Benzothiazole-Accelerated Sulfur Vulcanization. IV. Effect of ZnO and Bis(2-mercaptobenzothiazole)Zinc(II) on 2-Bisbenzothiazole-2,2′-polysulfide Formation in 2-Bisbenzothiazole-2,2′-disulfide and 2-Bisbenzothiazole-2,2-disulfide/Sulfur

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ABSTRACT: The effect of ZnO and bis(2-mercaptobenzothiazole)zinc(II) [Zn(mbt)$_2$] on 2-bisbenzothiazole-2,2′-polysulfide (MBTP) formation in 2-bisbenzothiazole-2,2′-disulfide (MBTS) and MBTS/sulfur, in the absence of rubber, was studied by heating mixes isothermally for various times and analyzing products by HPLC. Both compounds accelerate MBTP formation but do not affect equilibrium concentrations. It is proposed that ZnO induces opening of the sulfur ring, permitting more rapid sulfuration of benzothiazole radicals (BtS), while with Zn(mbt)$_2$, exchange between sulfurated Zn(mbt)$_2$ and BtS radicals promotes their sulfuration. MBTP of lower sulfur rank form first and in the highest concentrations, while MBTP of higher sulfur rank form sequentially and form from MBTP of immediately lower sulfur rank. The concentrations of MBTP of lower sulfur rank pass through a maximum before equilibrating at lower concentrations. Reaction mechanisms to account for MBTP formation and the role of ZnO and Zn(mbt)$_2$ in accelerating the reactions are proposed. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 1405–1412, 2000

Key words: 2-bisbenzothiazole-2,2′-disulfide; 2-bisbenzothiazole-2,2′-polysulfide; bis(2-mercaptobenzothiazole)zinc(II); ZnO; sulfur

INTRODUCTION

The interaction between curatives to form active sulfurating agents is generally regarded as the first step in accelerated sulfur vulcanization.[1] On heating, disulfidic accelerators such as 2-bisbenzothiazole-2,2′-disulfide (MBTS)[2,3] and tetramethylthiuram disulfide (TMTD)[4,5] form polysulfides and these are attributed the role of active sulfurating agents in the absence of ZnO.[6,7] However, not all authors[8,9,10] proposed 2-bisbenzothiazole-2,2′-polysulfide (MBTP) formation from MBTS alone, and it has been suggested that MBTS vulcanizes by a similar mechanism to 2-mercaptobenzothiazole (MBT). In the presence of sulfur, MBTP formation is generally recognized[2,3,11,12] and vulcanization mechanisms involving MBTP have been proposed.[7,13,14] Following Kapur et al.,[2] Gradwell et al.[3] suggested that MBTS cleaved homolytically and that, in the absence of sulfur, BtS radicals abstracted sulfur from MBTS to yield high concentrations of MBTM and BtSS radicals. The latter radicals would continue to exchange sulfur with MBTS to produce MBTM and radicals of higher sulfur rank. In the

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presence of sulfur, MBTM production is limited, while MBTP production is increased and is attributed to BtS radicals abstracting sulfur atoms from cyclic sulfur in preference to MBTS, leading to radicals of progressively higher sulfur rank.[3] Resonance and conjugation were suggested to account for the stability of radicals of sulfur rank greater than two.[15,16]

MBTP production was considered to result mainly from radical recombination reactions and, to a lesser extent, from sulfur exchange by polysulfidic radicals with MBTP [reaction (1)]:

$$\mathrm{BtS}_x^\bullet + \mathrm{BtS}_y\mathrm{Bt} \leftrightarrows \mathrm{BtS}_{(x-1)}^\bullet + \mathrm{BtS}_{(y+1)}\mathrm{Bt} \qquad (1)$$

Kapur et al.[2] proposed that MBTS and ZnO react within 1 min at 150°C and ascribed the broad peak at 1350–1400 cm^{-1} in Raman spectra as characteristic of the bis(2-mercaptobenzothiazole)zinc(II) [$\mathrm{Zn(mbt)_2}$] formed, while the formation of $\mathrm{ZnOBt^+}$ was suggested on similar grounds. MBTP formed rapidly. Other authors, employing DSC[17] and X-ray diffraction,[18] questioned the formation of $\mathrm{Zn(mbt)_2}$ at vulcanization temperatures.

