

# Sulfur Vulcanization of Polyisoprene Accelerated by Benzothiazole Derivatives. II. Reaction of 2-Mercaptobenzothiazole and Its Zinc Salt with Sulfur and ZnO in Polyisoprene

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## SYNOPSIS

Compounds of polyisoprene with sulfur and bis(2-mercaptobenzothiazole)zinc(II) ( $\text{Zn}(\text{mbt})_2$ ) or ZnO and 2-mercaptobenzothiazole (MBT) were vulcanized by heating in a differential scanning calorimeter. The reaction was stopped at points along the thermogram and the product analyzed. ZnO and MBT readily react, the reaction going to completion during compounding. The presence of  $\text{Zn}(\text{mbt})_2$  delays the onset of crosslinking compared to compounds without zinc. It is suggested that the induction period prior to crosslinking is occasioned by the inactivity of  $\text{Zn}(\text{mbt})_2$ , which must breakdown to MBT before it can participate in the vulcanization process. Such decomposition results from attack by anions generated when polysulfidic crosslinks, formed in the unaccelerated sulfur that occurs in the early stages of crosslinking, undergo scission. The effect of MBT, not bound to zinc, on the mechanism of the reaction is discussed. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

In a companion article<sup>1</sup> we reported on the 2-mercaptobenzothiazole (MBT) accelerated sulfur vulcanization of polyisoprene (IR) in the absence of ZnO. It is generally accepted that, in the presence of zinc, reaction between MBT and ZnO or zinc stearate forms a zinc-accelerator complex, bis(2-mercaptobenzothiazole) zinc(II) [ $\text{Zn}(\text{mbt})_2$ ]. There is considerable disagreement on subsequent reactions. Vulcanization does not occur in the absence of sulfur.

Broad  $\text{Zn}(\text{mbt})_2$  and  $\text{ZnOBT}^+$  peaks were observed in the 1350–1400  $\text{cm}^{-1}$  region in the Raman spectra of MBT/ZnO heated to 150°C. The line and shoulder that developed at 1350–1400  $\text{cm}^{-1}$  in an MBT/sulfur/ZnO mixture heated to 150°C for 1 min were interpreted by Kapur et al.<sup>2</sup> as evidence for the rapid formation of  $\text{Zn}(\text{mbt})_2$ . It should be

noted that Coran<sup>3</sup> also proposed the formation of Zn-accelerator complexes that included oxygen. Auerbach<sup>4</sup> assumed the formation of  $\text{Zn}(\text{mbt})_2$  during the induction period but he stated that this species was not the vulcanizing agent. Instead he assumed that the ZnS split off and that the MBT residue reacted as a radical or ion. Campbell and Wise<sup>5</sup> found an induction period of 3 min before the onset of crosslinking. A marked induction period applies in poly(butadiene-*co*-styrene) vulcanization and  $\text{Zn}(\text{mbt})_2$  does not reform despite the presence of excess ZnO in the compound.<sup>4</sup> Russell et al.<sup>6</sup> also referred to an induction period when using MBT.

In view of the ready anionic activation of sulfur and the regeneration of persulfenyl anions, Bateman et al.<sup>7</sup> suggested a reaction mechanism initiated by benzothiazole-2-thiolate anions ( $\text{BtS}^-$ ). Dogadkin et al.<sup>8</sup> suggested that MBT reacts with sulfur to form radicals that lead to vulcanization, while Shelton and McDonel<sup>9</sup> found that a polar mechanism dominates. Bruni and Romani<sup>10</sup> suggested that the MBT first reacted with ZnO in the presence of sulfur to give  $\text{Zn}(\text{mbt})_2$ .  $\text{Zn}(\text{mbt})_2$  in turn reacted with sulfur to give MBTS.

