Sulfur Vulcanization of Polyisoprene Accelerated by Benzothiazole Derivatives. IV. The Reaction of Polyisoprene with N-Cyclohexylbenzothiazole Sulfenamide, Sulfur, and Zinc Oxide

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SYNOPSIS

Polyisoprene was vulcanized with N-cyclohexylbenzothiazole sulfenamide (CBS), sulfur, and zinc oxide by heating in a Differential Scanning Calorimeter (DSC) at a programmed rate to given temperatures. The reaction was quenched and the product analyzed. Soluble curatives and reaction intermediates were analyzed by high-performance liquid chomatography (HPLC) and the crosslink density of the network determined by swelling. The delayed action of the CBS accelerator is explained in terms of an exchange reaction between benzothiazole terminated polysulfidic pendent groups on the polymer chain and CBS to yield unreactive amine terminated pendent groups and 2-bisbenzothiazole-2,2'-disulfide (MBTS). MBTS reacts with sulfur to form 2-bisbenzothiazole-2,2'-polysulfides (MBTPs), which also form pendent groups. Crosslinking does not commence until all of the CBS has been consumed and pendent groups are no longer deactivated. 2-Mercaptobenzothiazole (MBT) is released only on crosslinking. When MBT is present in the formulation at the outset of the reaction it traps cyclohexylamine released when CBS adds to the chain as a pendent group. The MBT-amine salt participates in a reaction that regenerates MBTS, which is, thus, not consumed in the vulcanization process. ZnO does not react with CBS, and its role in increasing the crosslink density is attributed to its promoting crosslinking reactions between pendent groups and neighboring chains rather than intramolecular reactions, which lead to cyclization. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

On heating, sulfenamides decompose to yield 2-bisbenzothiazole-2,2'-disulfide (MBTS) and 2-mercaptobenzothiazole (MBT).[1] When looking at sulfenamides as accelerators, the role of these two accelerators in the overall reaction sequence must, therefore, also be considered. Scheele and Helberg[2] vulcanized natural rubber (NR) with N-cyclohexylbenzothiazole sulfenamide (CBS) and sulfur and analyzed the extractable products. The dissociation of the sulfenamide was considered to be the first reaction, and the CBS was used up before any crosslinks were formed. The MBTS that formed also dis-

appeared before crosslinking took place. They found that at the same time as the sulfenamide is used up, the amine content of the vulcanizate reached its maximum value, while MBT reached its maximum value only when the number of crosslinks were at a maximum. Sulfenamides are well known delayed action accelerators, and Morita and Young,[3] who studied the vulcanization of pale crepe with various sulfenamides, sulfur, stearic acid, and ZnO, found that the sulfenamide/sulfur ratio was an important factor in scorch delay. The ratio was also found to affect the number of monosulfidic crosslinks formed.[4] Coran[5] suggested that sulfenamides reacted more rapidly than MBTS due to the formation of amine crosslink precursors, more hindered amines giving slower reaction rates. Kinetic investigations[6] of sulfenamide vulcanization have shown that the decomposition of the sulfenamides starts suddenly

and is accompanied by crosslinking which sets in just as suddenly.

Scheele[6] proposed the decomposition of sulfenamides to give radicals that would lead to carbon–carbon as well as sulfur crosslinks, while Shelton and McDonel[7] found that sulfur curing systems using CBS were slightly retarded by radical scavengers. They came to the conclusion that sulfenamide accelerators reacted via a mixed polar and free radical mechanism. In a later article Scheele and Helberg[2] proposed a different mechanism in which the amine salt was shown to have the same reactivity as the sulfenamides. Loo[8] claimed that the active sulfurating agent was the zinc mercaptide coordinated to cyclohexylamine. Fewer crosslinks form at higher temperatures because more pendent groups are desulfurated to inactive monosulfidic pendent groups before they can crosslink.[9]

This article reports on the decomposition of CBS in rubber and measures the formation of extractable reaction intermediates prior to and during crosslinking. The data are used to propose a mechanism for the delayed action observed with CBS and to explain the roles of sulfur, MBTS, MBT, and ZnO in the reaction sequence.