Coran[13] suggested that soluble zinc, produced from the reaction with fatty acids, changed the reaction pathway of MBTS-accelerated vulcanization, while Morrison[19] found more crosslinked products in 2-methyl-2-pentene when $\mathrm{Zn(mbt)_2}$ was present together with MBTS/sulfur. Benzothiazole-terminated pendent groups were not detected at 140°C and this was attributed to their rapid crosslinking in the presence of $\mathrm{Zn(mbt)_2}$. At 130°C, pendent groups were found.[19] $\mathrm{Zn(mbt)_2}$ is an accelerator in its own right, but if, as suggested,[17,18] it does not form in the reaction between MBTS and ZnO prior to the onset of crosslinking, MBTP must initiate the reaction. Thus, the accelerating effect of ZnO on vulcanization may, in part, be sought from its influence on MBTP formation. MBTP formation in the absence of ZnO has been reported in detail[3] and this article examined the influence of ZnO and $\mathrm{Zn(mbt)_2}$, frequently added to MBTS formulations, on MBTP formation in the absence of rubber.

EXPERIMENTAL

Materials

MBTS (chemical purity 93%, Orchem, Sasolburg, South Africa), $\mathrm{Zn(mbt)_2}$ (Bayer, Leverkusen, Germany), ZnO (Zinc Process, Cape Town, South Africa), and sulfur (98% soluble in $\mathrm{CS_2}$, AECI, Modderfontein, South Africa) were used. MBTS and $\mathrm{Zn(mbt)_2}$ were purified as described.[20] Mixes were prepared by grinding components with a pestle and mortar and the molar composition of each mix is given in parentheses in the text. Samples were heated in open DSC pans at 5°C/min or held isothermally for various times before dissolution in dichloromethane/methanol (5/95 v/v) and analyzed by HPLC as described.[3,21] In the present series of articles, an Altech Nucleosil C-18 reverse-phase column was used, as opposed to a μ-Bondapak C-18 reverse-phase column used in the study of MBTS reactions in the absence of ZnO.[3] The mobile phase was methanol/water (80/20 v/v) and was changed linearly to 100% methanol over a period of 2 h. In the figures, the initial concentration of reactants and products are expressed in terms of the initial concentration of the reactant.

RESULTS AND DISCUSSION

Mixes with ZnO

Heating MBTS/ZnO (1:1) in a DSC at 5°C/min produced a single MBTS melting endotherm with a maximum at 182°C. As reported earlier,[17,18] $\mathrm{Zn(mbt)_2}$ did not form as shown by the unchanged concentrations of MBTP formed on addition of ZnO. HPLC analysis showed the formation of MBTM and MBTP (Figs. 1 and 2), MBTP of higher sulfur rank forming sequentially (Fig. 2), as also found in the absence of ZnO.[3]

Holding MBTS/sulfur/ZnO isothermally at 152°C resulted in rapid MBTS and sulfur consumption (Fig. 3) with 20 and 55 mol %, respectively, remaining after 6 min. MBTP were produced rapidly from the outset (Fig. 4) and an additive concentration of 60 mol % was formed after 6 min. The system equilibrated at this point with only MBTM showing a slow, continued increase in concentration, although the total concentration attained was less than 2 mol % after 40 min; MBT was not detected.

MBTP of low sulfur rank are the most abundant, and the sequential formation of MBTP of higher sulfur rank, found in the absence of ZnO,[3] is also exhibited when ZnO is present (Figs. 2 and 4). Hence, we proposed that the addition of $\mathrm{S_8}$ to BtS[6,8,22] and the subsequent desulfuration of the highly sulfurated radical does not occur.

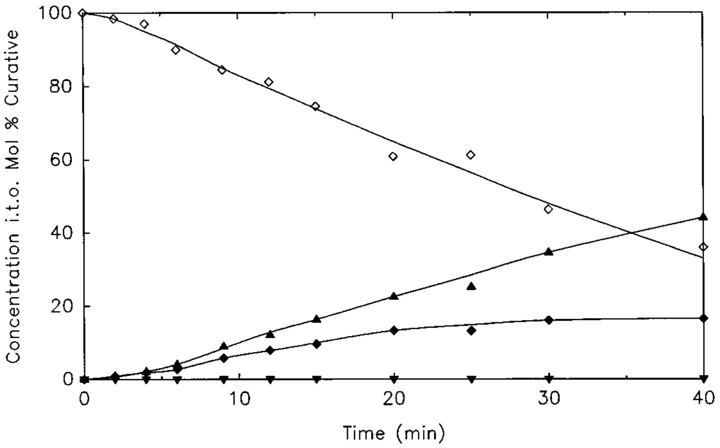


Figure 1 HPLC analysis of the MBTS/ZnO (1:1) system heated isothermally at 182°C: (▼) MBT; (◇) MBTS; (▲) MBTM; (◆) sum of BtS_xBt ($x = 3$–7).

