CHEMISTRY OF ACCELERATED SULFUR VULCANIZATION

List of Abbreviations

Bt	Benzothiazole group
MBT or BtSH	2- Mercaptobenzothiazole
MBTS or Br-SS-Bt	2-bisbenzothiazole-2,2′-disulfide
BTP or BtS-S_X-SBt	2-bisbenzothiazole-2,2′-polysulfide
BtS-Zn-S_X-SBt	Zinc-mercaptobenzothiazole polysufides
RH	Rubber
Bt-S_X*	Benzothiazole terninated polysulfidic radilcal
CDB	2-cyclohexyldithiobenzothiazole

- A- ACCELERATED CHEMISTRY
- B. CROSSLINKING CHEMISTRY
- C. POST-CROSSLINKING CHEMISTRY

A- ACCELERATED CHEMISTRY

- Formation of MBTS from MBS
- Reaction of sulfur with MBTS and other accelerator polysulfides
- Exchange reaction among accelerator-polysulfides
- Effect of ZnO-Formation of Zinc-Accelerator Complexes

B. CROSSLINKING CHEMISTRY

- Formation of crosslink precursors
- Conversion of crosslink precursors to crosslink
- Scorch delay reaction

C. POST-CROSSLINKING CHEMISTRY

- Crosslink desulfuration
- Crosslink degradation and main- chain-modification

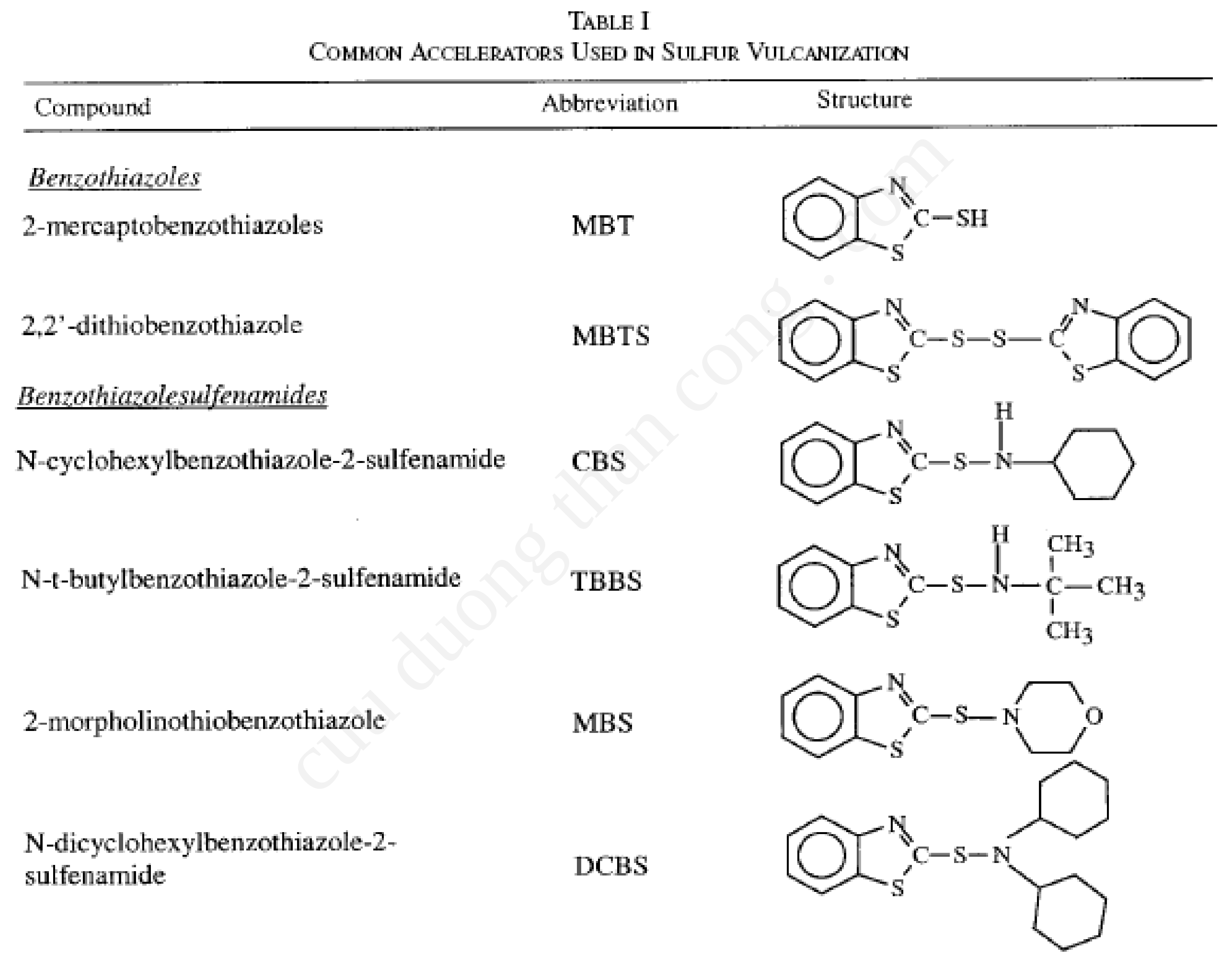


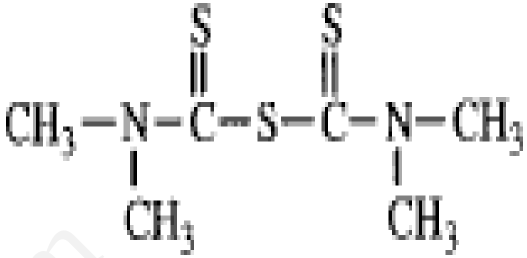
TABLE I
COMMON ACCELERATORS USED IN SULFUR VULCANIZATION

Compound	Abbreviation	Structure
Benzothiazoles		
2-mercaptobenzothiazoles	MBT	
2,2'-dithiobenzothiazole	MBTS	
Benzothiazolesulfenamides		
N-cyclohexylbenzothiazole-2-sulfenamide	CBS	
N-t-butylbenzothiazole-2-sulfenamide	TBBS	
2-morpholinothiobenzothiazole	MBS	
N-dicyclohexylbenzothiazole-2-sulfenamide	DCBS	

Thiurams

Tetramethylthiuram monosulfide

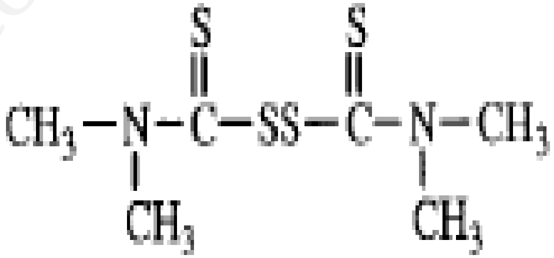
TMTM



$$CH_3-\underset{CH_3}{\underset{|}{N}}-\overset{S}{\overset{\|}{C}}-S-\overset{S}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{N}}-CH_3$$

