxide (100 mL, 40%), CS₂ (11.9 g) and dimethylamine (DMA)

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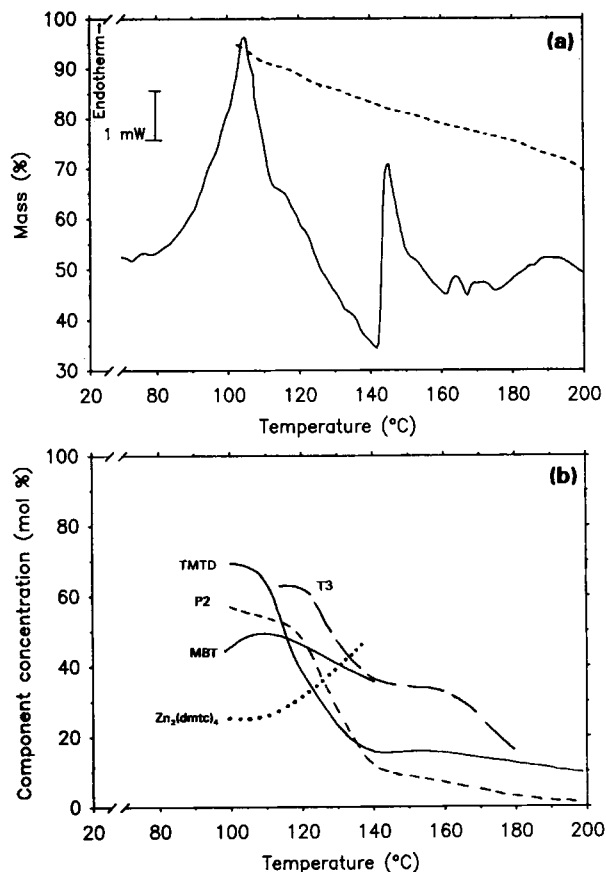


Figure 1 (a) TG(---), DSC curves and (b) HPLC analysis of TMTD(1)-MBT(1)-ZnO(1) heated at 5°C/min in sealed pans. Poor separation of TMTD and $Zn_2(dmte)_4$ above 140°C.

(28 mL, 25%) were reacted according to McCleverty and Morrison,³ a published procedure,⁶ to give tetra-*n*-butylammonium dimethylcarbamate, $[NBu^+][S_2CNMe_2]$ (55.1 g). Then $Zn(mbt)_2$ (3.0644 g, 0.0077 mol) and $[NBu^+][S_2CNMe_2]$ (2.8080 g, 0.0077 mol) were reacted² to give tetra-*n*-butylammonium bis(benzothiazole-2-thiolato)-(dimethyldithiocarbamate) zincate, $[NBu_4^+][Zn(S_2CNMe_2)(C_7H_4NS_2)_2]$ (5.1532 g, 0.0068 mol, 88%). Found: C 51.77, H 6.63, N 7.18%. Calculated: C 52.11, H 6.63, N 7.36%.

For zinc salts X-ray diffraction measurements were made using a Philips PW 1729 generator (40 kV, 30 mA) with a PW1840 diffractometer (CuK α radiation, 1.541 Å) and PW1840 diffractometer control. X-ray spectra were scanned at 0.02°2 θ /s, using a time constant of 5 s and slit of 0.2 mm between the angles of 7 and 80°2 θ . $Zn_2(dmte)_4$ and $Zn(mbt)_2$ were identified in solids by comparison with spectra obtained using the commercial mate-

rials as standards and the powder diffraction data file.

Interaction between curatives was studied by the heating samples in a DSC and products analyzed by HPLC as described earlier.¹

RESULTS AND DISCUSSION

TMTD-MBT-ZnO

In order to determine whether $Zn(mbt)_2$ forms in solution, a mixture of MBT(1)-ZnO(1) was added to a solvent mixture of 4 mL dichloromethane and 21 mL methanol, placed in an ultrasonic bath for 5 min at room temperature and the solid subsequently separated from the liquid. The solid was washed with methanol (3 \times 25 mL), dried under high vacuum, and X-ray analysis of the solid showed the presence of 13% $Zn(mbt)_2$ by mass. By comparison of the TG thermal curve for $Zn(mbt)_2$ with that of this solid, using O₂ as flow gas, the mass loss in the temperature region associated with the oxidative degradation of $Zn(mbt)_2$ showed the presence of 19% $Zn(mbt)_2$. Limited reaction had clearly occurred with the formation of a layer of $Zn(mbt)_2$ on the surface of ZnO particles inhibiting further reaction in solution.

A sample of TMTD(1)-MBT(1)-ZnO(1) was treated in a solvent in the same manner as the MBT-ZnO sample above. In a second sample, the powder mixture was heated in nitrogen atmosphere under ambient pressure at 150°C for 5 min. The X-ray and TG techniques showed the absence of $Zn(mbt)_2$ in both samples. The reason for this may reside in the exchange reactions of the type discussed below.