EXPERIMENTAL

The CBS was produced by Bayer (Germany) and the polyisoprene (IR) by Karbochem, a division of Sentrachem (South Africa). The compounding procedures have been described in previous articles in the series.[10-12] Vulcanization was conducted by heating samples to various temperatures at a programmed rate in a Differential Scanning Calorimeter (DSC). The network was characterized by swelling in benzene and the extractable curatives analyzed by high-performance liquid chromatography (HPLC).[13] CBS was found to react with sulfur even at room temperature, and for this reason the rubber cannot be extracted for long periods of time. The identification of the various products of CBS reactions have been described in a previous article.[1] The data for 2-bisbenzothiazole-2,2'-polysulfides (MBTPs) in this text is the total MBTP concentration: it includes the trisulfide, tetrasulfide, and any higher polysulfides that were detected by HPLC. 2-Bisbenzothiazole-2,2'-monosulfide (MBTM) was synthesized according to the method of D'Amico et al.;[14] NMR and sulfur analysis of the product confirmed the structure of MBTM. MBTS polysulfides were prepared by the method of Levi.[15]

RESULTS

CBS Accelerated Sulfur Vulcanization of Polyisoprene

IR/CBS

The vulcanization of IR by CBS in the absence of sulfur is limited ($1/2M_c = 0.45 \times 10^{-5}$ mol/mL at 220°C) and occurs only at a very high temperatures, the same temperature region in which Gradwell and McGill[1] found the sulfenamide to decompose. In the absence of rubber, the CBS decomposition exotherm starts at $T_o = 210°C$, with a peak at 215°C. In the presence of rubber, the initial degradation products of CBS are MBTS and MBTP, the MBTP being consumed before any crosslinking takes place (Fig. 1). MBT is formed as crosslinking commences. Some 2-N-cyclohexylaminobenzothiazole (CB) and MBTM, both of which are thermally more stable than the other species,[1] form above 215°C. Decomposition of CBS commences prior to the small exotherm.

IR/CBS/ZnO

The DSC curve of IR/CBS/ZnO (Fig. 2) is very similar to that of IR/CBS. The exotherm starts at 200°C with a peak at 214°C. In the presence of ZnO, crosslinking occurs slightly earlier and the crosslink density is somewhat higher, though still very low ($1/2M_c = 1.30 \times 10^{-5}$ mol/mL at 220°C). The extractable curatives are very similar to the previous compound except that less MBTS and MBTP are formed.

IR/CBS/Sulfur

On vulcanizing IR with CBS and sulfur in the DSC, an apparently single reaction exotherm is obtained starting at $T_o = 150°C$, with a peak at $T_p = 167°C$ (Fig. 3). Crosslinking starts at 155°C, only once all of the CBS has been consumed, and a maximum crosslink density is reached at 166°C (Table I). The crosslinking reaction proceeds very quickly up to 160°C, at which point no MBTS is available and the MBT concentration, which increases very rapidly during crosslinking, reaches its equilibrium value. Less than half of the sulfur has been used at this stage, and consumption of the rest of the sulfur must be attributed to crosslinking reactions involving MBT.[10] There is a small further increase in crosslink density before reversion reactions dominate over MBT promoted crosslinking and the overall crosslink density decreases, despite the
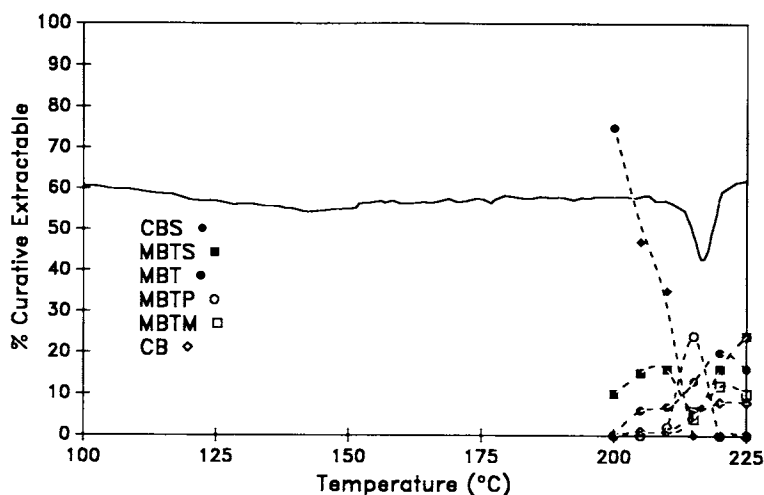
Figure 1 Analysis of the IR/CBS vulcanization system. DSC curve, heating rate 2.5°C/min, initial mass, M_i = 21.1213 mg, final mass, M_f = 20.8615 mg %. Curative extractable (– – –).

availability of elemental sulfur. Note that, as in the absence of elemental sulfur, decomposition of most of the CBS to MBTS and MBTP takes place prior to the onset of the vulcanization exotherm.

