The Reactions of 2-(4-Morpholinothio)- and 2-(4-Morpholinodithio) Benzothiazole in the Absence of Polyisoprene

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ABSTRACT: 2-(4-morpholinothio)benzothiazole (MOR) and 2-(4-morpholinodithio) benzothiazole (MDB) were heated with sulfur and ZnO in a DSC. The products formed at various temperatures were identified and analyzed by HPLC. At temperatures below 200°C, decomposition of the accelerator in the absence of other curatives was slow, degradation products being mainly 2-bisbenzothiazole-2,2'-disulfide (MBTS) and 2mercaptobenzothiazole (MBT). A rapid exothermic decomposition above 200°C resulted in the formation of MBT (or its amine salt) and 2-(4-morpholino)benzothiazole (MB). MOR and MDB reacted with sulfur to form higher polysulfides. MDB was shown to react more readily with sulfur than MOR and the delayed action of MOR in rubber can therefore not be ascribed to a stable polysulfide as suggested by other authors. Neither MOR nor MDB was found to react with ZnO. A limited reaction between MBT and ZnO was observed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1235–1240, 1999

Key words: MOR; polyisoprene; MBT; MBTS; ZnO

INTRODUCTION

Commercially, sulfenamides are important accelerators for the vulcanization of rubber. McGill et al.^{1–5} have suggested that a study of the interactions of curatives in the absence of rubber can contribute to understanding reactions that occur during the early stages of the vulcanization process. Gradwell and McGill¹ studied the reactions of *N*-cyclohexyl-2-benzothiazolesulfenamide (CBS), 2-(4-morpholinothio)benzothiazole (MOR), and 2-*t*-butylbenzothiazolesulfenamide (TBBS), in the absence of rubber. The sulfenamides decomposed rapidly between 200 to 220°C.¹ Below 200°C limited degradation occurred, in the case of MOR yielding 2-(4-morpholino)benzothiazole (MB), 2-bisbenzothiazole-2,2'disulfide (MBTS), 2-bisbenzothiazole-2,2'-monosulfide (MBTM), and 2-(4-morpholindithio)benzothiazole (MDB), while the final products were 2-mercaptobenzothiazole (MBT), possibly as the MBT-amine salt, and the unsulfurated, sulfenamide species, MB. Banks and Wiseman⁶ reported similar products, but like Gradwell and McGill,^{1,2} did not give quantitative data. Morita and Young⁷ suggested that the induction period observed with sulfenamides was due to the formation of more stable intermediates such as MDB in MOR systems.

This article compares the stability of MOR and MDB on heating in the absence of rubber and the interaction of the two sulfenamides with sulfur and ZnO. It presents quantitative data on the formation of reaction intermediates.

EXPERIMENTAL

Unrefined, industrial grade MOR, produced by Bayer (Barcelona), sulfur by AECI (South Af-

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Figure 1 DSC curves of MOR and MDB (\cdots) heated at 2.5°C/min.

rica), and ZnO by Zinc Process (South Africa) were used. MDB was synthesized as described by Hardman.⁸

Curatives and mixtures of curatives in 1:1 mol ratios were sealed in aluminium DSC pans and heated in a DuPont 9000 DSC at 2.5° C/min. Highpurity nitrogen, at a flow rate of 65 mL/min, was used as a purge gas. The reaction was stopped at points along the DSC curve and the mixture analyzed by High-Performance Liquid Chromatography (HPLC), as described previously.^{1,2,9}

Amounts of curatives and products found are given as a percentage of the original curative used that was converted to that particular species, for example, 1 mol MOR would yield at most 0.5 mol MBTS, and this would be referred to as 100% MBTS (i.e., 100% conversion of MOR to MBTS)

RESULTS

MOR

The DSC curve (Fig. 1) showed that MOR melted at 84° C (85° C¹) and decomposed at 206° C (219° C¹). MOR had initial impurities of MBT (6 mol %) and MBTS (1 mol %). Decomposition occurred gradually after melting, and at 180° C 79 mol % MOR remained with MBT (13 mol %), MBTS (8 mol %), and MDB (1 mol %). The MBT-(morpholine) salt could not be separated from MBT on the HPLC, and hence, all MBT values could reflect MBT or MBT-(morpholine) salt concentration. A sample heated to the decomposition temperature showed 4 mol % of the MOR remaining, with the following products: MBT (9 mol %), MB (25 mol %), MDB (17 mol %), MBTM (11 mol %), MBTS (21 mol %), and 2-bisbenzothiazole, 2,2'-polysulfides (MBTPs), (2 mol %). After the exotherm (Fig. 1), all of the MOR had decomposed and only MBT (or its amine salt) (48 mol %) and MB (48 mol %) were present. The mass loss of 6.1% at 225°C indicated that the amine fragment, which accounts for 34% of the mass of MOR, had not evaporated (b.p. morpholine = $128^{\circ}C^{10}$). Banks and Wiseman⁶ showed that the amine fragment is possibly trapped as the amine salt of MBT.