In a TMTD(1)-MBT(1)-ZnO(1) mixture (Fig. 1), mutual dissolution of the accelerators commences at 81°C, slightly earlier than in the absence of ZnO.¹ TG analysis shows that the sample starts to lose volatiles at much the same temperature as in the absence of ZnO. The DSC thermogram shows a broad endotherm followed directly by a broad exotherm, which is interrupted by a volatilization endotherm when the DSC pan bursts. (Instead of making a pinhole in the lid of the DSC pan to allow the escape of volatiles, the pressure was allowed to build up. This allowed the effect of volatiles on the reaction to be demonstrated.) Based on the mass of accelerators in the mix, the mass loss at 200°C is only about 36%, which is much less than that for the TMTD(1)-MBT(1) system. This is in agreement with the amine volatile evolution study of Tuan et al.⁴

Table I (Continued)

| Mixture | Temp (°C) | Component Concentration (mol %) | | | | | | | | | | | | | | | |
|----------------------------------|--------------|---------------------------------|------|------|----|----|----|------|-----|------|------|----|----|----|----|----|-----------------|
| | | S8 | TMTM | TMTD | T3 | T4 | T5 | TMTU | MBT | MBTM | MBTS | M3 | P1 | P2 | P3 | P4 | ZD ^a |
| [NBu ₄] ⁺ | 25 | 63 | | 26 | d | | | | 69 | | | | | | | | 73 ^d |
| [Zn(dmtc) ₂ | 117 | 76 | | 44 | d | | | | 73 | | | | | 8 | | | 57 ^d |
| (mbt)] ⁻ | 135 | 64 | | 42 | d | | | | 65 | | | | 10 | | | | 57 ^d |
| sulfur | 150 | 72 | | 28 | d | | | | 65 | | | 5 | 4 | | | | 70 ^d |
| | 160 | 76 | | 32 | d | | | | 69 | | | | 9 | | | | 69 ^d |
| | 180 | 63 | | 19 | d | | | | 66 | | | 5 | 2 | | | | 40 ^d |
| | 200 | 57 | | 3 | d | | | | 76 | 12 | | 9 | 1 | | | | 9 ^d |
| | 220 | 13 | | 1 | d | | | | 62 | 13 | 4 | 8 | | | | | |
| [NBu ₄] ⁺ | 25 | 83 | | 47 | d | 32 | | | 60 | | 8 | | 22 | | | | 38 ^d |
| [Zn(dmtc) | 120 | 78 | | 71 | d | 32 | 15 | | 55 | | 11 | | 19 | | | | 21 ^d |
| (mbt) ₂] | 150 | 77 | | 85 | d | | | | 66 | | 8 | | 10 | | | | 20 ^d |
| (1)- | 165 | 69 | | 95 | d | 17 | 22 | | 68 | | 6 | | 12 | | | | 22 ^d |
| sulfur(1) | 180 | 76 | | 72 | d | | | | 66 | | 4 | | 6 | | | | 19 ^d |
| | 200 | 46 | | 1 | d | | | | 88 | 18 | | 4 | 1 | | | | |

^a ZD = Zn₂(dmtc)₄.

^b Poor separation of MBT and Zn₂(dmtc)₄.

^c No separation of MBT and Zn₂(dmtc)₄.

^d No separation of T3 and Zn₂(dmtc)₄. Denoted as ZD.

^e No separation of MBT and TMTD. Denoted as TMTD.

HPLC analysis shows that the amount of P2 in the TMTD(1)-MBT(1)-ZnO(1) mixture heated to 100°C, is much higher than in the absence of ZnO, while the concentrations of TMTD and MBT are correspondingly lower (Fig. 1). As discussed in the previous article,¹ the exchange reaction between TMTD and MBT would lead to the formation of P2 and Hdmtc. Removal of the latter by reaction with ZnO⁵ would shift the equilibrium, increasing the yield of P2 and decreasing the amount of TMTD in solution. Problems were experienced in adequately separating MBT and Zn₂(dmtc)₄ on the HPLC and values are shown in Figure 1 only for those samples in which the peaks could be resolved to some extent. Trends in the concentrations of these species in the early stages of the thermal curve support the consumption of MBT and the formation of Zn₂(dmtc)₄.

Tetramethylthiuram trisulfide T3 also forms in rather high concentrations considering the absence of sulfur (Table I). However, unlike the TMTD(1)-MBT(1) and TMTD(1)-MBT(1)-sulfur(1) systems, in which it decomposes above 150°C, it persists to 180°C. On further heating, the TMTD, TMTP, and P2 concentrations decrease in sympathy as Zn₂(dmtc)₄ forms from Hdmtc and ZnO.⁵ P1 [presumably *N,N*-dimethylthiocarbonylbenzothiazole sulfide (DMTBS)],¹ would result from desulfuration of P2, while exchange between two P1 molecules would give 2-bisbenzothiazole-2,2'-monosulfide (MBTM) (and TMTM). As Hdmtc is trapped

by ZnO, TMTU forms in low concentration and only at 200°C.