IR/CBS/Sulfur/MBT

The addition of MBT to the IR/CBS/sulfur system brings about a slightly earlier initiation of crosslinking. The occurrence of two distinct events is now evident in the DSC curve (Fig. 4), the maximum crosslink density coinciding with the start of the second process. The CBS all decomposes before any crosslinking takes place, leaving only MBTP, MBTS, and MBT (as well as the amine fragment). Despite the crosslink density being similar to that in the absence of MBT, the amount of MBT liberated during crosslinking is very low (< 20%) and declines towards the end of the reaction. MBT is known[16–18] to catalyse the decomposition of CBS to MBTS and cyclohexylamine, and the MBTS concentration is high early in the heating program. Its concentration reaches a minimum at the onset of crosslinking but then increases again and reaches a value of about 55%, at which it remains constant up to 220°C.

IR/CBS/Sulfur/ZnO

The vulcanization exotherm of IR/CBS/sulfur/ZnO starts at T_o = 145°C (Fig. 5). The presence of ZnO changes the DSC curve associated with vulcanization and two exotherms are observed, one with a peak at 150°C, and the second with a peak at 165°C. Crosslinking occurs during the first exotherm and reversion dominates during the second. The CBS is utilized very quickly with the accompanying release of MBT. Very little MBTS is extractable in this system (Fig. 5). The crosslink density reaches a very high level, $1/2M_c$ = 16.5 × 10^{-5} (Table I). The sulfur efficiency is 11 sulfur atoms per crosslink at the maximum crosslink density. The crosslink density decreases very rapidly after the sulfur has been consumed.

DISCUSSION

IR/CBS and IR/CBS/Sulfur Systems

In the absence of rubber the products of the early stages of thermal degradation of CBS and sulfur are mainly the polysulfides of CBS (CBPs) together with small amounts of MBTS and its polysulfides (MBTP).[16] On heating an IR/CBS/sulfur compound, the CBS concentration initially decreases slowly and no CBPs are detectable in the extract, but the MBTS concentration, and later (150°C) the MBTP concentration, build up to very much higher values than are found in the absence of rubber[16] (Fig. 3). This points to the degradation of CBS being affected by interaction with rubber. As the highly reactive CBPs, the main degradation products of CBS,[16] are not detected, it is apparent that these rapidly add to the rubber chain. A substitution reaction would lead to polysulfidic benzothiazole terminated pendent groups, while cyclohexylamine would be liberated. Scheele and Helberg[2] report free
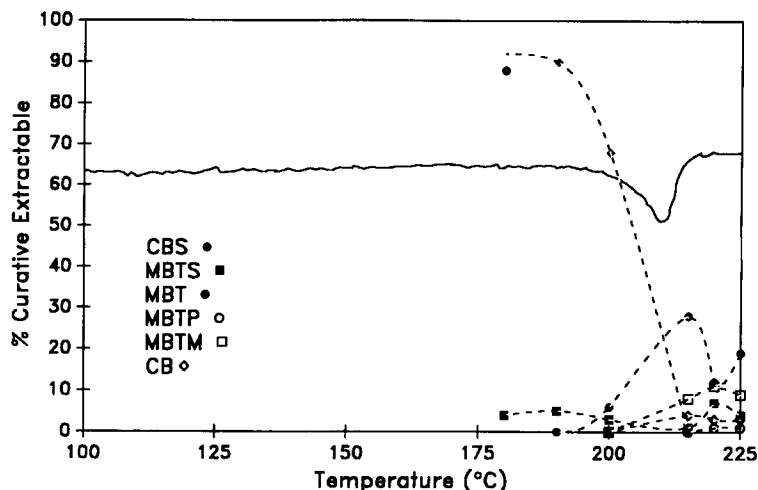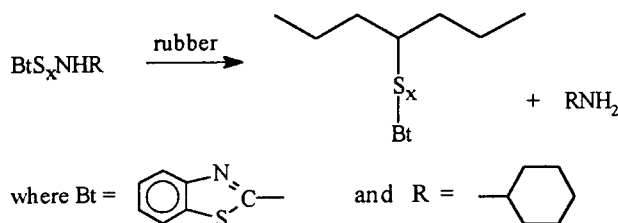
Figure 2 Analysis of the IR/CBS/ZnO vulcanization system. DSC curve, heating rate 2.5°C/min, initial mass, M_i = 21.4113 mg, final mass, M_f = 21.1275 mg %. Curative extractable (– – –).

amine in a CBS vulcanizate, which supports a substitutive rather than an additive reaction.