Tetramethylthiuram disulfide

TMTD

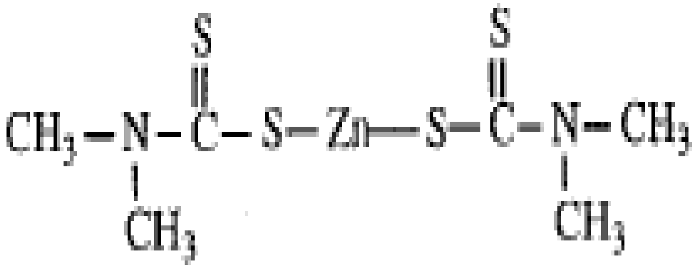


$$CH_3-\underset{CH_3}{\underset{|}{N}}-\overset{S}{\overset{\|}{C}}-SS-\overset{S}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{N}}-CH_3$$

Dithiocarbamates

Zinc Dimethyldithiocarbamate

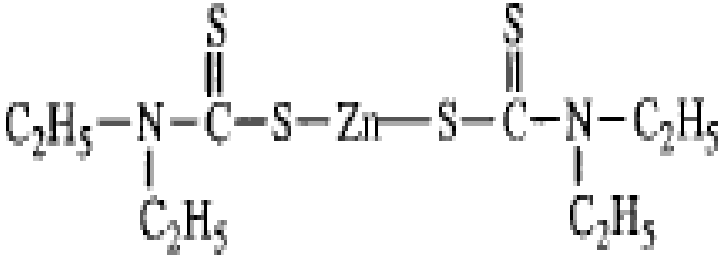
ZDMC



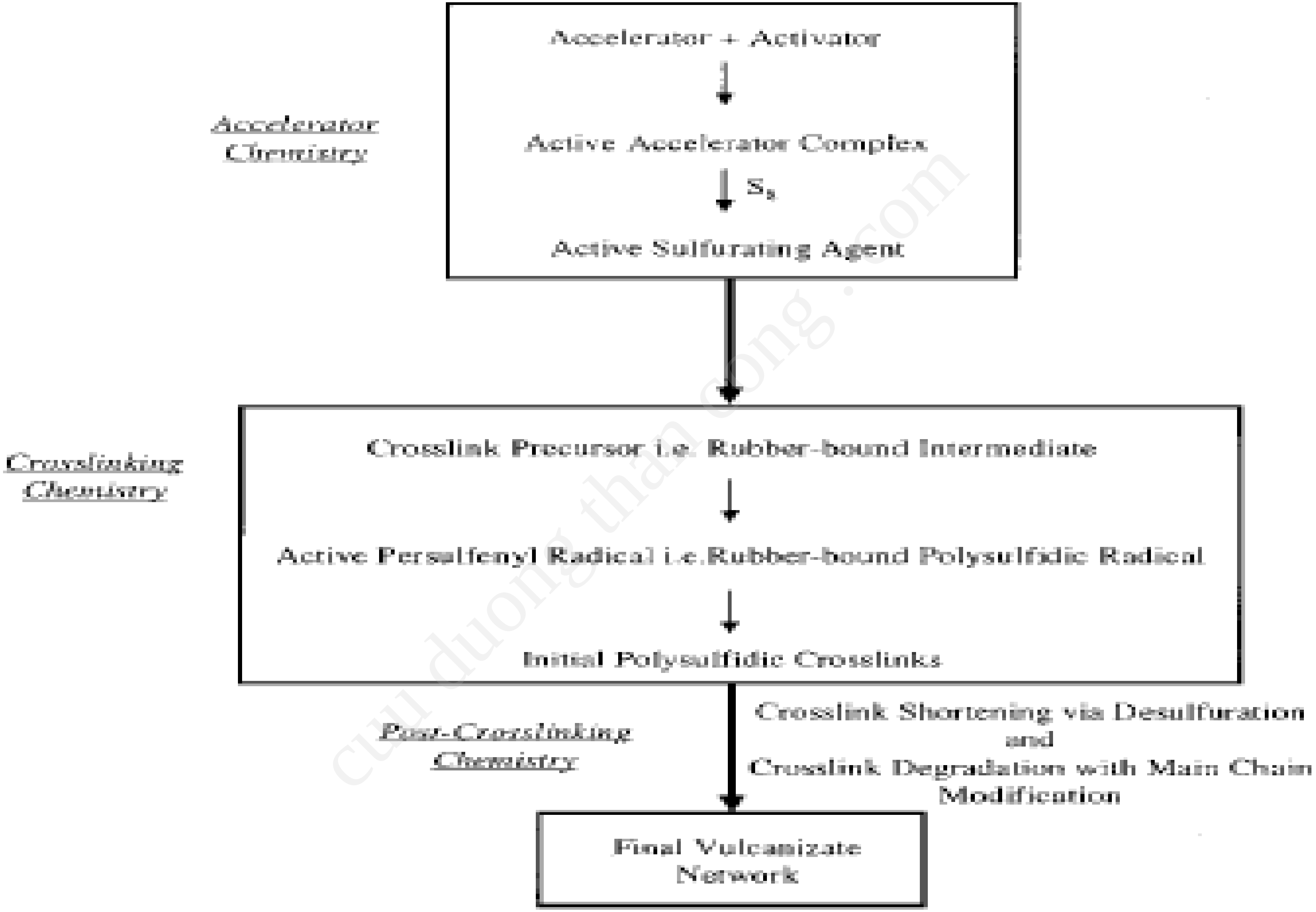
$$CH_3-\underset{CH_3}{\underset{|}{N}}-\overset{S}{\overset{\|}{C}}-S-Zn-S-\overset{S}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{N}}-CH_3$$

Zinc Diethyldithiocarbamate

ZDEC



$$C_2H_5-\underset{C_2H_5}{\underset{|}{N}}-\overset{S}{\overset{\|}{C}}-S-Zn-S-\overset{S}{\overset{\|}{C}}-\underset{C_2H_5}{\underset{|}{N}}-C_2H_5$$