MBTP formation appears to differ from that in the absence of ZnO (ref. 3) in that the concentration of MBTP of lower sulfur rank passes through a maximum before reaching equilibrium concentrations and the induction period[3] for MBTP formation is essentially removed. Equilibrium concentrations of MBTP were not affected by ZnO addition, showing that little or no $Zn(mbt)_2$ formed and, hence, the different behavior on addition of ZnO must originate from its influencing the reactivity of sulfur, rather than its interaction with MBTS. On heating sulfur with ZnO, up to 20 mol % of the sulfur could not be accounted for after rapid cooling, even if the solid residue was crushed and left for long periods to ensure complete dissolution in dichloromethane. Although sulfur may be adsorbed onto the surface of the ZnO particles, it is more likely that ZnO opened the sulfur ring and allowed the more ready formation of insoluble polymeric sulfur, accounting for the 20 mol % drop in extractable sulfur. Almost 100 mol % sulfur can be accounted for when heated to 150°C on its own.

It is proposed that reaction (1), previously[3] considered to be of lesser importance, is mainly responsible for the formation of MBTP of higher sulfur rank and that these form from MBTP of immediately lower sulfur rank :

$$BtSS^{\bullet} + BtS_3Bt \leftrightharpoons BtS_4Bt + BtS^{\bullet} \qquad (2)$$

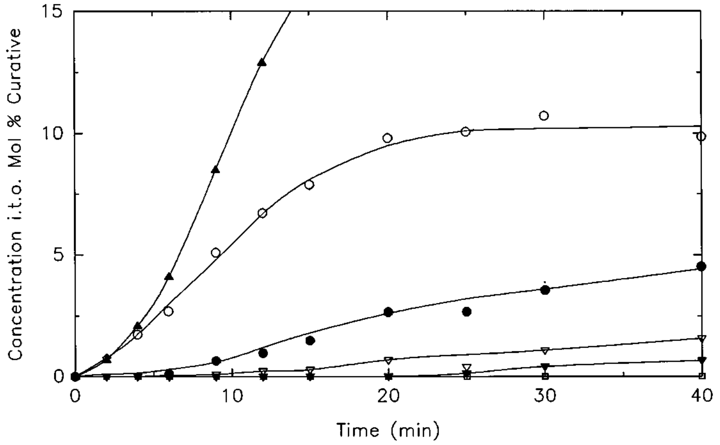


Figure 2 HPLC analysis of MBTM and MBTP formed when heating the MBTS/ZnO (1:1) system isothermally at 182°C: (▲) MBTM; (○) BtS_3Bt; (●) BtS_4Bt; (▽) BtS_5Bt; (▼) BtS_6Bt; (□) BtS_7Bt.

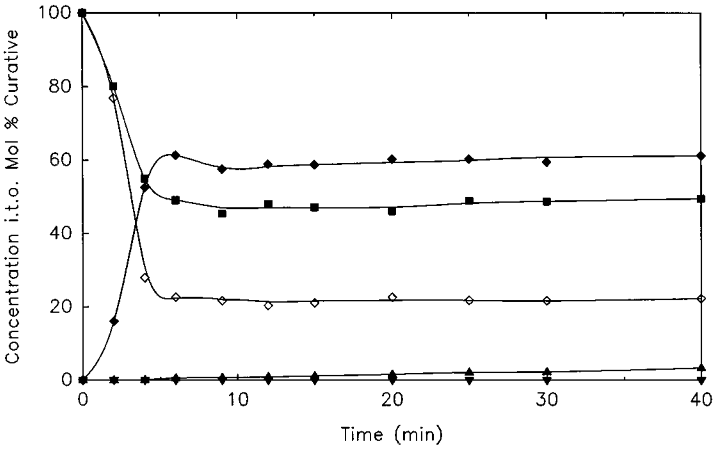


Figure 3 HPLC analysis of the MBTS/sulfur/ZnO (1:1:1) system heated isothermally at 152°C: (▼) MBT; (◇) MBTS; (▲) MBTM; (◆) sum of BtS_xBt (x = 3–12); (■) sulfur.