Note that up to this stage of the reaction the amount of extractable sulfur remains high, indicating the small amounts of sulfur involved in CBP and BtS_x—pendent group formation. This low sulfur consumption is in agreement with Scheele.[6] No crosslinking occurs until all of the CBS has decomposed in accord with CBS being a delayed action accelerator.[2,3,19,20] The delay in the onset of crosslinking and the high MBTS concentration present at this stage of the reaction can best be explained in terms of an exchange reaction involving CBS and BtS_x—pendent groups.

These BtS_x—pendent groups would initially be formed via a substitutive reaction involving CBP, but as the MBTS and MBTP concentrations increase, also via the reaction of MBTP with the rubber.[12]

Scheele and Helberg[2] found that the cyclohexylamine content in the vulcanizate reached a max-

imum (55%) when the CBS was used up. This would accord with the above scheme in which about 50% of the amine would be free and 50% bound to the rubber following the CBS/BtS_x—pendent group exchange. Indeed, changes in the concentration of extractables reported by Scheele and Helberg[2] are in good agreement with the data in Figure 3. The high MBTS and MBTP concentrations that develop should initiate crosslinking in accord with the reaction found in the IR/MBTS/sulfur system,[12] but any BtS_x—pendent groups formed would interact with CBS, delaying crosslinking.

Coran,[5] too, suggested the formation of amine crosslinking precursors as opposed to benzothiazole precursors but did not indicate how these formed or subsequently participated in the crosslinking process. Campbell and Wise,[21,22] in a similar study involving the sulfenamide 2-(4-morpholinodithio)-benzothiazole sulfenamide (MOR), suggested that the cure delay was due to the reaction of MOR with polysulfides rather than with rubber, the conversion to polymeric polysulfides (BtS_xBt) of higher sulfur rank increasing throughout the scorch delay period. This study supports the increase in MBTP prior to crosslinking, but it would be difficult to explain the high crosslink density that results if the crosslinking resulted merely from a build up of BtS_xBt. Lieb et al.[23] suggested that MBT (which, according to them, was not detected during the scorch delay because it was so active) would decompose CBS, giving MBTS that, on forming BtS_x—pendent groups, would release more MBT for the further attack on CBS. However, it is not clear from their theory why the BtS_x—pendent groups, that are subsequently in-
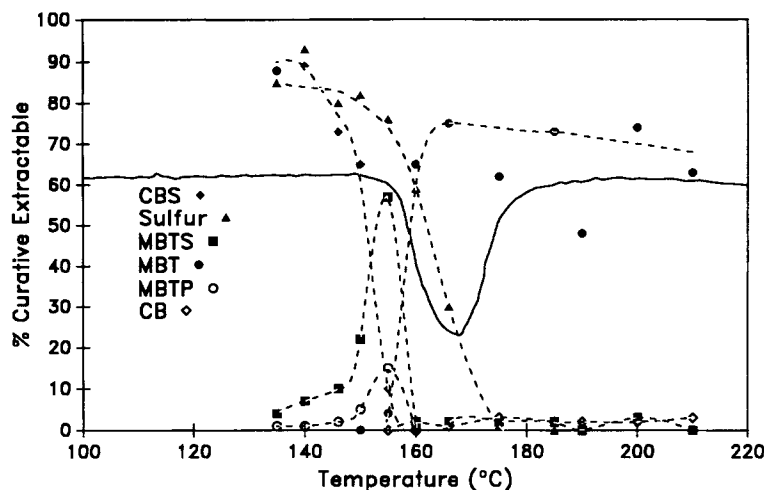
Figure 3   Analysis of the IR/CBS/sulfur vulcanization system. DSC curve, heating rate 2.5°C/min, initial mass, M_i = 21.2485 mg, final mass, M_f = 21.0290 mg %. Curative extractable (- - -).