The DSC thermogram of TMTD(1)-MBT(1)-ZnO(5) (Fig. 2) has the same general features as that for the mixture with 1 mol of ZnO, except that the dissolution/melting process is initiated later (89°C) than that with 1 mol of ZnO. This may be associated with poorer heat transfer in the presence of a large amount of ZnO powder. An exothermic reaction, accompanied by a 5% mass loss, occurs above 180°C. As in mixes without ZnO,¹ the thermal curve at higher temperatures is dependent on the temperature at which the pan bursts. As expected, the system shows a very small mass loss at 200°C, due to the ability of ZnO to trap Hdmtc. With 1 mol of ZnO, the mass loss was surprisingly high.

The product spectrum (Fig. 2 and Table I) of the mix shows good agreement with that for the 1 mol ZnO system. The persistence of TMTP at high temperatures is discussed below.

TMTD-MBT-Sulfur-ZnO

The melt/dissolution endotherm of TMTD(1)-MBT(1)-sulfur(1)-ZnO(1) (Fig. 3) occurs at about 80°C. Considering that both ZnO and sulfur lowered the mass loss of the TMTD-MBT mix, it is not unexpected that the mix containing both sulfur and ZnO should have the lowest mass loss of all mixes (16.8% at 200°C, expressed in terms of the

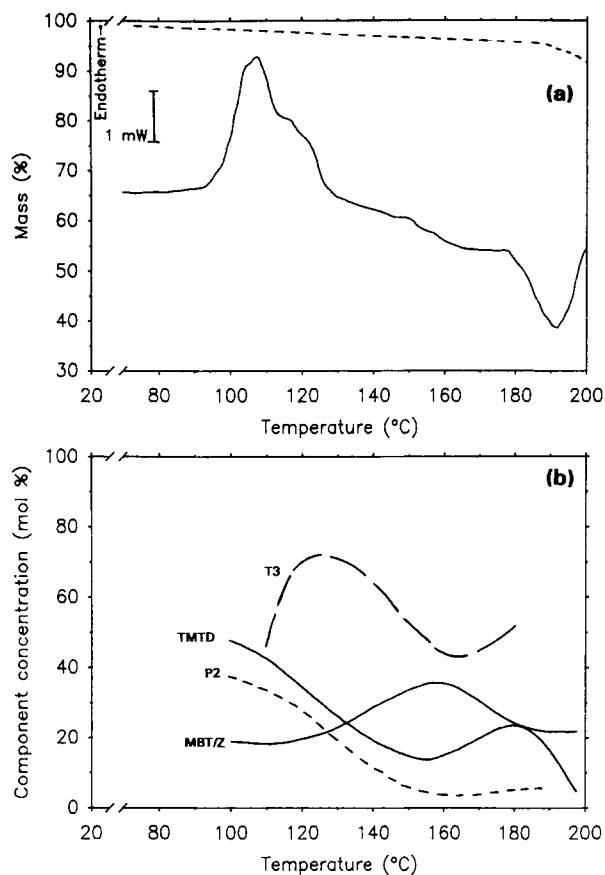


Figure 2 (a) TG (---), DSC (—) curves and (b) HPLC analysis of TMTD(1)-MBT(1)-ZnO(1) heated at 5°C/min in sealed pans. No separation of MBT and $Zn_2(dmtc)_4$, shown here as MBT/Z.

accelerator plus sulfur masses). As in all previous mixes, the start of mass loss coincides with the onset of the melt/dissolution endotherm.

As in the TMTD(1)-MBT(1)-ZnO(1) system, the concentration of P2 in a room temperature solution is high due to the removal of Hdmtc by ZnO (Fig. 1). The presence of free sulfur allows the ready formation of T3 even in the room temperature solution and on heating large amounts of TMTP and PP form (Table I). As in the TMTD(1)-MBT(1)-ZnO(1) system, the concentration of P2 decreases less rapidly at high temperatures. The free sulfur concentration decreases slightly at temperatures around 100° to 140°C when the concentrations of polysulfidic accelerator complexes are high. MBT and $Zn_2(dmtc)_4$ could not be separated in this experiment. X-ray analysis of the solid separated from an unheated TMTD-MBT-sulfur-ZnO mixture in a solution of 2 mL dichloromethane and 21 mL methanol showed the presence of small quantities of $Zn(mbt)_2$.