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In contrast to Taneja and Banerjee,<sup>11</sup> Lorenz and Echte<sup>12</sup> found that the amount of MBT consumed is independent of the MBT or  $\text{Zn}(\text{mbt})_2$  loading. One  $\text{Zn}(\text{mbt})_2$  molecule is consumed for every 11 sulfur molecules reacted. Once all of the sulfur has been used up no further MBT consumption occurs.<sup>8,12</sup> The decrease in sulfur concentration, rate of crosslinking, and the crosslink density are unaffected by the  $\text{Zn}(\text{mbt})_2$  concentration.<sup>13</sup> This is said to be due to its insolubility in rubber. However, Lorenz and Echte<sup>12</sup> found that the rate constant for sulfur consumption is 2.5 times greater than with MBT/ZnO. Reported amounts of extractable MBT at the end of the reaction vary greatly, depending on the compound studied, but it is generally concluded that little MBT is consumed.<sup>4,5,8,12</sup>

It was suggested previously<sup>1</sup> that in MBT accelerated vulcanization the reaction was similar to that for unaccelerated sulfur vulcanization,  $\text{SH}^+$  cations from MBT merely acting as additional centers for initiating the reaction. This article reports on a differential scanning calorimetry (DSC) study of the effect of ZnO on the vulcanization.

## EXPERIMENTAL

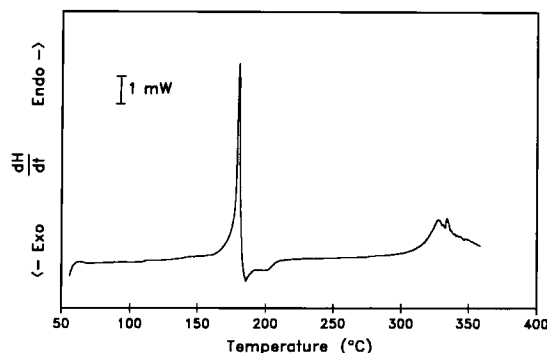
The MBT was produced by Monsanto (Belgium), the  $\text{Zn}(\text{mbt})_2$  by Bayer (Germany), and the zinc oxide (active grade, 99.72% purity) by Zinc Process (South Africa). The commercial grade  $\text{Zn}(\text{mbt})_2$  was found to contain  $\pm 18\%$  MBT (by mass). The  $\text{Zn}(\text{mbt})_2$  was washed by dissolving the MBT in methanol. The two samples of  $\text{Zn}(\text{mbt})_2$ , pure and impure, were used in the vulcanization of IR leading to very different vulcanization reactions.

The experimental procedures were described previously.<sup>1</sup> The curing characteristics of various rubber samples were tested in a Monsanto Rheometer, (MDR 2000E) with an arc of  $\pm 0.5^\circ$ . Temperatures are indicated in the text.

## RESULTS

### MBT/ZnO Interactions

The DSC thermogram in Figure 1 of MBT/ZnO (1 : 1 mole ratio) shows the melting of MBT at  $178^\circ\text{C}$ , slightly below that of MBT, in the absence of ZnO. At  $180^\circ\text{C}$  the DSC trace abruptly drops to below the baseline. This is due to the formation of  $\text{Zn}(\text{mbt})_2$  as soon as the MBT melts. The DSC melting endotherm of  $\text{Zn}(\text{mbt})_2$  is seen at  $320^\circ\text{C}$  ( $330^\circ\text{C}$ <sup>14</sup>). High-performance liquid chromatography (HPLC)



**Figure 1** DSC thermogram. Heating rate  $5^\circ\text{C}/\text{min}$ . MBT/ZnO (1.1 mole ratio),  $M_i = 8.660$  mg.

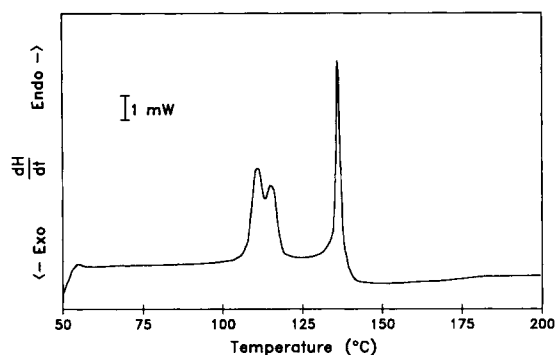
analysis of this mix, after being heated to  $200^\circ\text{C}$ , showed that only 12 mass % of the original MBT remained unreacted. Failure of the reaction may be ascribed to the coating of ZnO particles by  $\text{Zn}(\text{mbt})_2$ . The formation of  $\text{Zn}(\text{mbt})_2$  above the MBT melting point was confirmed by X-ray diffraction<sup>14</sup> and by Raman spectroscopy.<sup>2</sup>

The DSC thermogram of MBT/sulfur/ZnO (1 : 1 : 1 mole ratio) drops abruptly after the MBT dissolution peak due to the MBT/ZnO reaction (Fig. 2). A mass loss of 10% was found on heating the mixture to  $170^\circ\text{C}$  at  $5^\circ\text{C}/\text{min}$  and HPLC analysis showed that 19 mass % of the MBT remained unreacted. This shows that the only reaction to have taken place was that between MBT and ZnO to form  $\text{Zn}(\text{mbt})_2$ .