volved in crosslinking, delay doing so until all of the CBS has been consumed. As in this article, Scheele and Helberg[2] suggested CBS attack on groups present on the chain at this stage. Their mechanism was, however, quite different to that proposed here. In their view, the induction period was due to attack of sulfur on rubber via a radical mechanism as originally suggested by Farmer and Shipley.[24] This would lead to polysulfidic pendent groups terminated by hydrogen (perthiols) abstracted from a neighboring chain. In the presence of CBS, crosslinking will not occur until all of the sulfur has been consumed because CBS will react with the hydrogen on the perthiol. However, it should be remembered that

initiation of crosslinking by sulfur is a slow process, while CBS accelerated vulcanization is fast.

Once all of the CBS has been consumed, destruction of benzothiazole pendent groups ceases. Note that at the point at which all of the CBS has reacted more than 85% of the benzothiazole groups can be accounted for in the extract. This supports the contention that BtS_x—pendent groups on the chain are replaced by $RNHS_x$—groups. The high concentration of MBTS and MBTP present at this stage, together with the availability of 80% of the sulfur, will lead to a rapid crosslinking process similar to that which applies to the MBTS accelerated system.[12] This involves BtS_x—pendent groups, resulting from

Table I   Crosslink Density, $\frac{1}{2}M_c$ ($\times 10^5$), for CBS Accelerated Vulcanization Systems

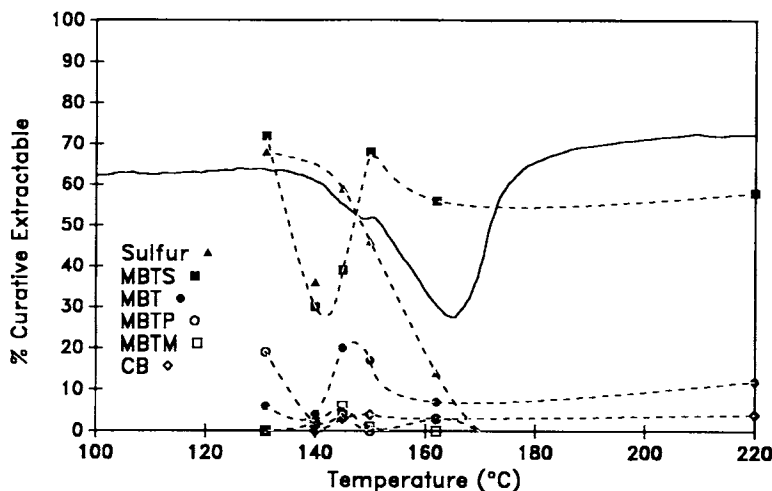| Temperature (°C)	IR/CBS/Sulfur	IR/CBS/Sulfur/MBT	IR/CBS/ZnO/Sulfur
140	0	Gel	0
146	0	3.95	Gel
150	0	6.95	3.54
155	Gel	—	16.50
160	5.70	4.36	13.72
166	7.35	—	8.54
175	2.30	—	—
176	—	—	4.75
180	—	—	4.95
185	2.16	—	—
190	2.31	—	4.67
200	2.64	—	—
210	1.10	—	—
212	—	—	3.61

Figure 4 Analysis of the IR/CBS/sulfur/MBT vulcanization system. DSC curve, heating rate 2.5°C/min, initial mass, M_i = 23.3366 mg, final mass, M_f = 22.7208 mg %. Curative extractable (– – –).

MBTP addition, crosslinking with neighboring chains, releasing MBT. As in the IR/MBTS/sulfur system,[12] the appearance of MBT is coupled with the formation of the first gel and its concentration builds up rapidly.

The maximum crosslink density is very similar to that in the IR/MBTS/sulfur compound[12] (1/ $2M_c$ = 6.48 × 10⁻⁵ mol/mL for MBTS/sulfur vs. 7.35 × 10⁻⁵ mol/mL for CBS/sulfur) as are the initial reaction temperatures and crosslink efficiencies. However, because 1 mol of CBS can at most form 1/2 mol of MBTS, the MBTS concentration in the CBS system would be much lower than in the MBTS formulation. In comparing the IR/CBS and IR/