MDB

The decomposition of MDB was analogous to that of the MOR system; MDB melted at 130°C and decomposed at 205°C (Fig. 1). As rapid decomposition occurred in the same temperature region as MOR, it appeared that the MOR and MDB have similar stabilities. Below 200°C decomposition of the MDB occurred slowly, and when heated to 170°C larger amounts of the major products, MBTS (13 mol %) and MBTM (11 mol %) were observed than were obtained with MOR. A mass loss of 2.9% at 225°C indicated that the amine had not evaporated. The exotherm at 205°C was smaller than that obtained with MOR. The final decomposition products of MDB were MBT (or its amine salt) and MB.

MOR/Sulfur

The addition of sulfur to MOR caused the thermal events observed with MOR to occur slightly earlier. The DSC curve of a 1 : 1 molar mixture of MOR and sulfur was characterized by two large endotherms and two exotherms (Fig. 2). The melting of MOR occurred at 78°C and that of sulfur at 105°C, while decomposition occurred at 199°C, compared to that of 205°C in the absence of sulfur. The exotherm at 160°C has been identified as the reaction of MOR with sulfur to form MDB.¹¹ This was verified by HPLC analysis; at 165°C, 16 mol % of MOR was in the form of the disulfide, MDB, and its higher polysulfides. Other products at 165°C were MBT (9 mol %), MBTM (12 mol %), MBTS (14 mol %), and MBTPs (7 mol %), and MB (2 mol %). As in the absence of sulfur, subsequent heating caused the decomposition of the thermally less stable species, shown by the strong exotherm, peaking at 199°C. MBT (51 mol %) and MB (43 mol %) were the final decomposition products at 225°C. Only 57 mol % sulfur remained, and a mass loss of 16.2 % was recorded at 225°C.

MDB/Sulfur

The DSC curve of MDB and sulfur (Fig. 2) showed an endotherm occurring at 81°C. The melting of MDB, which occurred at 130°C in the absence of sulfur, and that of sulfur, normally occurring at 105°C, both having decreased. Under the hot stage-optical microscope, the MDB crystals were seen to float in the sulfur, which liquified at 77°C, and then to dissolve completely by 92°C. The formation of the eutectic permitted intimate mixing of the two liquids, thus leading to the intermediate products forming more readily. HPLC analysis at 125°C showed the formation of MBT (20 mol %). MBTS (17 mol %). MBTM (21 mol %). and MBTPs (6 mol %). Decomposition also occurred earlier, starting at 175°C (Fig. 2) compared to 195°C (Fig. 1) in the absence of sulfur. The lower stability of MDB/sulfur mixes, compared to MOR/ sulfur, was evident from larger amounts of degradation products formed.

MOR/Sulfur/ZnO

The addition of ZnO to a MOR/sulfur mix had very little effect on the DSC curve (cf. Fig. 3 vs. Fig. 2). The MOR melt (77°C) and the sulfur melt (105°C) were still evident. The exotherm due to the formation of MDB was seen at 155°C and rapid decomposition of MOR occurred at 205°C. HPLC analysis showed the formation of an identical product spec-



Figure 2 DSC curve of MOR/Sulfur and MDB/Sulfur (\cdots) heated at 2.5°C/min.



Figure 3 DSC curve of MOR/Sulfur/ZnO and MDB/ Sulfur/ZnO (····) heated at 2.5°C/min.

trum to that of the MOR/sulfur system, at 155°C MOR (4 mol %), MDB (14 mol %), MORPs (3 mol %), MBT (9 mol %), MBTM (13 mol %), MBTS (15 mol %), MBTPs (3 mol %), and MB (2 mol %). At 225°C MBT (38 mol %), MB (50 mol %), and sulfur (63 mol %) remained, and a mass loss of 16.5% was recorded. The only noticeable change brought about the addition of ZnO was the lower MBT concentration. MBT has been shown² to react very readily with ZnO to form zinc mercaptoben-zothiazole $Zn(mbt)_2$, which was not soluble in the solvents used and, therefore, was not detected by HPLC.