Kok<sup>15</sup> did not observe the melting of MBT, but only a strong exotherm in the region where MBT and ZnO react. The line and shoulder that developed at  $1350\text{--}1400\text{ cm}^{-1}$  in the Raman spectra of an MBT/sulfur/ZnO mixture heated to  $150^\circ\text{C}$  for 1 min were interpreted by Kapur et al.<sup>2</sup> as evidence for the rapid formation of  $\text{Zn}(\text{mbt})_2$ .

### IR/Sulfur/ZnO

On adding ZnO to an IR/sulfur compound<sup>1</sup> the DSC exotherm shifts to very slightly lower temperatures, but the onset of crosslinking and curves of sulfur consumption coincide with those for vulcanization in the absence of ZnO (Fig. 3). A much higher crosslink density is attained with ZnO (DSC peak maximum  $6.58 \times 10^{-5}$  vs.  $3.26 \times 10^{-5}$  mol/mL), but the initial rate of crosslink formation (slope of crosslink density vs. temperature plot) is the same. As the crosslink density is higher, the Moore-Tregoe efficiency of sulfur utilization is better in the presence of ZnO and remains good over a wider temperature range (Table I). Bhaumik et al.<sup>16</sup> found



**Figure 2** DSC thermogram. Heating rate 5°C/min. MBT/sulfur/ZnO (1 : 1 : 1 mole ratio),  $M_i = 18.246$  mg,  $M_f = 16.374$  mg.

that the natural rubber (NR)/sulfur vulcanization exotherm started at 160°C; and in the presence of ZnO the initiation temperature was 155°C. The effect of ZnO on the initiation temperature in the NR/sulfur system may be attributed to its interaction with natural accelerators in NR. (The temperatures at which crosslinking was first observed by Bhaumik and those of the present study cannot be compared directly because the sulfur loading and DSC scanning rate will influence the temperature at which crosslinking can be detected.)

### IR/MBT/Sulfur/ZnO

In the absence of sulfur, MBT and ZnO cannot vulcanize IR, no crosslinks are formed, and no thermal events are visible on the DSC curve. The MBT is not extractable from the rubber. It appears that the MBT reacts with the ZnO during mixing, a sample extracted without having been heated yielding less than 5% extractable MBT.

The addition of ZnO to an IR/MBT/sulfur system<sup>1</sup> delays the onset of the vulcanization exotherm (Fig. 4) that is also slightly narrower than for the IR/sulfur system. As in the IR/sulfur system, crosslinking can be detected prior to the exotherm. Sulfur is consumed very rapidly and no free sulfur is detectable at the peak of the exotherm. Measurement of crosslink density shows that crosslinking is delayed with respect to the IR/MBT/sulfur<sup>1</sup> system and commences at the same temperature as in the IR/sulfur system. However, once initiated crosslinking is more rapid and the maximum crosslink density attained before reversion is the same as for unaccelerated sulfur vulcanization.

ZnO and MBT readily react to form  $Zn(mbt)_2$ <sup>4,12</sup> and initially there is essentially no free MBT in the

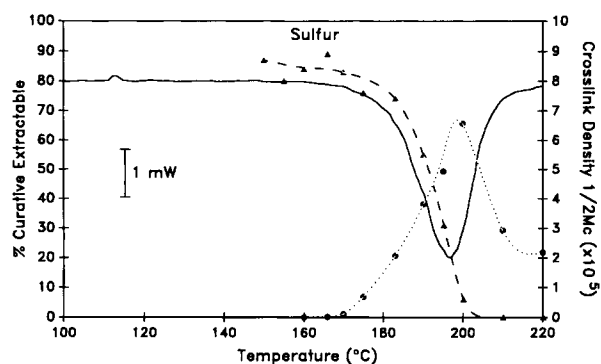
compound. However, MBT is rapidly released during reaction and its concentration reaches a peak just after all of the sulfur has been consumed (Fig. 4). At this point 90% of the MBT in the original compound has been liberated, after which the MBT concentration decreases slightly.