MBTS systems,[12] where the same would apply, it is noted that the crosslink density in the former system is 10 times that in the latter system. Crosslinking is particularly rapid in the CBS/sulfur system, much more so than in the MBTS/sulfur system, while the MBTS and MBTP concentrations drop to virtually zero immediately crosslinking commences. Sulfur decreases more slowly. The difference between the CBS system and a MBTS accelerated system must be ascribed to the amine fragment of the accelerator which, in terms of the reaction sequence proposed above, is attached to the chain as pendent groups following the CBS/BtS$_x$—pendent group exchange reaction. It is unlikely that these groups would, on
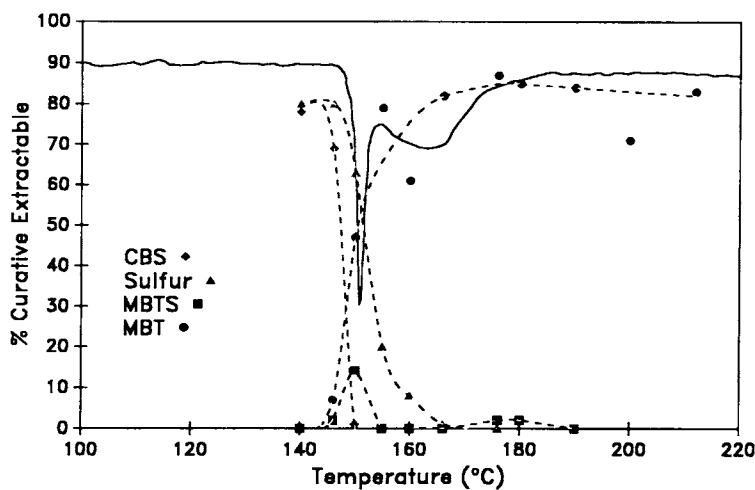

Figure 5 Analysis of the IR/CBS/ZnO/sulfur vulcanization system. DSC curve, heating rate 2.5°C/min, initial mass, M_i = 18.8780 mg, final mass, M_f = 18.4393 mg %. Curative extractable (– – –).

their own, lead to crosslinking, for if they did so, it is difficult to see why this reaction does not also take place prior to the CBS being consumed. Crosslinking could involve reaction between benzothiazole and amine terminated polysulfidic pendent groups, regenerating CBS that is rapidly decomposed by MBT[16] present in the system at this stage.

BtSNHR + BtSH ⟶ BtSSBt + RNH₂
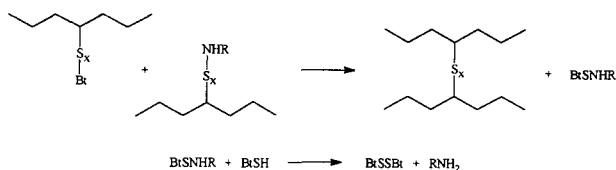
However, the above reaction is not likely to be a major route to crosslinking. Reaction between such pendent groups will not increase the crosslink density beyond that achievable by BtS_x—groups reacting with neighboring chains, though the regeneration of MBTS will lead to some further crosslinking.

Instead, it is suggested that an exchange reaction occurs between MBT, liberated when BtS_x—pendent groups crosslink, and the $RNHS_x$—pendent groups.

The CBS produced will suffer very rapid degradation by MBT, the concentration of which is now very high.

BtSNHR + BtSH ⟶ BtSSBt + RNH₂
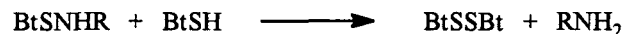
(MBTS formed on degradation of CBS will initiate further crosslinking via MBTP and pendent group formation and, thus, is not regenerated.)

Crosslinking may now occur between BtS_x—and HS_x—pendent groups, nitrogen in the benzothiazole group abstracting hydrogen from the HS_x—group rather than from a neighboring polymer chain.
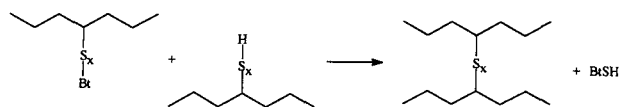
Once all of the MBTS (MBTP) has been consumed, crosslinking will be initiated mainly by MBT (or the amine salt of MBT), the concentration of which is high at this point. Despite the formation of crosslinks via the MBT accelerator, the overall crosslink density decreases as was also found when all of the MBTS had reacted in the IR/MBTS/sulfur system.[12] Scheele and Helberg,[2] too, note that

reversion occurs just before all of the sulfur has been consumed.