Accelerator + Activator

Active Accelerator Complex

S_8

Active Sulfurating Agent

Accelerator Chemistry

Crosslink Precursor i.e. Rubber-bound Intermediate

Active Persulfenyl Radical i.e. Rubber-bound Polysulfidic Radical

Initial Polysulfidic Crosslinks

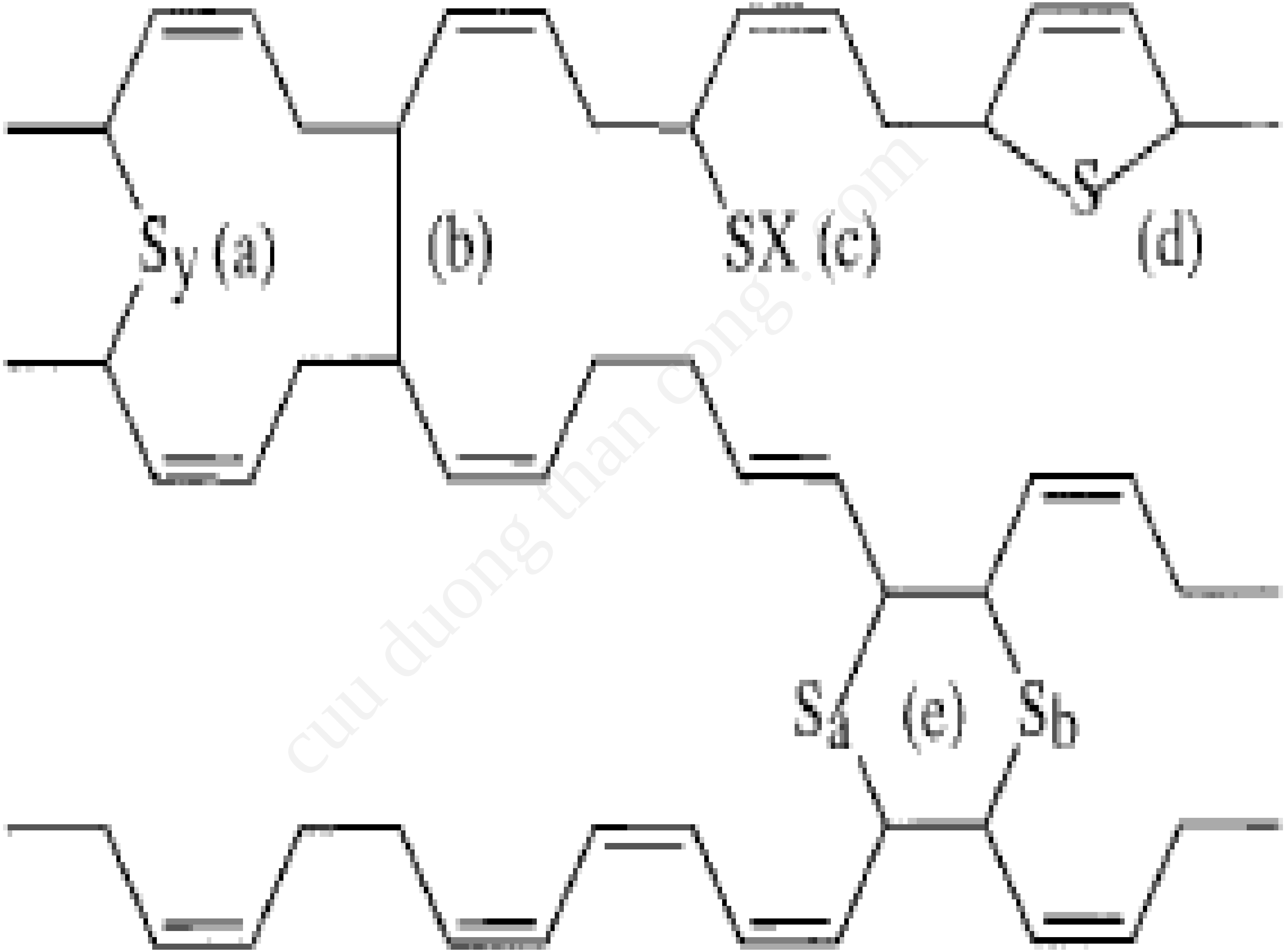
Crosslinking Chemistry

Crosslink Shortening via Desulfuration
and
Crosslink Degradation with Main Chain Modification

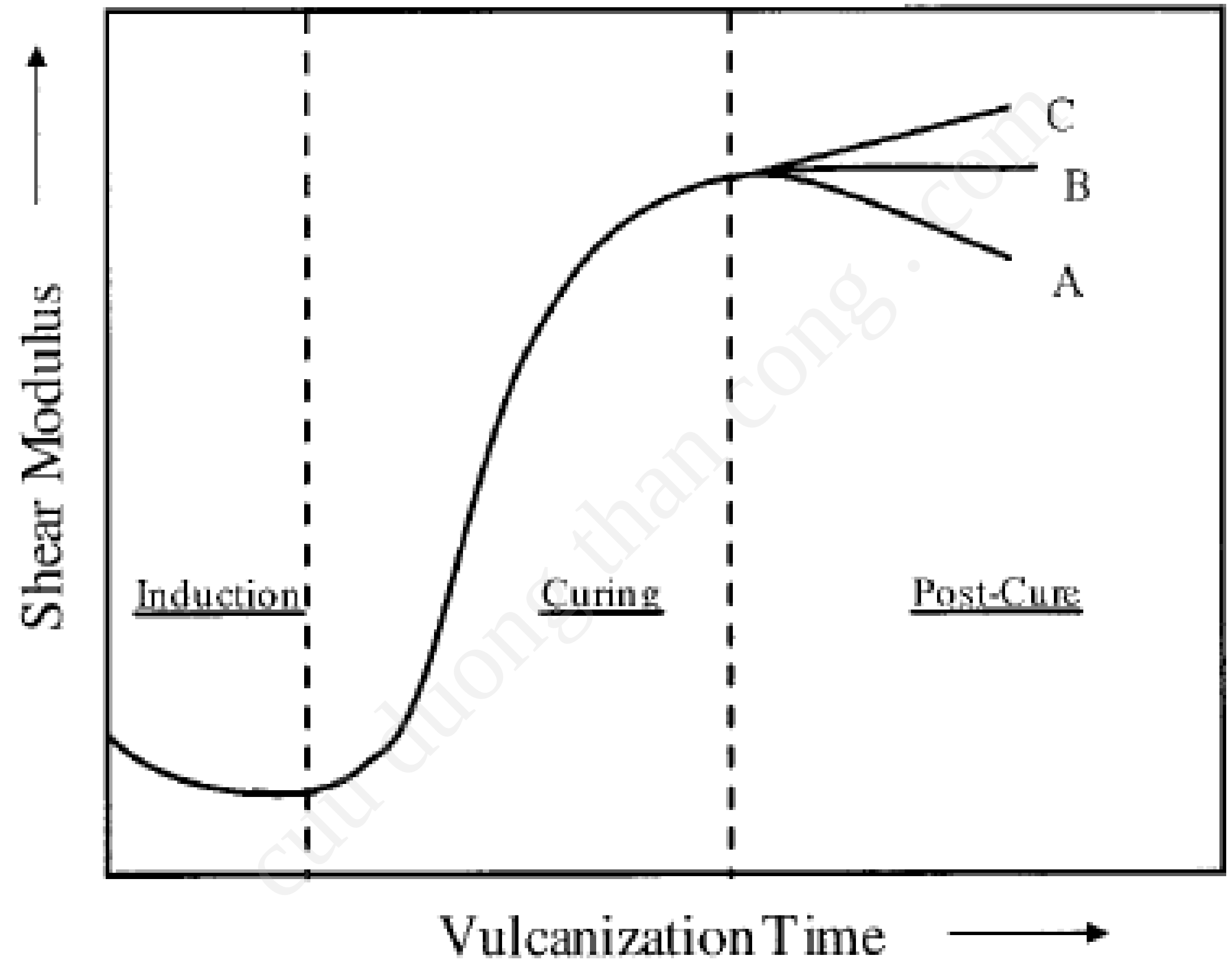
Post-Crosslinking Chemistry

Final Vulcanizate Network

FIG. 1. — General mechanism for accelerated sulfur vulcanization. Mechanism adapted from that of Morrison and Porter.[16]