MDB/Sulfur/ZnO

The DSC curve was essentially unaltered by the addition of ZnO to the MDB/sulfur mix. The eutectic melt was still seen at 89°C with decomposition occurring at 208°C (Fig. 3). The products of the reaction between MDB and sulfur in the presence of ZnO were the same as in its absence.

DISCUSSION

Decomposition of MOR and MDB

Both MOR and MDB decomposed at approximately 206°C (Fig. 1) to give similar products. CBS decomposed in the same temperature region,¹ suggesting an identical initiating step. The decomposition exotherms were very narrow, indicating a rapid reaction, as was also evident from HPLC analysis before and after the exotherm. Dogadkin et al.¹² proposed that, at vulcanization temperatures (140–160°C), N,N-diethylbenzothiazole dissociated to form benzothiazole and diethylamine radicals by scission of the weaker S—N bond. The product spectrum was explained in terms of S—N bond scission involving an analogous series of reactions to those proposed by Gradwell and McGill¹ for CBS decomposition.

$$\begin{array}{l} BtSNR_2 \Leftrightarrow BtS^{\bullet} + {}^{\bullet}NR_2\\ BtS^{\bullet} + BtS \Leftrightarrow BtSSBt\\ BtS^{\bullet} + BtSSBt \Leftrightarrow BtSBt + BtSS^{\bullet}\\ BtSSBt \Leftrightarrow Bt^{\bullet} + BtSS^{\bullet}\\ BtS^{\bullet} + Bt^{\bullet} \Leftrightarrow BtSBt\\ BtSS^{\bullet} + BtSS^{\bullet} \Leftrightarrow BtSSSBt\\ BtSS^{\bullet} + {}^{\bullet}NR_2 \Leftrightarrow BtSSNR_2 \end{array}$$

The amine fragment was not satisfactorily accounted for in the above reaction sequence. Cyclohexylamine boils at $134^{\circ}C^{10}$ and morpholine at $128^{\circ}C^{10}$ and should readily have escaped from the system at 200°C, yet only small mass losses were recorded. In line with other workers, Gradwell and McGill¹ also suggested that the amine may, in part, be trapped as the amine salt of MBT.

MDB, MBTM, MBTS, and MBTPs, detected before the apex of the reaction exotherm, were not present at higher temperatures. The reactions leading to formation of MB, which occurred at temperatures well above those of interest to vulcanization chemistry, was difficult to establish. Gradwell and McGill¹ showed that heating MBTS or MBTM with cyclohexylamine to 150°C led to the formation of CB and MBT (or its amine salt).

$$\begin{split} BtSSBt + HNR_2 \Rightarrow BtSH + BtNR_2 + S \\ BtSBt + HNR_2 \Rightarrow BtSH + BtNR_2 \end{split}$$

However, on heating MBTS with an excess of morpholine (a secondary amine) in an open tube in an oil bath, isothermally at 200°C for 5 min, the main product was MOR, together with MBT and a small amount of MDB. Failure of morpholine to decompose MBTS may account for the larger amounts of MBTS in MOR systems compared to CBS systems at temperatures below the decomposition exotherm. In the presence of sulfur, MOR was decomposed by morpholine at 200°C to yield MB, MBT, and H₂S. MDB, sulfur, and morpholine, also yielded MB, MBT, and H₂S. MB does not result from the decomposition of the amine salt because, in the absence of sulfur, the amine salt of MBT should also form when MOR decomposes, yet no H₂S was liberated and no mass loss was recorded. As the amount of MBT in the system at the peak of the exotherm was only 9 mol %, it is likely that most of the amine fragment was in fact present as dimorpholine, (R₂NNR₂). Banks and Wiseman⁶ suggested the formation of N,N'-dicyclohexyl hydrazine (HRNNRH) on decomposition of CBS. MB may be produced by the interaction of MBTS and dimorpholine.

 $BtSSBt + R_2NNR_2 \Rightarrow 2BtNR_2 + 1/4S_8$

The formation of small amounts of free sulfur (2%) was detected at these temperatures in the MOR systems.