In an effort to retrap the MBT after the  $Zn(mbt)_2$  had decomposed, three times the ZnO loading used in the above experiments was added (3 mol ZnO/1 mol MBT). Although a decrease in the amount of MBT extracted was found (approx. 25% less at the peak), the reaction exotherm was unchanged. The crosslink density achieved was the same as with lower ZnO loadings ( $1/2M_c = 4.06 \times 10^{-5}$  vs.  $4.14 \times 10^{-5}$  mol/mL), but the efficiency was slightly better (43 vs. 54).

### IR/ZMBT/Sulfur

The IR/Zn(mbt) system does not cause the vulcanization of IR. No MBT is extractable and no crosslinks are formed.

The behavior of the IR/Zn(mbt)<sub>2</sub>/sulfur system is very similar to that of the IR/MBT/sulfur/ZnO system. A narrow exotherm is observed with sulfur consumption and rapid crosslinking being recorded before the onset of the exotherm (Fig. 5). Crosslinking commences slightly later (2–5°C) than in the system where  $Zn(mbt)_2$  results from the interaction of MBT and ZnO. The maximum crosslink density is slightly higher than with the IR/MBT/ZnO/sulfur system ( $1/2M_c = 5.13 \times 10^{-5}$  vs.  $4.14 \times 10^{-5}$  mol/mL at 180°C). The release of extractable MBT coincides with crosslinking. The small amount of MBT present prior to crosslinking at 155°C must be generated during compounding.



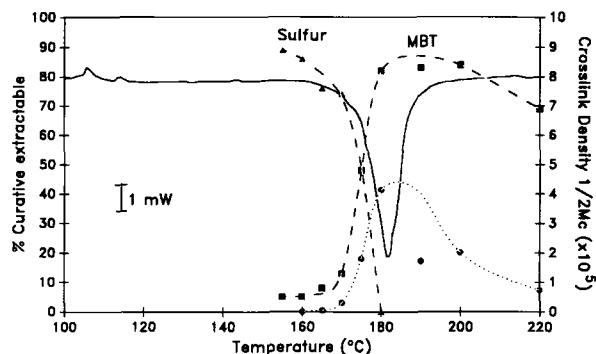
**Figure 3** Analysis of the IR/sulfur/ZnO vulcanization system. DSC thermogram, heating rate 2.5°C/min,  $M_i = 21.0784$  mg,  $M_f = 21.0362$  mg. (· · ·) Crosslink density  $1/2M_c (\times 10^5)$ . (---) % curative extractable.

**Table I Moore-Tregoe Efficiency for Different Curative Systems**

Temp (°C)	IR/Sulfur/ZnO (100/9.5/3)	Ir/MBT/Sulfur/ZnO (100/6.2/9.5/3)	IR/ZMBT/Sulfur (100/14.7/9.5)	IR/ZMBT/MBT/Sulfur (100/12.2/2.5/9.5)
140				81
150				30
160				34
170	373	196	108	50
175	85	64		
180	31	54	36	79
190	29	132	78	94
200	35	113	97	

In an attempt to retrap the MBT released and hence modify the vulcanization, ZnO was added to the compound. This did not, however, change the vulcanization exotherm at all. The MBT did not appear to react with the excess ZnO, the exotherm did not shift, the MBT was extractable, and the crosslink density was of the same order as in the absence of ZnO.

MBT was present as an impurity in the commercial Zn(mbt)<sub>2</sub> sample and, if not removed, leads to a totally different vulcanization reactivity. If 2.5 phr MBT is added to an IR/sulfur/Zn(mbt)<sub>2</sub> compound a broad exotherm is obtained (Fig. 6), peaking some 18–20°C earlier than in the systems with purified Zn(mbt)<sub>2</sub>. Crosslinking commences at 130°C, much earlier than in any other systems (Fig. 6). The release of MBT is slower, but in the end 75% of the MBT in the Zn(mbt)<sub>2</sub> complex has been released.



**Figure 4** Analysis of the IR/sulfur/MBT/ZnO vulcanization system. DSC thermogram, heating rate 2.5°C/min,  $M_i = 29.5417$  mg,  $M_f = 28.8368$  mg. (· · ·) Crosslink density  $1/2M_c$  ( $\times 10^5$ ). (---) % curative extractable.