If any CB were formed in the crosslinking sequence, this would equate to a minor event and the small amount of CB found in these systems can be considered to be a product of CBS degradation.[1] In the absence of sulfur, where the amounts of MBTS that result via CBP addition to the chain and CBS exchange are lower, the CB and MBTM concentrations are higher. Both are stable degradation products.

Effect of MBT

Figure 4 shows that degradation of CBS occurs rapidly at a lower temperature in the presence of MBT and the DSC curve of the IR/CBS/sulfur/MBT system shows that the first exotherm shifts to a correspondingly lower temperature. It remains difficult to ascribe a particular event to the second exotherm.

MBT will catalyze the degradation of CBS,[16] leading to high MBTS concentrations at lower temperatures. Pendent groups now form mainly via a MBTS additive reaction as the CBP concentration soon decreases to zero (Fig. 4). Note that the sulfur concentration had decreased to 36% before gel formation as opposed to sulfur concentrations in excess of 65% in cases where BtS_x—pendent groups form via CBP. As MBT was added to the system, the amine released on catalyzed degradation of CBS can now be trapped as the amine salt. It is proposed that the MBTS concentration does not decrease to zero as MBTS is regenerated when the amine salt exchanges with BtS_x—pendent groups to give a perthiol that participates in the crosslinking process.
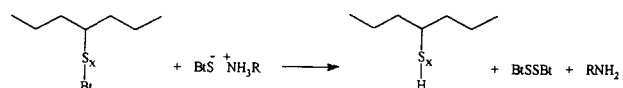
As CBS degraded, rather than added, to the polymer, most of the pendent groups are BtS_x—formed via MBTS addition rather than $RNHS_x$—formed via CBP exchange reactions. Thus, interaction with the amine salt will ensure regeneration of larger amounts of MBTS. Indeed, the MBTS concentration increases after reaching a minimum value at 145°C (Fig. 4). As suggested earlier, reaction between the perthiol and a BtS_x—pendent group will lead to crosslinking.

BtSH + RNH₂ ⟶ BtS⁻ + ⁺NH₃R
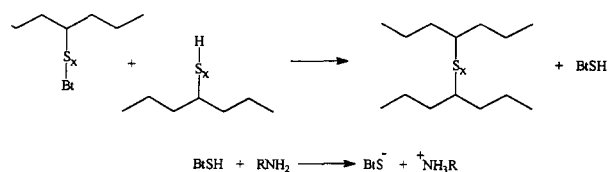
The MBT (salt) concentration does not continue to increase, as occurs when the amine salt does not form. Instead, it is involved in the exchange reaction, and though regenerated, there is a small decrease in its concentration as the reaction progresses.

Notice that in the IR/CBS system (i.e., in the absence of sulfur) the MBTS concentration does not decrease to zero at high temperatures, but in fact, increases after a minimum at 215°C (Fig. 1). At these temperatures MBTS will lead to rapid vulcanization[12] and the fact that its concentration remains high can be explained as follows. In the absence of sulfur, the formation of CBP is more difficult and reaction occurs only at very high temperatures (> 200°C). The disappearance of CBS is slower and a small amount of MBT is produced as a high temperature degradation product[1] while the CBS concentration is still high. Thus, cyclohexylamine liberated by the addition of CBP to the chain and by MBT catalyzed degradation[1] of CBS to MBTS will, in the presence of this MBT, be trapped as the amine salt. The amine salt and BtS_x—pendent groups will undergo a sulfide exchange reaction to yield a polysulfidic pendent group terminated by hydrogen (perthiol), MBTS, and cyclohexylamine as discussed above. In IR/CBS/ZnO, IR/CBS/sulfur, and IR/CBS/sulfur/ZnO compounds there is no free MBT present early in the reaction and cyclohexylamine liberated during degradation of CBS escapes from the system. Following the consumption of all of the MBTS formed in the reaction process, the remaining sulfur is consumed via a MBT type reaction. In IR/CBS and IR/CBS/sulfur/ MBT compounds there is some free MBT present at the outset of the reaction, and this results in some of the amine formed being trapped as an amine salt of MBT. As crosslinking progresses, the sequence of reactions is altered and the MBTS concentration does not fall to zero but MBTS is regenerated.