Sy (a)
(b)
SX (c)
S
(d)
Sa
(e)
Sb

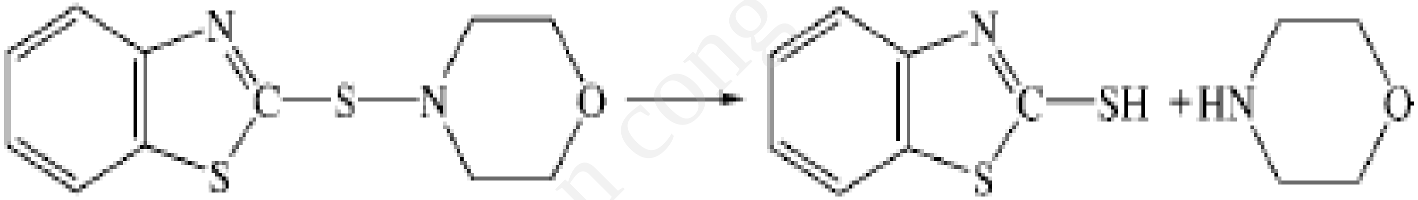
- (a) sulfur crosslinks ($y=1$ mono, $y=2$ di, $y>2$ polysulfide crosslinks
- (b) carbon-carbon crosslink
- © Pendant accelereator sulfide where X is the accelerator moiety
- (d) Cyclic sulfide
- (e) Vicinal crosslinks


Shear Modulus
C
B
A
Induction
Curing
Post-Cure
Vulcanization Time

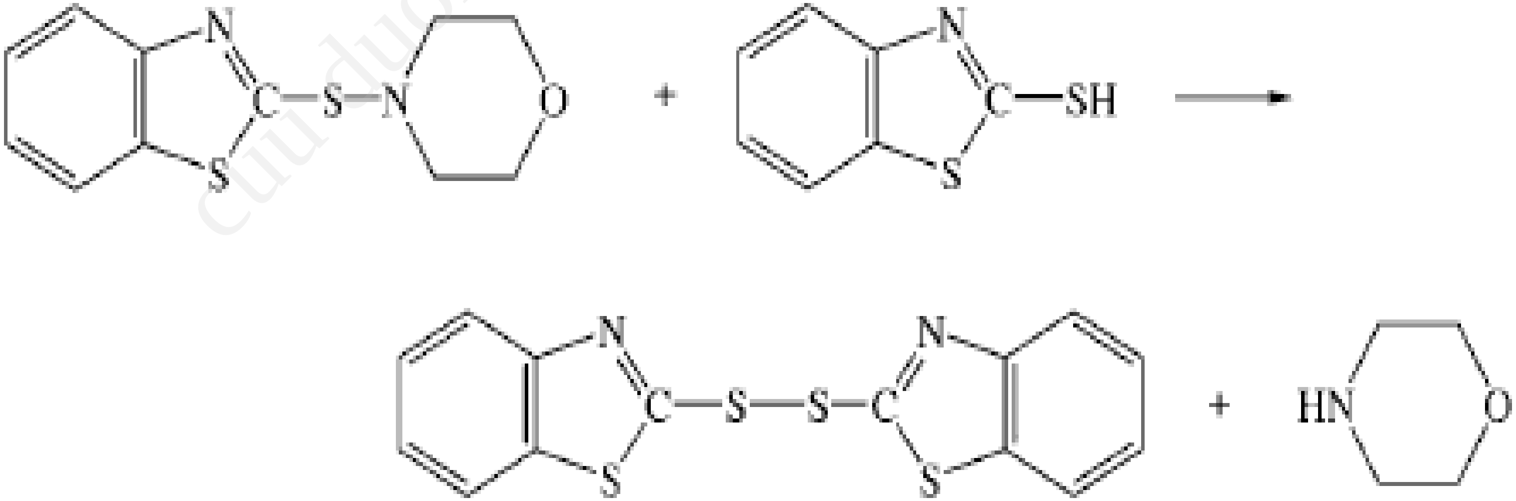
A- ACCELERATOR CHEMISTRY

Formation of MBTS from MBS

For an MBS accelerated system, these two reactions are



and



Reaction of sulfur with MBTS and other Accelerator-polysulfides

A key intermediate that reacts with elemental sulfur is MBTS

$$\text{Bt-S-S-Bt} \rightleftharpoons \text{Bt-S}\bullet + \text{Bt-S}\bullet$$

$$\text{Bt-S}\bullet + S_8 \longrightarrow \text{Bt-S-}S_8\bullet$$

$$\text{Bt-S}^{\bullet} + S_8 \longrightarrow \text{Bt-S-S}^{\bullet} + S_7$$

$$\text{Bt-S-S}^{\bullet} + S_x \longrightarrow \text{Bt-S-S-S}^{\bullet} + S_{x-1}$$