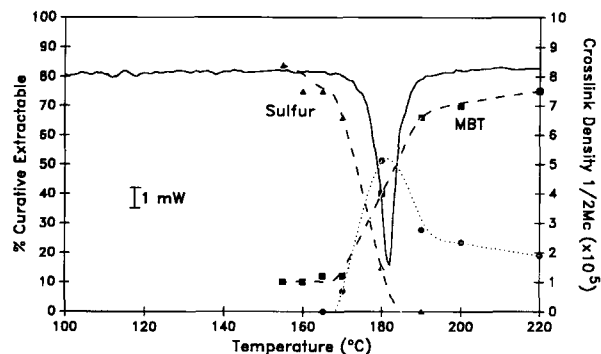
## DISCUSSION

### MBT/ZnO and MBT/Sulfur/ZnO

In the both the MBT/ZnO and MBT/sulfur/ZnO systems, the ready formation of Zn(mbt)<sub>2</sub> was demonstrated but no further reaction was detected; specifically HPLC analysis showed that no MBTS was formed. Thus, as noted earlier, the formation of MBTS in the vulcanizate implies the participation of the rubber molecule. Luyt<sup>17</sup> extracted MBTS from polyisoprene vulcanizates and found similar amounts of MBTS in vulcanizates both with and without ZnO.

### IR/Sulfur/ZnO

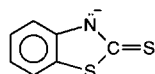
The addition of ZnO has a minimal effect on the vulcanization process, but does affect the crosslink



**Figure 5** Analysis of the IR/sulfur/Zn(mbt)<sub>2</sub> vulcanization system. DSC thermogram, heating rate 2.5°C/min,  $M_i = 29.1402$  mg,  $M_f = 29.0823$  mg. (· · ·) Crosslink density  $1/2M_c$  ( $\times 10^5$ ). (---) % curative extractable.



that sulfur attacked  $\text{Zn}(\text{mbt})_2$  to form MBTS and  $\text{ZnS}$ , but most authors<sup>4,5,8</sup> report only MBT formation. Radical attack on  $\text{Zn}(\text{mbt})_2$  cannot be excluded and the small amount of MBT present in the rubber mix after compounding may result from attack by chain end radicals or persulfenyl radicals at chain ends on  $\text{Zn}(\text{mbt})_2$ . On transferring a sulfide anion to  $\text{Zn}^{2+}$  the persulfenyl anion is transformed into a persulfenyl cation that can initiate the vulcanization chain reaction by adding to the double bond in a process analogous to that suggested for unaccelerated sulfur vulcanization. The mercaptobenzothiazolyl sulfide anions generated from  $\text{Zn}(\text{mbt})_2$  may abstract a proton from the rubber chain to form MBT. Although the C—H bond (on the rubber chain) is stronger than the S—H bond (in MBT), abstraction may occur via the highly electronegative N in the MBT ion.



Although some MBT is present even at 150°C, the rapid formation of MBT coincides with the onset of crosslinking and its release is very rapid once crosslinking commences. The resulting carbon anion on the polymer chain, or the original mercaptobenzothiazolyl sulfide anion may, as an alternative to MBT formation, react with sulfur to form persulfenyl anions that can decompose more  $\text{Zn}(\text{mbt})_2$  and are, in the process, converted to persulfenyl cations that can participate in initiating the crosslinking process. Thus  $\text{Zn}(\text{mbt})_2$  will be decomposed very rapidly, while the resulting high concentration of persulfenyl cations will lead to rapid attack on the polymer chain initiating reaction with sulfur.

### IR/MBT/Sulfur/ZnO

In the IR/MBT/sulfur/ZnO system the onset of vulcanization, when compared to the IR/MBT/sulfur system,<sup>1</sup> is delayed by the presence of ZnO; and the effect of MBT in facilitating the initiation of crosslinking by sulfur at lower temperatures is removed. As noted, MBT and ZnO readily react to form  $\text{Zn}(\text{mbt})_2$ , and in IR/sulfur/MBT/ZnO compounds there is essentially no free MBT at the onset of vulcanization. One would therefore expect the behavior of the system to mimic that of the IR/ $\text{Zn}(\text{mbt})_2$ /sulfur system. Indeed the exotherms closely coincide; the curves peak at the same temperature although the exotherm for the IR/MBT/ZnO/sulfur system is very slightly narrower (cf.