The sequential formation of MBTP of higher sulfur rank is quite clear in Figures 2 and 4, as well as in similar systems in the absence of ZnO.[3] The formation of BtSS radicals requires only one sulfur abstraction from MBTS or from elemental sulfur, giving a species that can form higher-ranked MBTP at the expense of lower-ranked MBTP via reaction (2), as observed.

It is noticeable in Figure 4 that between 2 and 4 min the BtS_4Bt concentration increases more than does the BtS_3Bt concentration. The apparent lower increase in BtS_3Bt was due to its partial conversion to BtS_4Bt. Indeed, at 4 min, all MBTP showed a greater increase in concentration, compared to their concentrations at 2 min, than did BtS_3Bt. BtS_3Bt may form by recombination of the more plentiful BtS and BtSS radicals and partly via exchange between BtSS and MBTS [reaction (1)], while other MBTP will form essentially by reaction (1). As the MBTS concentration decreases, the rate of BtS_3Bt formation from radical recombination will decrease and its progressive conversion to BtS_4Bt will lead to a decrease in its initially high concentration. The formation of MBTP of progressively higher sulfur rank does not continue indefinitely, as suggested by reaction (1). MBTP of higher sulfur rank are less stable and will decompose more rapidly, giving radicals of different degrees of sulfuration that can recombine at random. Radical recombination and exchange reactions between MBTP of different sulfur rank assume increased importance as the

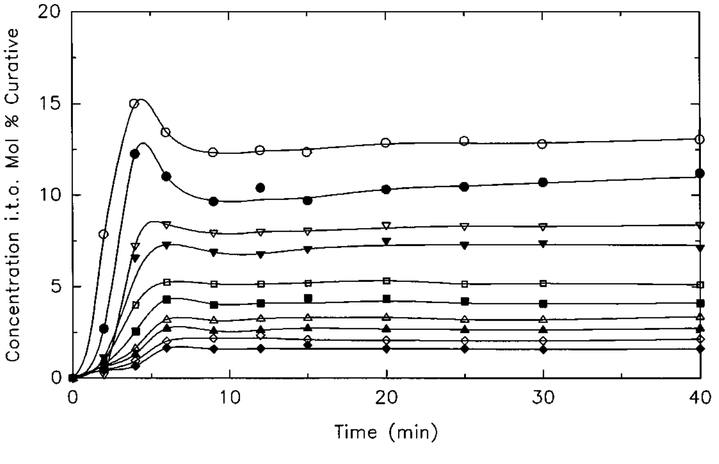


Figure 4 HPLC analysis of MBTP formed when heating the MBTS/sulfur/ZnO (1:1:1) system isothermally at 152°C: (○) BtS_3Bt; (●) BtS_4Bt; (▽) BtS_5Bt; (▼) BtS_6Bt; (□) BtS_7Bt; (■) BtS_8Bt; (△) BtS_9Bt; (▲) $BtS_{10}Bt$; (◇) $BtS_{11}Bt$; (◆) $BtS_{12}Bt$.

reaction proceeds and will determine the equilibrium concentrations that prevail. Comparison of the data in Figures 3 and 4 with those in Figure 4 of ref. 3 shows that at equilibrium MBTS/sulfur mixes contain 25 mol % MBTS, 13 mol % BtS_3Bt, 7 mol % BtS_4Bt, 6 mol % BtS_5Bt, and 5 mol % BtS_6Bt and that MBTS/sulfur/ZnO mixtures contain 20 mol % MBTS, 13 mol % BtS_3Bt, 11 mol % BtS_4Bt, 7 mol % BtS_5Bt, and 5 mol % BtS_6Bt. The total MBTP concentration in Figure 3 is higher than that reported for MBTS/sulfur mixes, but this is due to the use of a different HPLC column and eluting solvent that allowed MBTP of higher sulfur rank to be detected in the more recent study.

Thus, ZnO affects the rate at which the system reaches equilibrium by facilitating sulfuration of BtS radicals by facilitating opening of the sulfur ring. Equilibrium concentrations of MBTP are, however, determined by the slower exchange reactions. Comparison of the MBTS/ZnO system (Figs. 1 and 2) with the MBTS system (Fig. 2, ref. 3) shows the similarity in the ratios of products formed, although reaction in the presence of ZnO is noticeably faster. ZnO may facilitate scission of the S—S bond in MBTS in an analogous manner to its ring-opening activation of elemental sulfur.