Zinc-Accelerator Complexes

Neither TMTD nor MBT undergo exchange reactions with the zinc-accelerator complexes. A methanol/dichloromethane (21/4 v/v) solution was added to a mixture of TMTD-Zn(mbt)₂ and placed in an ultrasonic bath for 5 min and allowed to stand for 19 h at room temperature. Little reaction occurred, only 3% $Zn_2(dmtc)_4$ being found in solution. Likewise, a methanol/dichloromethane (21/4, v/v) solution was added to a mixture of MBT- $Zn_2(dmtc)_4$, placed in an ultrasonic bath for 5 min, and allowed to stand for 90 h at room temperature. The remaining solid was filtered off and washed. X-ray analysis showed no $Zn(mbt)_2$ to be present.

The binary systems accelerator-sulfur, zinc salt-accelerator, and zinc salt-sulfur are stable in solution at room temperature, the latter also being stable on heating up to 200°C. This is in agreement with studies using radioactive sulfur.⁶ TMTD and sulfur form TMTP at vulcanization temperatures. Ex-

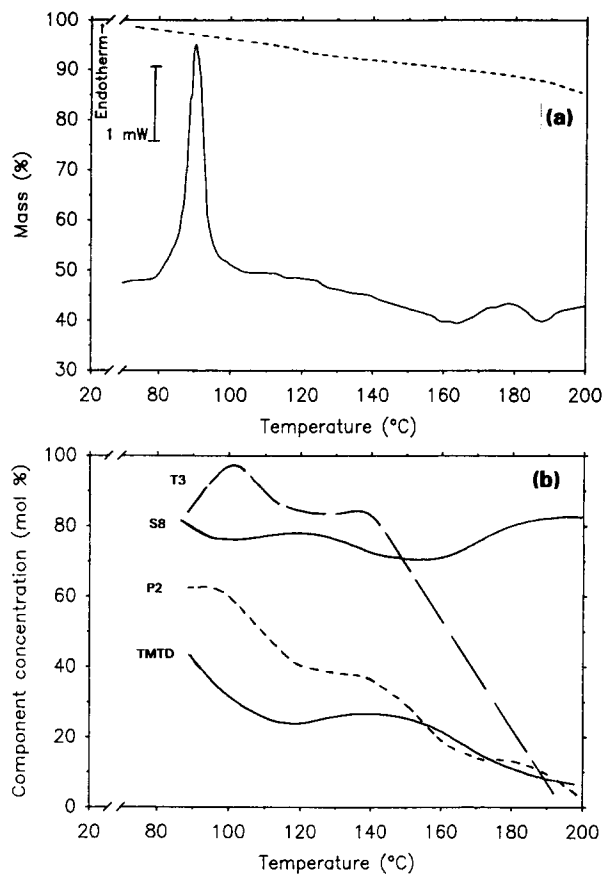


Figure 3 (a) TG (---), DSC (—) curves and (b) HPLC analysis of TMTD(1)-MBT(1)-sulfur(1)-ZnO(1) heated at 5°C/min in sealed pans. No separation of MBT and $Zn_2(dmtc)_4$. See Table I.

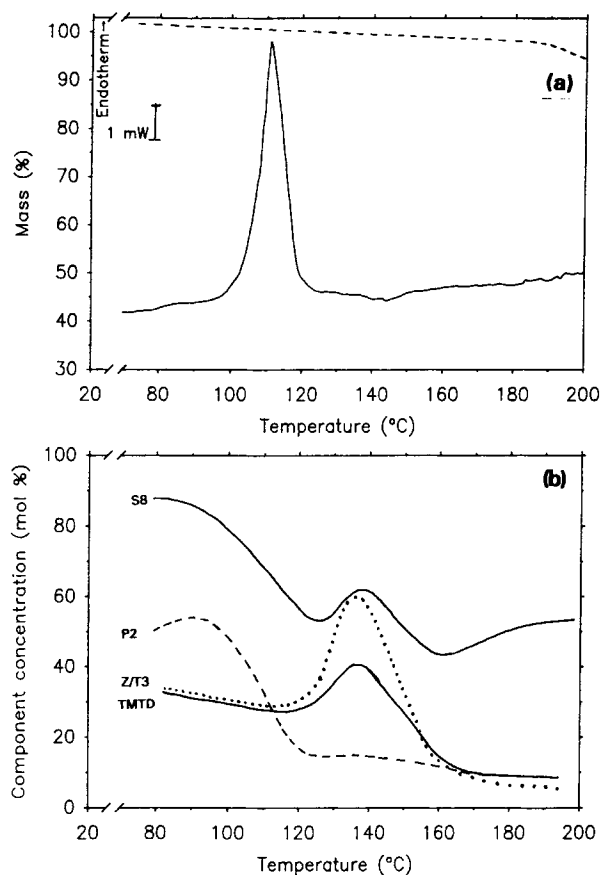
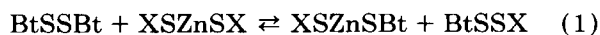