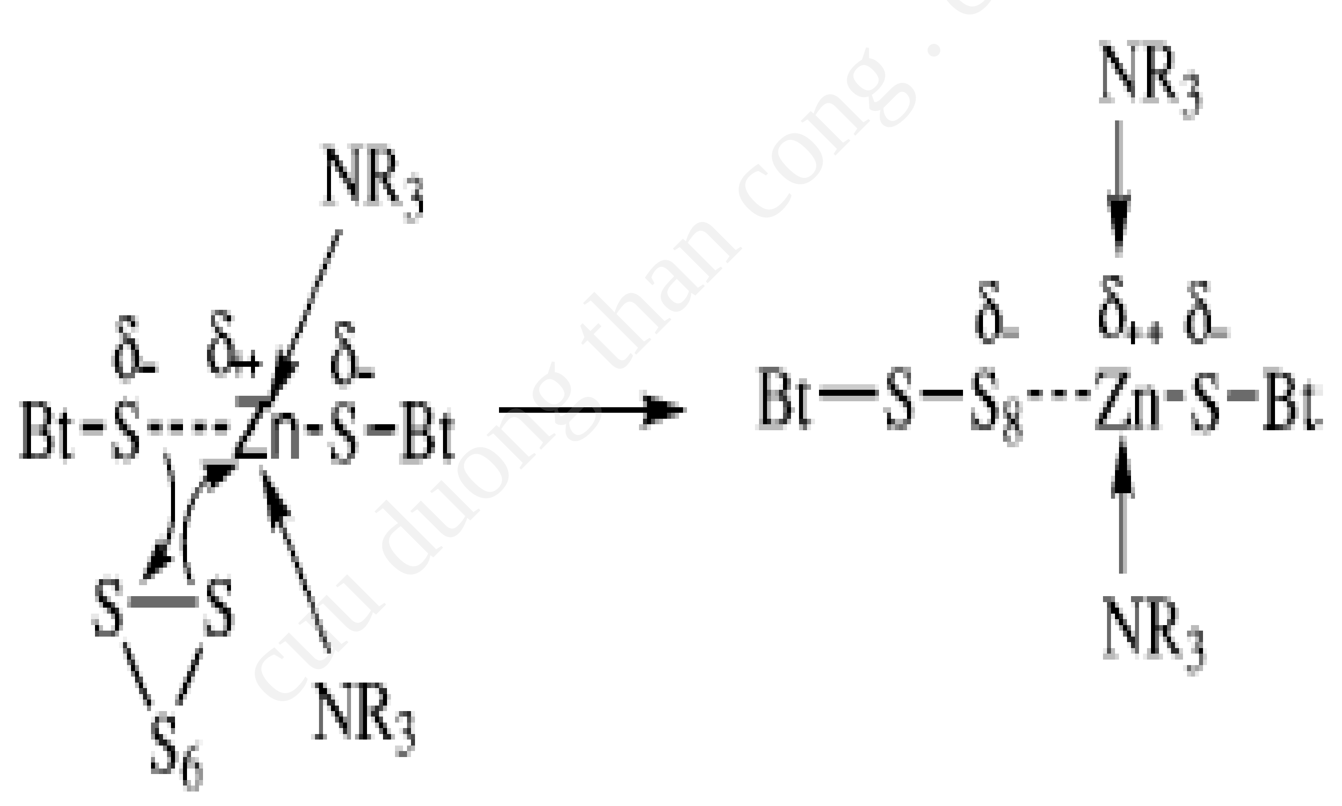
$$\text{Bt-S-S-Bt} + S_x \longrightarrow \text{Bt-S-S-S-Bt} + S_{x-1}$$

$$\text{Bt-S-}S_y\text{-S-Bt} + S_x \longrightarrow \text{Bt-S-}S_{y+1}\text{-S-Bt} + S_{x-1}$$

Exchange reaction among accelerator polysulfide

$$\mathrm{Bt\text{-}S_x\text{-}Bt + Bt\text{-}S_y\text{-}Bt \longrightarrow Bt\text{-}S_z\text{-}Bt + Bt\text{-}S_{x+y-z}\text{-}Bt}$$

Effect of ZnO-Formation of Zinc-Accelerator Complexes



Zinc-accelerator complexes may also undergo exchange reactions with other zinc-accelerator complexes to yield a distribution of Zn-accelerator species

$$\begin{array}{c}\mathrm{Bt\text{-}Zn\text{-}S_{X}\text{-}Bt} + \mathrm{Bt\text{-}Zn\text{-}S_{Y}\text{-}Bt} \\ \Big\downarrow \\ \mathrm{Bt\text{-}S_{Z}\text{-}Zn\text{-}Bt} + \mathrm{Bt\text{-}S_{X+Y\text{-}Z}\text{-}Zn\text{-}Bt}\end{array}$$

B- Crosslink chemistry

Formation of crosslink precursors

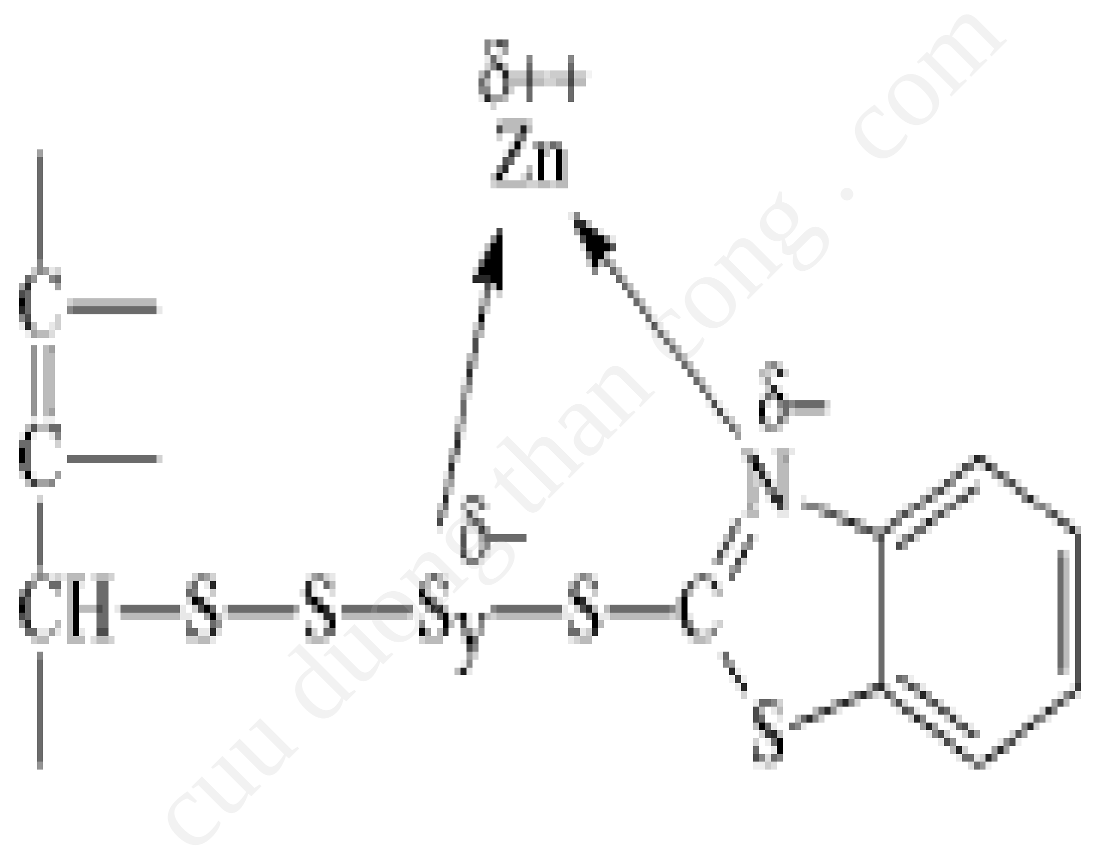
- Crosslink precursors are formed when the accelerator polysulfides react with the rubber chains, resulting in structures RS_X-SBt
- If Zinc is complexed to the accelerator polysulfide, the crosslink precursors can be BtS-Zn-S_XSBt