Mixes with $Zn(mbt)_2$

During the mixing of the curatives [MBTS/$Zn(mbt)_2$ 1:1 and MBTS/$Zn(mbt)_2$/sulfur 1:1:1] in a pestle and mortar, an odor was observed (not H_2S) that dissipated quickly. Subsequent HPLC analysis revealed the formation of 5 mol % MBT, which remained constant during subsequent heating.

Heating MBTS/$Zn(mbt)_2$ (1:1 mol ratio) in a DSC at 5°C/min produced a single MBTS melting endotherm with a peak maximum at 176°C, although the onset of melting (150°C) was much earlier than in the absence of $Zn(mbt)_2$. On heating at 176°C, rapid MBTS consumption occurred from the outset and an equilibrium concentration of 20 mol % was attained after 15 min (Fig. 5). MBTP formed rapidly from the outset, although MBTP of higher sulfur rank were produced later and in lower concentrations, the additive equilibrium concentration being 18 mol % after 9 min. MBTP with a sulfuration of up to 9 were detected with BtS_3Bt being formed in highest concentration, its concentration passing through a maximum before equilibrating at a slightly lower value (Fig. 6). Reaction rates were very much faster than those obtained with either MBTS[3] or MBTS/ZnO systems (Fig. 1).

Heating MBTS/$Zn(mbt)_2$/sulfur (1:1:1) in a DSC at 5°C/min produced endothermic peaks at 113°C, associated with the melting of sulfur, and at 141°C, reflecting the dissolution of MBTS in the molten sulfur. MBTP formation at 141°C was much more rapid than in any of the other systems studied; equilibrium concentrations were achieved after 6 min (Figs. 7 and 8) and MBTP with a sulfuration of up to 12 were detected. The concentrations of lower sulfurated MBTP passed through a maximum.

The MBTS and MBTS/sulfur systems studied earlier[3] contained 3 mol % MBT as an impurity. MBT at this level had little effect on the rate of the reaction when compared to $Zn(mbt)_2$ (with 5 mol % MBT) in this study. Indeed, the MBTS/$Zn(mbt)_2$/sulfur mixture reacted much faster than

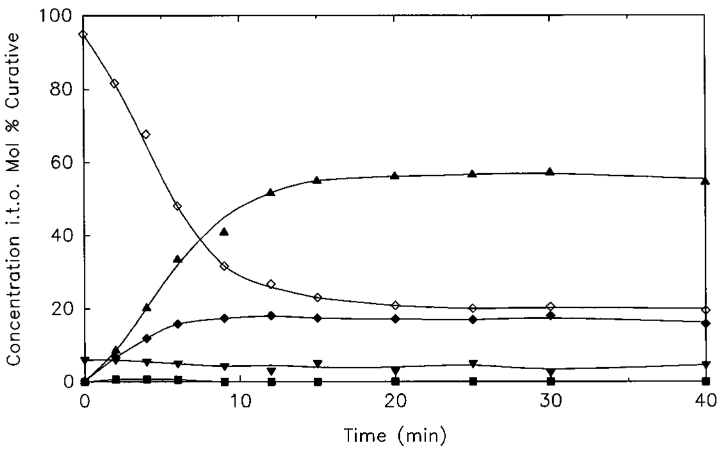


Figure 5 HPLC analysis of the MBTS/$Zn(mbt)_2$ (1:1) system heated isothermally at 176°C: (▼) MBT; (◇) MBTS; (▲) MBTM; (◆) sum of BtS_xBt (x = 3–9); (■) sulfur.

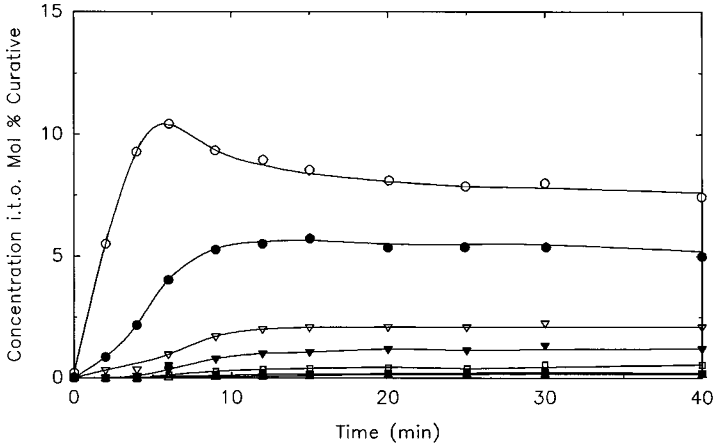


Figure 6 HPLC analysis of MBTP formed when heating the MBTS/Zn(mbt)$_2$ (1:1) system isothermally at 176°C: (○) BtS$_3$Bt; (●) BtS$_4$Bt; (▽) BtS$_5$Bt; (▼) BtS$_6$Bt; (□) BtS$_7$Bt; (■) BtS$_8$Bt; (△) BtS$_9$Bt.