Figure 4 (a) TG (---), DSC (—) curves and (b) HPLC analysis of $\text{Zn}_2(\text{dmtc})_4(0.5)\text{-MBTS}(0.5)\text{-sulfur}(1)$ heated at $5^\circ\text{C}/\text{min}$ in sealed pans. No separation of $\text{Zn}_2(\text{dmtc})_4$ and T3, shown here as Z/T3.

change experiments with tagged TMTD⁶ showed exchange between $\text{Zn}_2(\text{dmtc})_4$ and TMTD at elevated temperatures, while McCleverty et al.,² too, reported ligand exchange. However, the ternary system of accelerator-sulfur-zinc salt rapidly undergoes exchange reactions in solution (Figs. 4, 5, and 6). The most ready evidence for the exchange is the appearance of P2 in the product spectrum. The rapid formation of P2 in relatively high concentrations suggests that it results directly from an exchange involving the zinc complex, e.g.,



where Bt = benzothiazole and X = $(\text{CH}_3)_2\text{C}(\text{S})\text{S}-$

Ligand exchange also occurs between two zinc salts in the presence of sulfur, which suggests the transient formation of a perthio zinc accelerator complex. It is postulated that in the absence of any other agent, dissociation of the complex will yield

sulfur and reform the original zinc salt (i.e., the system appears stable), but in the presence of a second accelerator (or its zinc salt) the latter may add to zinc in place of the sulfurated ligand. MBT, too, appears in the product spectrum, (Table I), indicating the involvement of an intermediate capable of extracting hydrogen, the most likely source being from water adsorbed onto the zinc salt. Exchange reactions involving P2 formed from TMTD and MBTS do not lead to MBT,¹ and it must be concluded that MBT originates from a ligand on the zinc salt, i.e., dissociation of the excluded sulfurated ligand will lead to sulfur and a benzothiazole species that can abstract hydrogen from its environment. (A dmtc ligand may likewise form Hdmtc. While the acid is not detected, it will lead to MBT and P2 via the exchange reactions outlined earlier.)¹

It was noted earlier that high TMTD concentrations develop and persist to elevated temperatures in the TMTD-MBT-sulfur-ZnO system, higher than in the absence of ZnO. The ligand released from

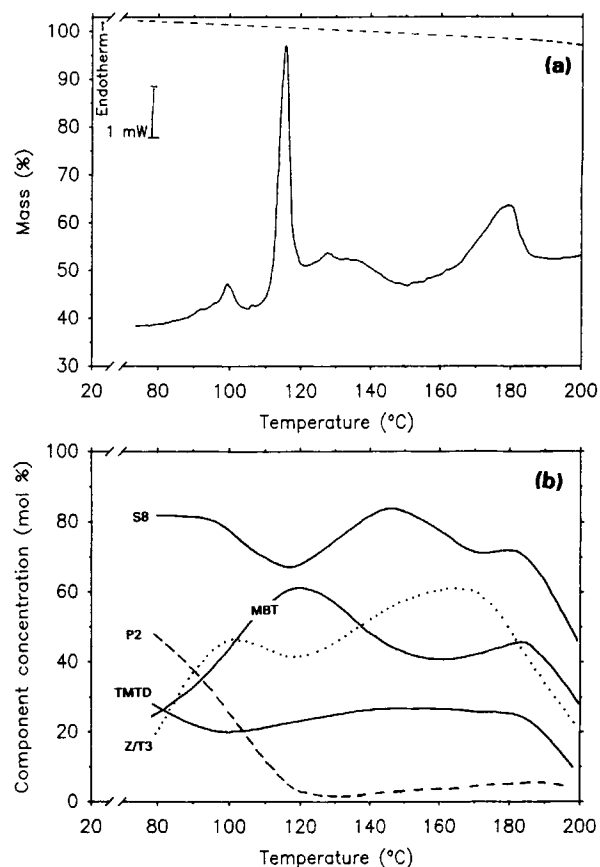


Figure 5 (a) TG (---), DSC (—) curves and (b) HPLC analysis of $\text{Zn}_2(\text{dmtc})_4(0.5)\text{-Zn}(\text{mbt})_2(0.5)\text{-sulfur}(1)$ heated at $5^\circ\text{C}/\text{min}$ in sealed pans. No separation of $\text{Zn}_2(\text{dmtc})_4$ and T3, shown here as Z/T3.