Conversion of crosslink precursors to crosslinks

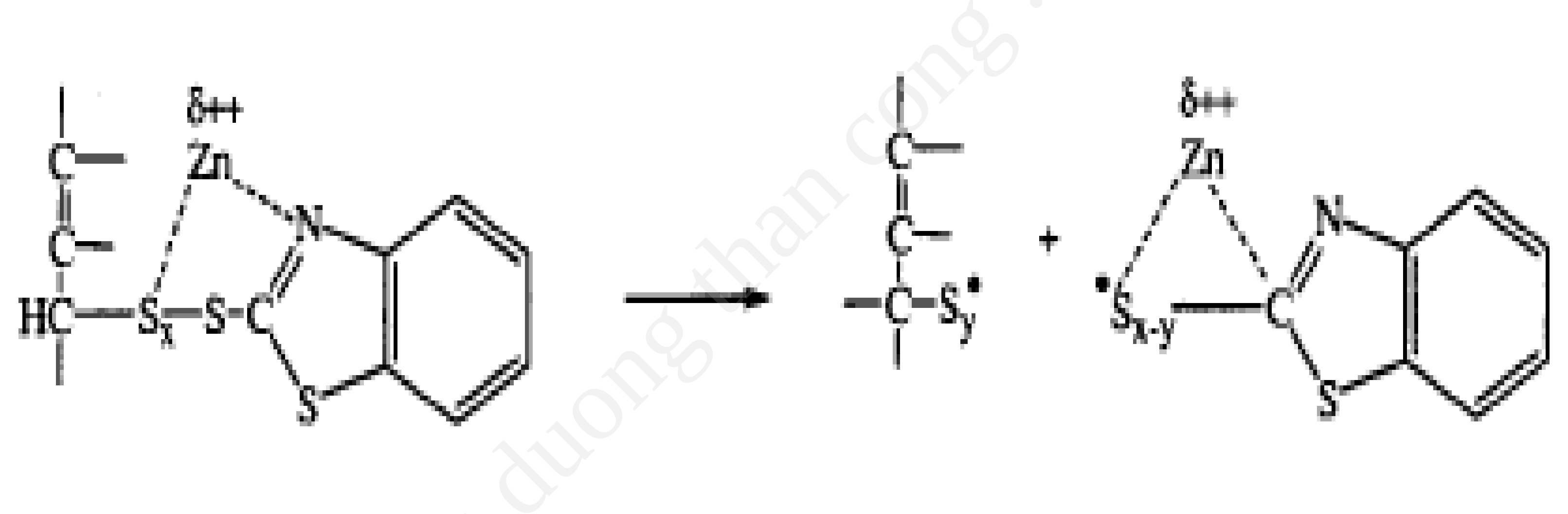
$$RS_XSBt \longrightarrow RS_Y^* + BtS_Z^*$$

$$RS_Y^* + \text{Rubber} \longrightarrow RS_YR$$

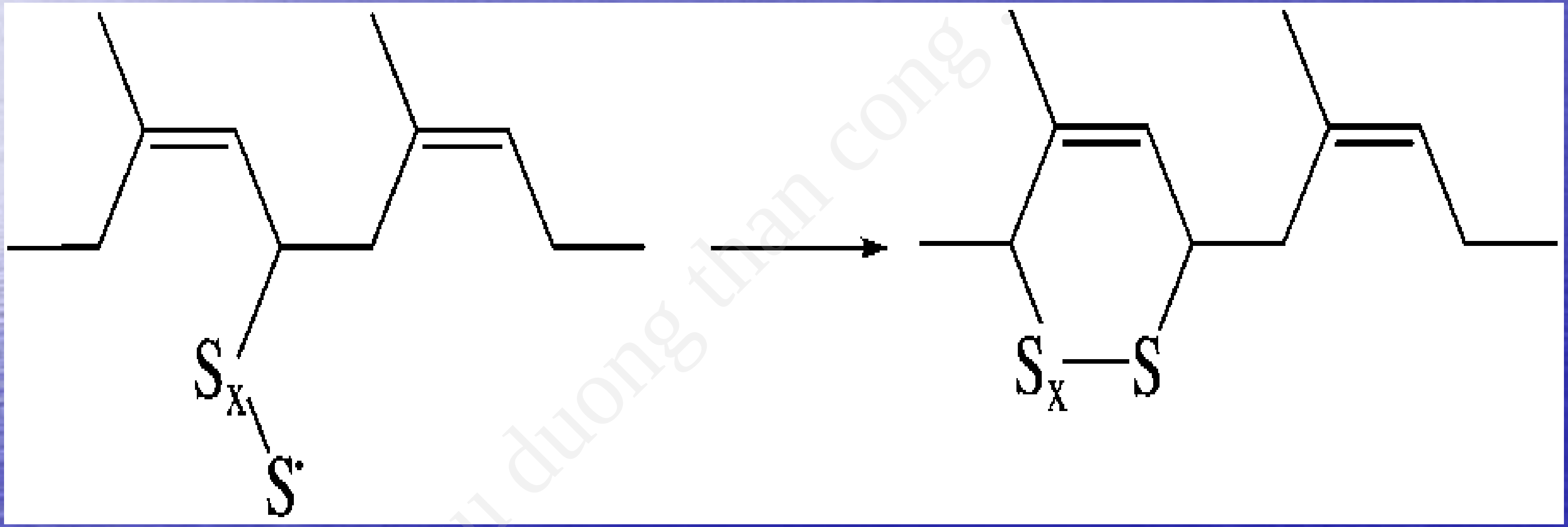
BtS_Z^* can undergo a variety of reaction like radical recombination to yield $BtSS_XSBt$


δ++
Zn
δ−
δ−
C
C
CH
S
S
Sy
S
C
N
S

The Zinc chelation can stabilize other sulfur bonds. Thus, in the presence of Zinc many of S-S bonds can break