The decomposition of the disulfidic accelerator, MDB, followed a closely similar route to MOR decomposition. The exotherms, indicating rapid decomposition of MOR and MDB, occurred at much the same temperature (Fig. 1), yet MBTS and MBTM formed more readily prior to the exotherm in MDB. 2-Bisbenzothiazole-2,2'-tetrasulfide was the most prominent MBTP that formed, and this points to the scission of the S—N bond in MDB.

$$BtSSNR_2 \Rightarrow BtSS^{\bullet} + {}^{\bullet}NR_2 \Rightarrow BtS_4Bt + R_2NNR_2.$$

Scission of the S—S bond would have resulted in the formation of 4,4'-dithiodimorpholine (DTDM), which could readily be detected by HPLC, but was not found. DSC analysis showed that DTDM is stable, decomposing rapidly only at 220°C. The high concentration of MBTM was surprising, and must have resulted from the breakdown of the less stable MBTPs.

Only MB and MBT (together with a small amount of sulfur) were present at temperatures above the exotherm. At no stage during MDB decomposition was MOR detected.

Reactions of MOR and MDB with Sulfur

Sulfur initiates the formation of intermediate species MBT, MBTS, MBTM, MBTPs, MDB, and MORPs in the temperature region where vulcanization takes place. The decomposition products were very similar to those found in the ab-

sence of sulfur, except for the higher concentration of polysulfidic species of the accelerator, namely MDB, MORPs, and MBTPs. BtS' radicals, formed on the breakdown of MOR or MDB, can abstract sulfur atoms from elemental sulfur as proposed by Gradwell et al.,¹³ and recombination reactions involving these radicals can lead to the formation of more highly sulfurated species. Gradwell et al.¹³ have shown that MBTS reacts much faster in the presence of sulfur than its absence and attributed this to the ease with which BtS' radicals can abstract sulfur atoms from elemental sulfur, thus decreasing the rate of BtS[•] radical recombination (the cage effect). Sulfur would similarly inhibit recombination of BtS[•] radicals from MOR or MDB decomposition, thus encouraging the reaction at lower temperatures and the formation of more highly sulfurated products.

In a MDB/sulfur mixture the sulfur and MDB melting endotherms merge into a single endotherm at 81° C. Polysulfide formation was observed at 125° C, indicating the ease with which the S—S bond in MDB is broken. At no stage was the formation of MOR observed. Clearly, the induction period observed with MOR accelerated vulcanization systems cannot be ascribed to the stability of MDB,⁷ the disulfide being more reactive towards sulfur than MOR (Fig. 2).

Reactions of MOR and MDB with ZnO

Almost all commercial formulations include ZnO, yet ZnO was found not to influence the reaction between curatives in the absence of rubber. In agreement with Gradwell and McGill,² the DSC curve (Fig. 3) did not indicate any new events nor did HPLC analysis reveal any change in the products. No reaction occurred between MOR and ZnO.

MBT reacts very readily with ZnO to form $Zn(mbt)_2$.² Although in some samples a decrease in the number of extractable Bt groups was noticeable, in the presence of ZnO, the MBT formed on decomposition of MOR in general did not react with ZnO. This can be attributed to the formation of the amine salt of MBT, which effectively blocked the MBT from reactions with ZnO.² However, more recent work in these laboratories¹⁴ have shown that, at vulcanization temperatures, the reaction between MBT ans ZnO is limited. Only during compounding, where $Zn-(mbt)_2$ formed around ZnO particles is sheared away, does the reaction go to completion.² A similar restriction on the reaction between stearic acid and ZnO has been reported.¹⁵

CONCLUSIONS

MOR and MDB decomposed rapidly above 200°C to yield MB and MBT (or the amine salt of MBT). The small mass loss at those temperatures was largely due to the evaporation of MB and MBT from DSC pans. At lower temperatures (120–180°C), where decomposition was less rapid, it could be seen that MDB decomposed more rapidly and was less stable than MOR, especially in the presence of sulfur. Thus, suggestions in the literature⁷ that the scorch delay in MOR accelerated vulcanization may be due to the stability of MDB, which forms from MOR prior to crosslinking, could not be substantiated.

The main degradation products of both MOR and MDB below 200°C were (1) the polysulfides of MOR, viz. MDB and MORP, (2) MBTS and its lower (MBTM) and higher sulfides (MBTP), (3) MBT or its amine salt, and (4) diamine (R_2NNR_2). The formation of the latter was implied and not proven.

Zinc-accelerator complexes are attributed to a major role in accelerated sulfur vulcanization, but it was shown that MOR (or MDB) and ZnO did not react to form $Zn(mbt)_2$. MBT and ZnO readily react, but no reaction occurred between MBT, liberated on decomposition of MOR, and ZnO and was attributed to the formation of $Zn(mbt)_2$ around the ZnO particle.

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