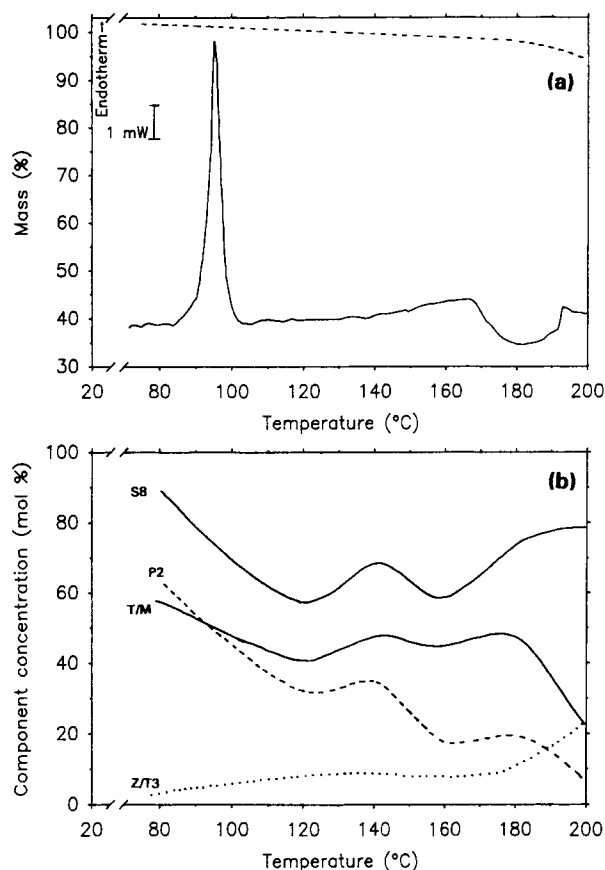
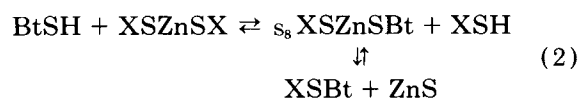


Figure 6 (a) TG (---), DSC (—) curves and (b) HPLC analysis of $\text{Zn}(\text{mbt})_2(0.5)\text{-TMTD}(0.5)\text{-sulfur}(1)$ heated at $5^\circ\text{C}/\text{min}$ in sealed pans. No separation of $\text{Zn}_2(\text{dmtc})_4$ and T3, shown here as Z/T3 and of MBT and TMTD, shown here as T/M.

the zinc salt during the exchange reaction [and that was shown to form Hdmtc (or MBT) on abstraction of a hydrogen from water], may initiate a sulfur exchange sequence. This would generate the high TMTD (and correspondingly low TMTM) concentrations observed (Figs. 1 and 3, Table I).

The products detected by HPLC result from exchanges in solution and it does not follow that similar reactions occur in the mixture prior to dissolution. It was shown¹ earlier that, on heating TMTD(1)-MBT(1)-sulfur(1) in the absence of zinc, polysulfides of TMTD and P2 form above the melting endotherm, the formation of the former being favored when MBT, and consequently Hdmtc, are present. In the present systems, all of which contain zinc, these species are also present in mixtures heated to above the endotherm. This change in product spectrum from that observed in the room temperature solution can only be brought about by exchange reactions in the melt. The equilibria be-

tween the different species are further complicated by the presence of zinc salts that participate in exchange reactions. It was seen earlier¹ that polysulfides of TMTD are favored in the presence of Hdmtc, and the decrease in P2 and the increase in TMTD and $\text{Zn}_2(\text{dmtc})_4$ would be consistent with this trend. As the temperature is raised, further changes occur. Notably the $\text{Zn}_2(\text{dmtc})_4$ and TMTD concentrations decrease again while changes in the sulfur concentration produce a W-shaped curve. It would appear that above 160°C exchange reactions involving the zinc salt lead to its decomposition as in eqs. (2) or (3), and that substitution of the leaving ligand does not occur. A mass loss would result from the volatilization or decomposition of Hdmtc.



At first glance, exchange does not appear to occur in the $\text{Zn}_2(\text{dmtc})_4(0.33)\text{-MBT}(0.67)\text{-sulfur}(1)$ mixture (Fig. 7 and Table I), i.e., no P2 forms, though separation of certain components was difficult. However, this is the only system in which a very large mass loss occurs above the melting endotherm and can be explained in terms of an exchange in which Hdmtc is liberated [eq. (3)].

A most important point that does emerge from the data in Figures 4, 5, and 6 is the formation of MBT (or possibly Hdmtc). The mechanism of $\text{Zn}_2(\text{dmtc})_4$ accelerated sulfur vulcanization is unclear, and aspects are currently being studied in these laboratories. It is significant that polysulfidic pendent groups, commonly believed to be precursors to crosslinking, are not formed in $\text{Zn}_2(\text{dmtc})_4$ vulcanizates.⁷ The formation of MBT implies the possibility of hydrogen abstraction from the polymer chain and may provide a route for initiation of the reaction.

Zinc Complexes with Three Ligands

$[\text{NBu}_4^+][\text{Zn}(\text{dmtc})_2(\text{mbt})]$ was synthesized as described. On heating a $[\text{NBu}_4^+][\text{Zn}(\text{dmtc})_2(\text{mbt})]$ (1)-sulfur(1) mixture, the zinc salt melts at 88°C , but shows little interaction with sulfur, the typical sulfur solid-solid and solid-liquid transitions being observed in the DSC (Fig. 8 and Table I).