R-S_Y* can react with an allylic carbon on a parent chain to form a crosslink



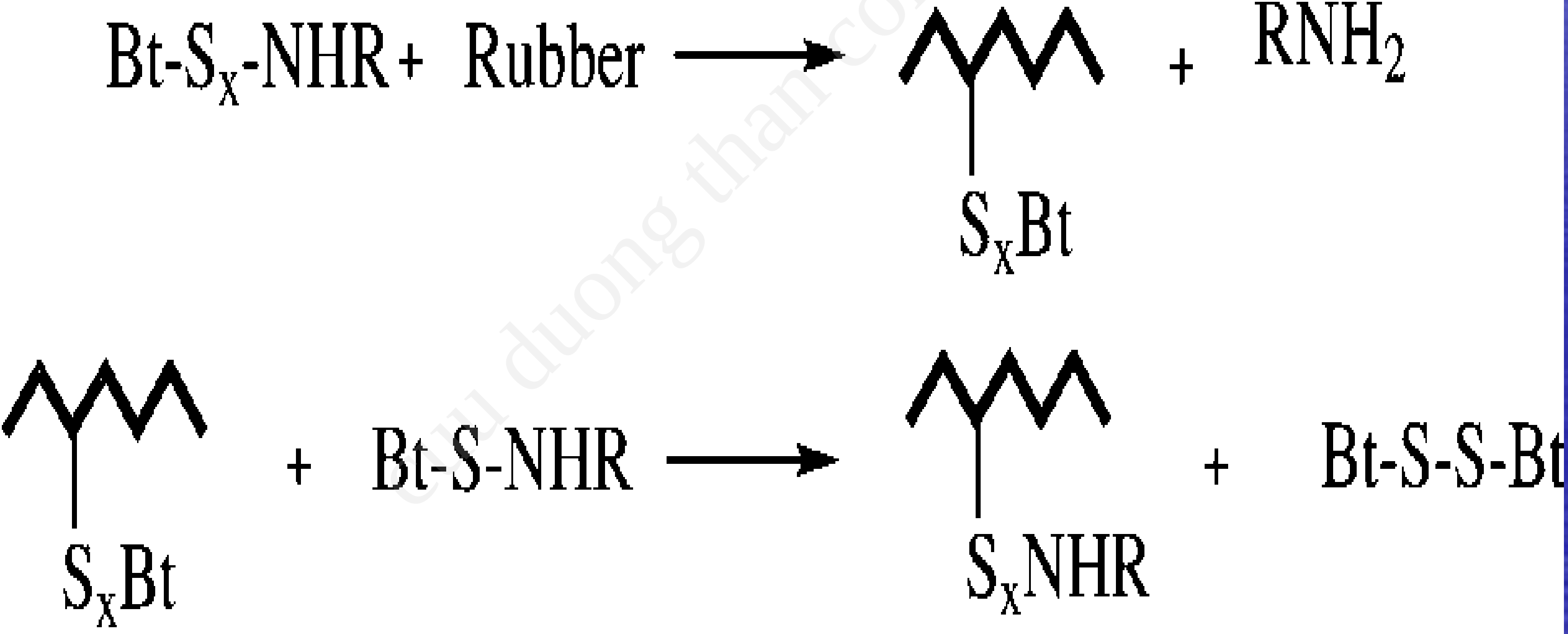
Scorch delay reaction

two different explanation have been proposed to account for scorch delay:

-Thermal stability of the accelerator

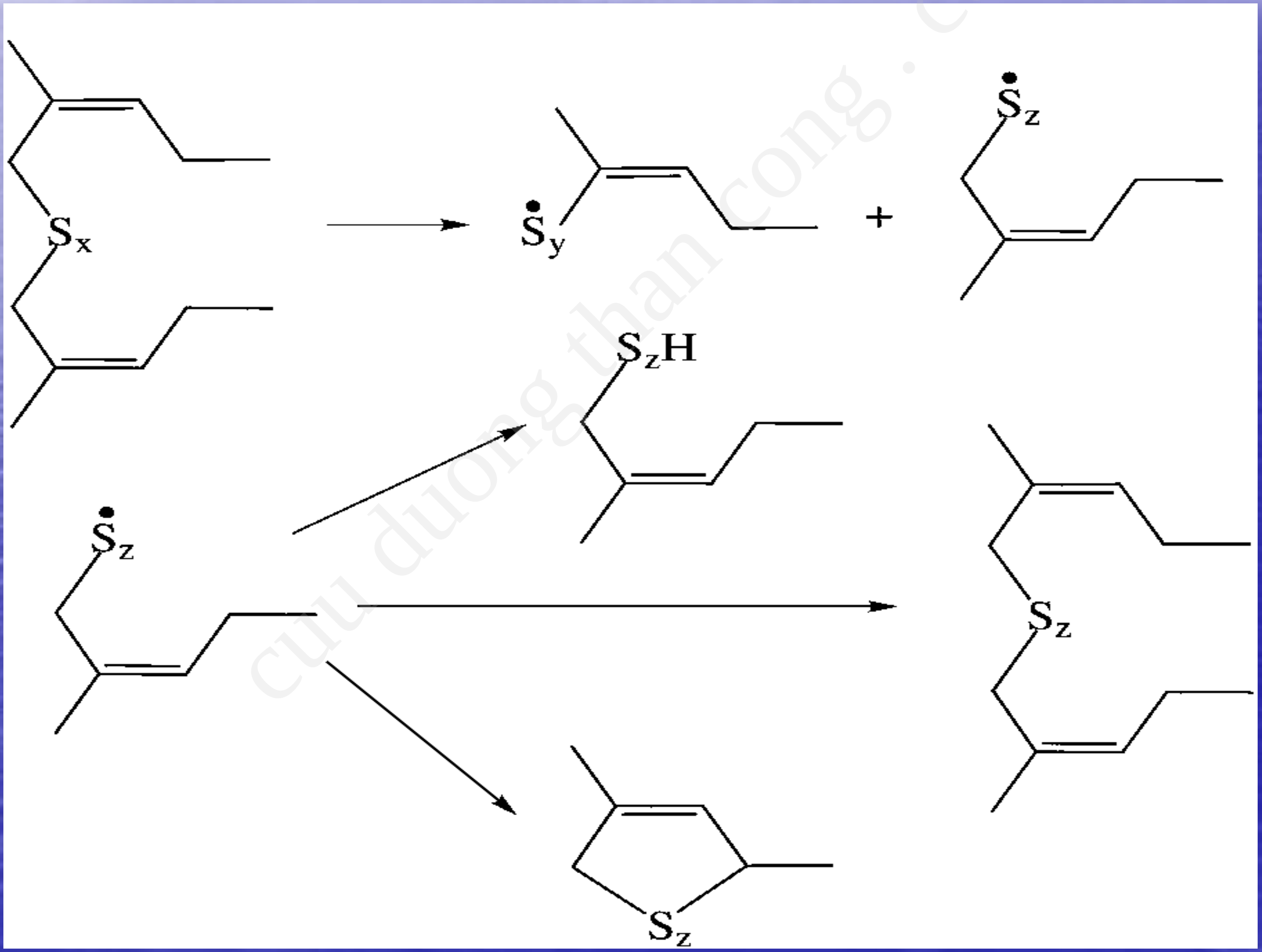
- Exchange reaction between accelerator-derived intrmediates