Figs. 4, 5). Crosslinking commences at the same temperature and plots of the consumption of sulfur are closely similar. MBT is released more rapidly from the system in which  $\text{Zn}(\text{mbt})_2$  is formed during compounding and this may be associated with the size of the  $\text{Zn}(\text{mbt})_2$  particles in the compounds. The  $\text{Zn}(\text{mbt})_2$  used was fairly large grained compared to the ZnO powder and, because the release of MBT results from the attack by persulfenyl anions on  $\text{Zn}(\text{mbt})_2$ , a depletion of elemental sulfur (needed for the formation of these anions) in the vicinity of the particles will slow down the rate of  $\text{Zn}(\text{mbt})_2$  decomposition. Note that, as in the IR/ $\text{Zn}(\text{mbt})_2$ /sulfur system, the formation of MBT accompanies crosslinking, that is, MBT is a by-product of the crosslinking process and, although it may participate in vulcanization once liberated, the onset of crosslinking is not dependent on the build-up of a certain concentration of MBT as is frequently reported in the literature.<sup>3,5,26,27</sup>

### Comparison of IR/ $\text{Zn}(\text{mbt})_2$ /Sulfur and IR/MBT/Sulfur/ZnO

In the IR/sulfur,<sup>1</sup> IR/ $\text{Zn}(\text{mbt})_2$ /sulfur (Fig. 5), and IR/MBT/sulfur/ZnO (Fig. 4) systems crosslinking is observed before the onset of the exotherm, again indicating the similarity in the crosslinking process. Lorenz and Echte<sup>12</sup> reported similar activation energies for the latter two reactions, slightly lower than that for sulfur vulcanization. A number of articles<sup>4,13,23,28</sup> state that it is "evident" that the zinc or amine salt of the thiazole is the actual accelerator in MBT/sulfur/ZnO systems. Scheele<sup>13</sup> also notes that in the NR/MBT/sulfur/ZnO system,  $\text{Zn}(\text{mbt})_2$  is the real accelerator but does not suggest how it functions. Dogadkin et al.<sup>8</sup> suggest a free radical type mechanism involving MBT that is essentially similar to that put forward by Taneja and Banerjee<sup>11</sup> for a MBT/sulfur system.

Some authors<sup>29</sup> suggest that the induction period, or delay in vulcanization, is due to the reaction of MBT and ZnO to form  $\text{Zn}(\text{mbt})_2$ . We have shown this to be a fast reaction that occurs very easily, even during compounding. The present study shows that the induction period is not due to the formation of  $\text{Zn}(\text{mbt})_2$  but rather to its inactivity.  $\text{Zn}(\text{mbt})_2$  is activated by persulfenyl cations generated during the early stages of unaccelerated sulfur vulcanization, which is a slow process. At higher temperatures this induction period is less noticeable.

The maximum crosslink density in the IR/ $\text{Zn}(\text{mbt})_2$ /sulfur system is higher than in the IR/MBT/sulfur/ZnO system ( $1/2M_c = 5.13 \times 10^{-5}$

vs.  $4.14 \times 10^{-5}$  mol/mL). The number of mercapto-benzothiazole groups in the  $\text{Zn}(\text{mbt})_2$  system is double that in the MBT/ZnO system (1 mol  $\text{Zn}(\text{mbt})_2$  releases 2 mol benzothiazole groups) and the larger number of chain initiating steps would explain the higher crosslink density. This is consistent with the higher crosslink density obtained in IR/MBT/sulfur systems where higher MBT loadings ensure more chain initiating events.<sup>1</sup> The crosslink density in the IR/MBT/sulfur/ZnO system is the same as that found in the absence of ZnO ( $1/2M_c = 4.24 \times 10^{-5}$  vs.  $4.14 \times 10^{-5}$  mol/mL) that would be expected if the crosslinking process were essentially the same, the only variable being the rate of supply of the species (persulfenyl cations) initiating the crosslinking reaction sequence.