was achieved on addition of 60 mol % MBT (MBTS/sulfur/MBT 1:1:0.6) in the earlier study.[3] Acceleration of the reaction must therefore be associated with Zn(mbt)$_2$. Ligand exchange between zinc-accelerator complexes was reported[23,24] and it is proposed that the ready exchange reactions between Zn(mbt)$_2$ and MBTS lead to the rapid formation of MBTM and the transient formation of sulfurated Zn(mbt)$_2$:

$$\text{BtSZnSBt} + \text{BtSSBt} \leftrightarrows \text{BtSZnSSBt} + \text{BtSBt} \quad (3)$$

$$\text{BtSZnSSBt} + \text{BtSSBt} \leftrightarrows \text{BtSZnSBt} + \text{BtS}_3\text{Bt} \quad (4)$$

This reaction may be indirect evidence for the transient formation of sulfurated Zn(mbt)$_2$ complexes. A further exchange between sulfurated Zn(mbt)$_2$ and MBTS will result in BtS$_3$Bt. The reaction will eliminate the induction period found with MBTS and will rapidly lead to high MBTM and BtS$_3$Bt concentrations (Figs. 5 and 6). Trace amounts of sulfur were detected in the early stages as would be expected if some BtSZnSSBt were to desulfurate without reacting further. MBTP of higher sulfur rank would form by sulfuration of lower MBTP, either by reaction with sulfurated Zn(mbt)$_2$ [reaction (4)] or with BtSS radicals [reaction (1)], thus accounting for the sequential formation of MBTP of higher sulfur rank and the concentration of MBTP of lower

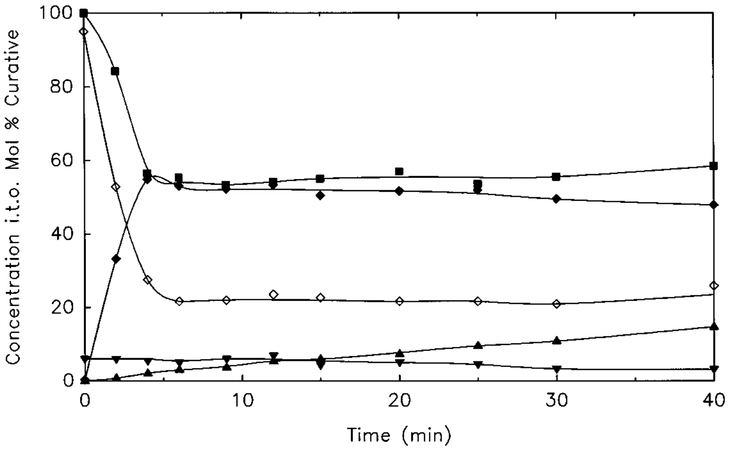


Figure 7 HPLC analysis of the MBTS/Zn(mbt)$_2$/sulfur (1:1:1) system heated isothermally at 141°C: (▼) MBT; (◇) MBTS; (▲) MBTM; (◆) sum of BtS$_x$Bt (x = 3–12); (■) sulfur.