The addition of sulfur has little effect on the complex product spectrum that $[\text{NBu}_4^+][\text{Zn}(\text{dmtc})_2(\text{mbt})]$ forms on its own in solution; TMTD,

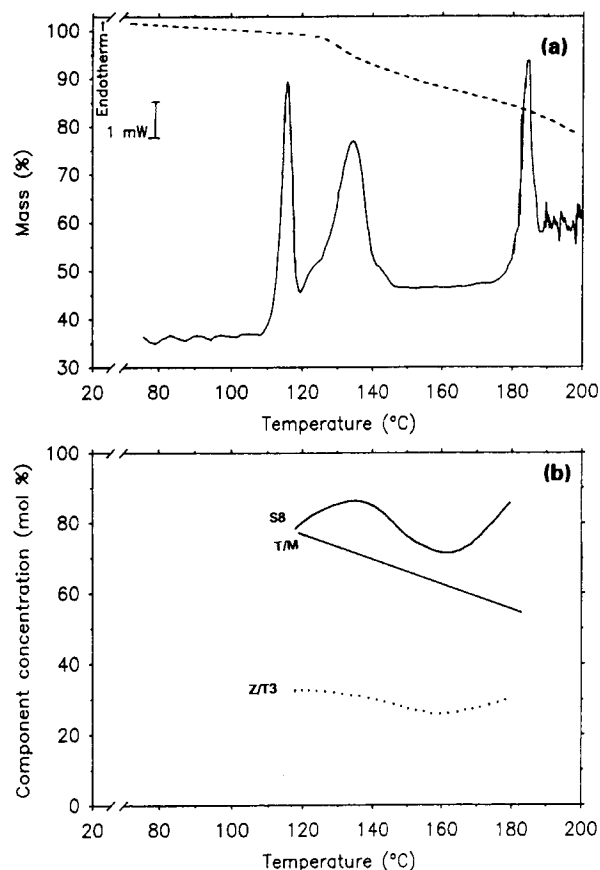


Figure 7 (a) TG (---), DSC (—) curves and (b) HPLC analysis of $\text{Zn}_2(\text{dmtc})_4(0.33)\text{-MBT}(0.67)\text{-sulfur}(1)$ heated at $5^\circ\text{C}/\text{min}$ in sealed pans. No separation of $\text{Zn}_2(\text{dmtc})_4$ and T3, shown here as Z/T3 and of MBT and TMTD, shown here as T/M.

MBT, and $\text{Zn}_2(\text{dmtc})_4$ are formed (Fig. 8). Only small changes occur below 160°C , P1 forming with TMTD decreasing. Above 160°C , mass losses begin and TMTD and $\text{Zn}_2(\text{dmtc})_4$ decrease as Hdmtc decomposes.

$[\text{NBU}_4^+][\text{Zn}(\text{dmtc})(\text{mbt})_2]\text{-Sulfur}$

$[\text{NBU}_4^+][\text{Zn}(\text{dmtc})(\text{mbt})_2]$ was also synthesized. On heating a $[\text{NBU}_4^+][\text{Zn}(\text{dmtc})(\text{mbt})_2](1)\text{-sulfur}(1)$ mixture in the DSC, the sulfur transitions merge into a single peak and the complex melts above 140°C (Fig. 9). It does not interact with sulfur. The noninteraction of these zinc complexes towards sulfur is consistent with the stability of $\text{Zn}_2(\text{dmtc})_4$ and $\text{Zn}(\text{mbt})_2$ towards sulfur.

Again, the three ligand complex forms a number of products on its own in solution, and the addition of sulfur has little effect on the product spectrum (Fig. 9). Rapid changes occur only above 165°C and

coincide with the mass loss. Polysulfides (MBTS, T4 and tetramethylthiuram pentasulfide (T5)) are more prominent than in the $[\text{NBU}_4^+][\text{Zn}(\text{dmtc})_2(\text{mbt})](1)\text{-sulfur}(1)$ system (Table I).

CONCLUSION

A complex series of equilibria are set up between the accelerator species in the presence of ZnO. A major role of ZnO is to trap Hdmtc and thereby prevent its decomposition to DMA and CS_2 , the former giving rise to destruction of polysulfidic pendent groups, which are precursors to crosslink formation. Secondly, the zinc salt formed in the course of the reaction sequence will act as an accelerator in its own right. In the presence of sulfur, ligands on both $\text{Zn}_2(\text{dmtc})_4$ and $\text{Zn}(\text{mbt})_2$ can be exchanged with the accelerators. Mixed zinc salts $(\text{Zn}(\text{dmtc})_x(\text{mbt})_y)$ are possible. The liberation of Hdmtc appears to be the main driving force in favoring