It appears that the MBT liberated is not re-trapped by ZnO, despite the compound containing an excess of ZnO [only half of the ZnO is involved in forming  $\text{Zn}(\text{mbt})_2$ ]. A similar IR/MBT/sulfur/ZnO compound was prepared and, after mixing, during which process the MBT would have been trapped as  $\text{Zn}(\text{mbt})_2$ , a further 6 phr of ZnO was added. On vulcanization the behavior of the system did not differ markedly from that of the earlier system. Crosslinking commenced some 5°C later (possibly as any free MBT had been mopped up more effectively), although the same crosslink density was achieved ( $1/2M_c = 4.24 \times 10^{-5}$  vs.  $4.06 \times 10^{-5}$  mol/mL). The release of MBT was somewhat more gradual than with a lower ZnO loading, but ultimately 70% of the original MBT was accounted for. Auerbach<sup>4</sup> also found that  $\text{Zn}(\text{mbt})_2$  did not reform in the compound despite an excess of ZnO and he attributed this to the high reactivity of  $\text{Zn}(\text{mbt})_2$  with sulfur preventing its accumulation. However, it is not the reactivity of  $\text{Zn}(\text{mbt})_2$  with sulfur that prevents its accumulation [a  $\text{Zn}(\text{mbt})_2$ /sulfur mix is stable], but its decomposition by persulfenyl anions present during vulcanization. The apparently slower release of MBT in the presence of excess ZnO suggests that re-trapping does occur and that MBT is released again following attack on the  $\text{Zn}(\text{mbt})_2$ .

### Effect of MBT

In the absence of rubber the  $\text{Zn}(\text{mbt})_2$ /sulfur/MBT mix is stable when heated at 5°C/min to 150°C. Only on heating in the presence of KOH does 50% of the  $\text{Zn}(\text{mbt})_2$  decompose by 150°C. It was suggested<sup>1</sup> that MBT accelerated vulcanization is initiated by the addition of an  $\text{SH}^+$  cation across the double bond to form a cyclic cation. MBT does not add to rubber in the absence of sulfur implying

the Bt anion would decompose the cyclic cation to reform MBT rather than add MBT to the rubber chain. In the presence of sulfur the ion pair may be separated and the Bt anion could open the sulfur ring, forming a persulfenyl anion that can attack and decompose  $\text{Zn}(\text{mbt})_2$  in an autocatalytic reaction as detailed above. The addition of MBT to the  $\text{Zn}(\text{mbt})_2$ /sulfur system leads to the very much earlier onset of vulcanization (Fig. 6). Decomposition of  $\text{Zn}(\text{mbt})_2$  would lead not only to an increase in MBT concentration [1 mol  $\text{Zn}(\text{mbt})_2 = 2$  mol of MBT], but also to the generation of more persulfenyl cations that activate crosslinking. It is found that when decomposition of  $\text{Zn}(\text{mbt})_2$  was initiated only at high temperatures (Figs. 4, 5) and the very rapid increase in the number of chain initiating species resulted in the rate of the crosslinking reaction being higher than for compounds without  $\text{Zn}(\text{mbt})_2$ ; and even when MBT initiates  $\text{Zn}(\text{mbt})_2$  breakdown at lower temperatures (Fig. 6), plots of crosslink density and elemental sulfur vs. temperature can be brought into coincidence with those for the MBT/sulfur system by shifting by 20°C along the temperature axis. This again suggests that the same reaction mechanism<sup>1</sup> is operative, the only difference being in the larger number of activators for the reaction sequence now present at the lower temperature.

### CONCLUSIONS

MBT and ZnO readily react to form  $\text{Zn}(\text{mbt})_2$ , the reaction in rubber occurring during compounding. Trapping of MBT by ZnO delays the onset of crosslinking compared to an IR/MBT/sulfur system.  $\text{Zn}(\text{mbt})_2$  does not accelerate vulcanization until it is decomposed to MBT. This decomposition is occasioned by the scission of polysulfidic crosslinks formed as a result of unaccelerated sulfur vulcanization. Persulfenyl anions formed in the scission lead to  $\text{Zn}(\text{mbt})_2$  decomposition. The reaction mechanism is similar to that which applies to unaccelerated sulfur (and MBT accelerated) vulcanization, MBT accelerating the reaction by the cationic addition of  $\text{SH}^+$  ions across the carbon-carbon double bond in the rubber. MBT appears not to be re-trapped by an excess of ZnO but any  $\text{Zn}(\text{mbt})_2$  formed by re-trapping is again degraded by persulfenyl anions.

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