$$\text{Bt-S-NHR} + S_8 \longrightarrow \text{Bt-}S_x\text{-NHR}$$



C-POST-CROSSLINKING CHEMISTRY

Crosslink desulfuration and main-chain-modification

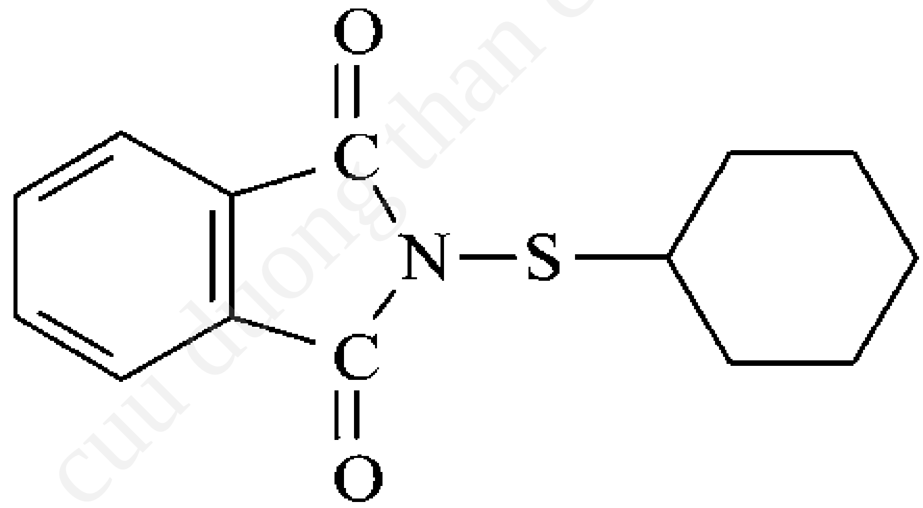


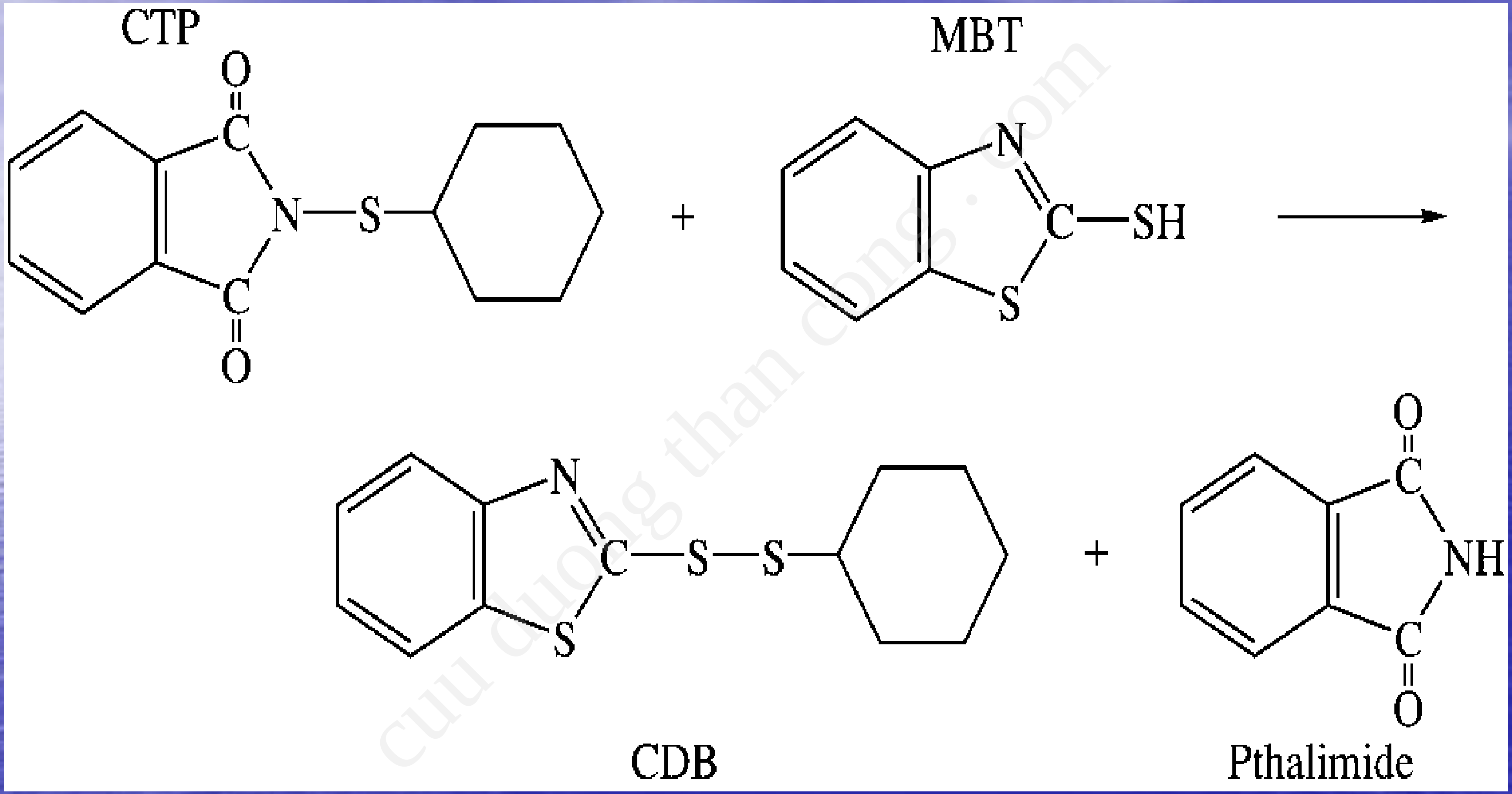
The degradation of the polysulfide crosslink RS_YR is more likely to proceed via the radical RS_X* and RS_Z* than RS_Y* and $R*$ (S-S bond is more easily broken than C-S bond)

RETARDER CHEMISTRY

- Increasing in scorch delay can be achieved by adding small amounts (0.1-o.4 phr) of a retarder (pre-vulcanization inhibitor, PVI)
- A typical PVI has an R-S-N group, where R does not contain the proton acceptor site common to the accelerator species

- A common industrial PVI is N-(cyclohexylthio)pthalimide (CTP)




CTP
O
C
N
S
C
O
+
MBT
N
C
SH
S
N
C
S
S
S
+
O
C
NH
C
O
CDB
Pthalimide

- The rate of this reaction is faster than the rate at which MBT reacts with MBS to form MBTS.
- MBTS formation is delayed and as a consequence crosslink formation is also delayed

$$\mathrm{MBS} \xrightarrow{\quad} \mathrm{MBT} + \mathrm{Amine}$$

$$\mathrm{MBS} + \mathrm{MBT} \xrightarrow[\text{Slow}]{} \mathrm{MBTS} + \mathrm{Amine}$$

$$\mathrm{CTP} + \mathrm{MBT} \xrightarrow[\text{Fast}]{} \mathrm{CDB} + \mathrm{Phtalimide}$$