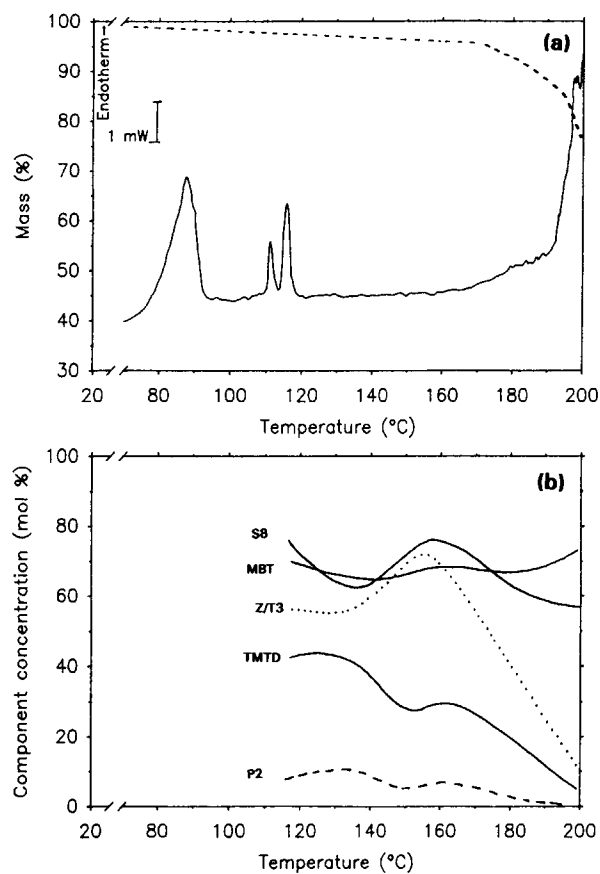


Figure 8 (a) TG (---), DSC (—) curves and (b) HPLC analysis of $[\text{NBU}_4^+][\text{Zn}(\text{dmtc})_2(\text{mbt})](1)\text{-sulfur}(1)$ heated at $5^\circ\text{C}/\text{min}$ in sealed pans. No separation of $\text{Zn}_2(\text{dmtc})_4$ and T3, shown here as Z/T3.

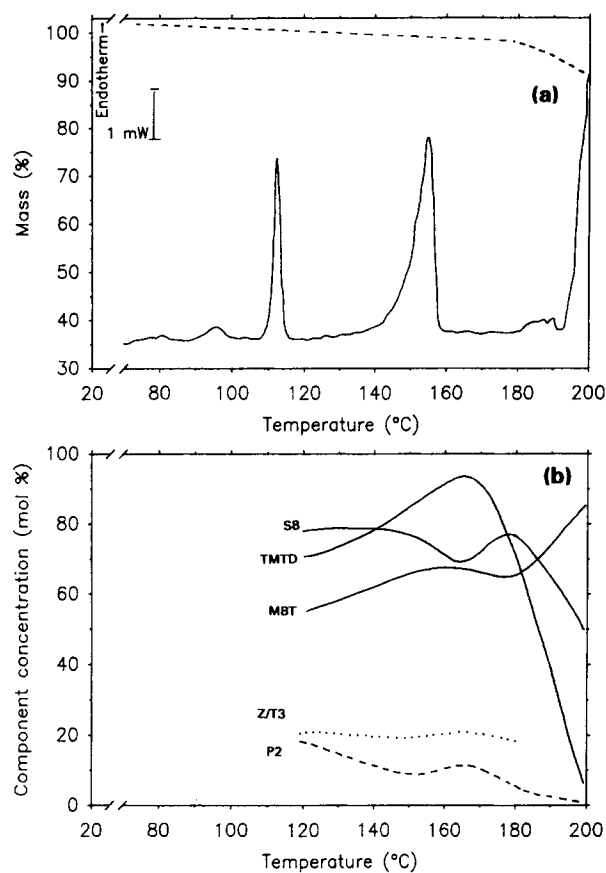


Figure 9 (a) TG (---), DSC (—) curves and (b) HPLC analysis of $[\text{NBu}_4][\text{Zn}(\text{dmtc})(\text{mbt}_2)](1)$ -sulfur(1) heated at $5^\circ\text{C}/\text{min}$ in sealed pans. No separation of $\text{Zn}_2(\text{dmtc})_4$ and T3, shown here as Z/T3.

$\text{Zn}_2(\text{dmtc})_4$ formation at higher temperatures. At still higher temperatures, the zinc salt decomposes in the presence of sulfur and free accelerator. The dmtc group released on decomposition may abstract

hydrogen from a suitable source or initiate sulfur exchange reactions that lead to high TMTP concentrations. Zinc salts with three ligands readily decompose in solution with sulfur leading to a complex series of equilibria.

With the binary accelerator system, the vulcanization process can be expected to be influenced by the presence of P2 and $\text{Zn}(\text{dmtc})_x(\text{mbt})_y$, both of which should act as accelerators, and by the fact that exchange reactions between the binary accelerators and their zinc salts influence the concentrations of accelerator polysulfides that form on heating.

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