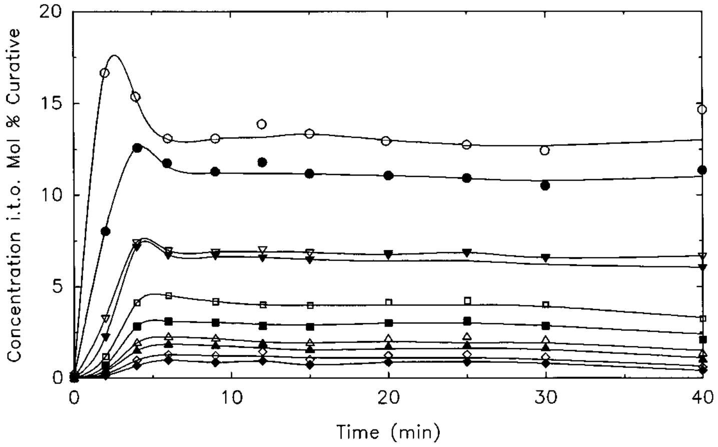


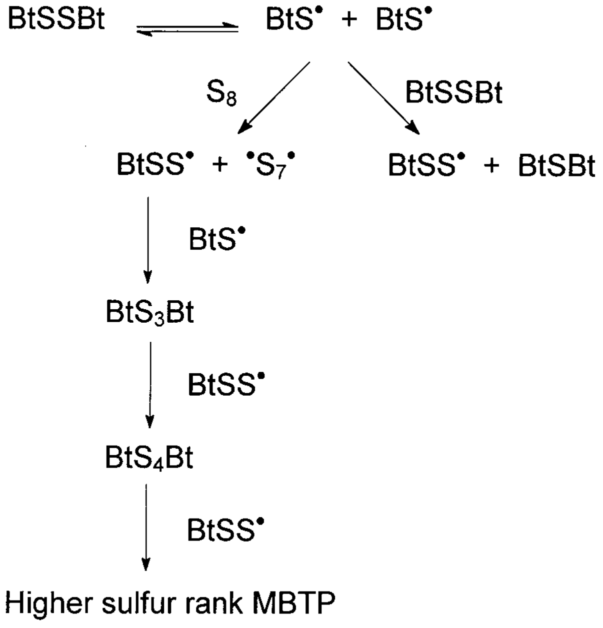
Figure 8 HPLC analysis of MBTP formed when heating the MBTS/Zn(mbt)$_2$/sulfur (1:1:1) system isothermally at 141°C: (○) BtS$_3$Bt; (●) BtS$_4$Bt; (▽) BtS$_5$Bt; (▼) BtS$_6$Bt; (□) BtS$_7$Bt; (■) BtS$_8$Bt; (△) BtS$_9$Bt; (▲) BtS$_{10}$Bt; (◇) BtS$_{11}$Bt; (◆) BtS$_{12}$Bt.

sulfur rank passing through a maximum. Ligand exchange is very rapid in the presence of sulfur[24] and it is proposed that the very rapid reaction in MBTS/Zn(mbt)$_2$/sulfur mixes results from the sulfuration of Zn(mbt)$_2$ by elemental sulfur. The sequential formation of MBTP of higher sulfur rank points to the incorporation of only one sulfur atom into Zn(mbt)$_2$, BtS$_4$Bt forming from the interaction of BtS$_3$Bt with sulfurated Zn(mbt)$_2$ or BtSS.

CONCLUSIONS

MBTP formation from MBTS and MBTS/sulfur is accelerated by the addition of ZnO and Zn(mbt)$_2$. It is proposed that the reaction is initiated by the homolytic dissociation of MBTS, BtS radicals abstracting a sulfur atom from MBTS, or preferentially from sulfur, when present, to give BtSS radicals. Recombination with BtS, the most plentiful radical in the system, leads to BtS$_3$Bt. It is proposed that BtS$_x$ radicals with $x > 2$ do not form by sulfuration. The sequential formation of MBTP of higher sulfur rank and the decrease in the initially high concentration of MBTP of lower sulfur rank are attributed to higher MBTP forming from lower MBTP via sulfur exchange with BtSS radicals. In the absence of an agent that will accelerate BtS$_3$Bt formation [ZnO, Zn(mbt)$_2$, MBT], a maximum in the concentration of MBTP of lower sulfur rank is not observed. This is solely due to their slower formation, allowing their conversion to higher sulfurated MBTP to more closely match their rate of formation. The accelerating effect of ZnO is ascribed to its opening of the cyclic sulfur ring, permitting the more rapid sulfuration of BtS radicals, and that of Zn(mbt)$_2$ to the exchange of ligands with MBTS, giving rise to sulfurated Zn(mbt)$_2$. Further exchange between the latter and MBTS yields BtS$_3$Bt. The reaction sequence is summarized in Scheme 1.

The equilibrium concentration of MBTP of different sulfur rank is not influenced by ZnO or Zn(mbt)$_2$ but is determined by more rapid disso-



Scheme 1 Proposed MBTP formation.

ciation of MBTP of higher sulfur rank and the random recombination of BtS_x radicals.

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