Effect of ZnO

Interestingly, the shape of the DSC exotherm for the IR/CBS/sulfur/ZnO (Fig. 5) system equates to that found in the absence of rubber.[16] This suggests that the thermal events are associated with the degradation of CBS and the formation of its degradation products, rather than with crosslinking. The first sharp exotherm coincides with the very rapid disappearance of CBS, followed almost immediately by the very rapid increase in crosslink density. Reversion occurs during the second exotherm though, as a similar exotherm was obtained in the absence of rubber, it is difficult to ascribe it

to any particular event. In the absence of rubber, the degradation curves for the CBS/sulfur and CBS/sulfur/ZnO are identical,[16] there being no interaction between CBS and ZnO. In the presence of rubber, these exotherms differ (cf. Figs. 3 and 5). With no ZnO, the first sharp exotherm appears to be absent, though as rapid degradation of CBS occurs only at higher temperatures in this system, the exotherm may well have merged with the second exotherm.

CBS does not react with ZnO to form a zinc–accelerator complex.[32] In the presence of ZnO, the overall reaction sequence is not much affected, crosslinking occurs somewhat earlier, is very rapid, and a high crosslink density is attained (Table I). The formation of CBP and its addition to the chain occurs very rapidly above 146°C, somewhat earlier than in the absence of ZnO. CBS/BtS_x—pendent group exchange again leads to MBTS. Once all of the CBS has been consumed rapid crosslinking and MBT release follows. The high crosslink density can be attributed to ZnO particles facilitating abstraction of pendent groups and favoring crosslinking rather than cyclization.[12] MBT will react with ZnO to form zinc mercaptobenzothiazole $(Zn(mbt)_2)$, but this will decompose rapidly under vulcanization conditions where it is attacked by persulferyl anions that will form on scission of polysulfidic crosslinks.[11] Hence, the MBT remains extractable $(Zn(mbt)_2$ is insoluble). MBTS is not regenerated in crosslinking, suggesting that, as in the absence of ZnO, cyclohexylamine produced at the stage when CBS added BtS_x—groups to the chain, escaped from the system and the amine salt of MBT was not formed.

In the absence of sulfur (IR/CBS/ZnO system), extractable MBT is not found in the early stages of reaction despite the fact that some must be produced in the high temperature degradation of CBS (Fig. 2). This can be explained by its being trapped as $Zn(mbt)_2$. $Zn(mbt)_2$ degradation occurs via polysulfidic anions[11] and none are present in the system at this point. Once crosslinking starts MBT is found in the extract. Conditions are now favorable for $Zn(mbt)_2$ decomposition and liberation rather than trapping of MBT. The same high concentration of MBTS as is found in the absence of ZnO (Fig. 1) does not apply here, the MBTS being consumed but not regenerated. This indicates that MBT was initially trapped by ZnO and could not trap cyclohexylamine to yield the amine salt needed for MBTS regeneration. Its liberation from the $Zn(mbt)_2$ occurred only once there was little or no amine left with which it could interact. Yet, as the MBTS concentration does not fall quite to zero at higher tem-

peratures, a small amount of amine salt, which re-generates MBTS by reaction with $RNHS_x$—pendent groups, is probably present.

CONCLUSIONS

It is proposed that CBS adds BtS_x—pendent groups to the polymer chain via CBPs in a substitutive re-action, but that these do not crosslink as they are rapidly exchanged for $RNHS_x$—pendent groups by reaction with CBS. The latter groups will not initiate crosslinking. The exchange reaction leads to the rapid buildup of MBTS and MBTPs in the system. Only once all of the CBS is consumed does the deac-tivation of BtS_x—pendent groups cease and a rapid crosslinking occurs via a MBTS type reaction. Crosslinking releases MBT. When free MBT is present in the system at the beginning of the reac-tion, it catalyzes the decomposition of CBS. This limits the amount of $RNHS_x$—pendent groups that end up on the chain, most of the CBS being degraded directly to MBTS and cyclohexylamine. Most im-portantly, this amine is now trapped by the available MBT to form the MBT-amine salt. This salt ex-changes with BtS_x—pendent groups to yield per-thiols that crosslink with BtS_x—groups. The ex-change reaction regenerates MBTS, the concentra-tion of which remains high as vulcanization progresses.

Vulcanization systems that contain ZnO lead to very high crosslink densities. This is attributed to the effect of ZnO in assisting in the removal of pen-dent groups during crosslinking and favoring inter-molecular reactions over the analogous intramolec-ular process.

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