Contribution to the Mechanism of the Thiuram Vulcanization. I. Polymerization of Styrene in the Presence of Tetramethylthiuram Disulfide and Natural Rubber

J. BENISKA, G. KYSELÁ, and E. ŠTAUDNER,

Chemical Faculty of the Slovak Technical University,
Bratislava, Czechoslovakia

Synopsis

The influence of the concentration of tetramethylthiuram disulfide (TMTD) on grafting of natural rubber by styrene at 80°, 95°, 115°, and 130°C and constant molar ratio of rubber and styrene was studied. It was found that the dependence $R_p = f([TMTD]^{1/2})$ at all followed temperatures goes through a maximum and that TMTD substantially decreases the amount of bound rubber in the graft copolymer. The analysis of the kinetic data and the results of separation of polymer mixtures showed the significant role in the process of the termination reactions of the growing polymer and the rubber radicals with the RS· radicals. The derived kinetic relation is in good agreement with the experimental results and allows calculation of the transfer rate constants of RS· radical on rubber.

INTRODUCTION

The theory of the radical mechanism of the tetramethylthiuram disulfide (thiuram, TMTD) vulcanization was formed mainly on the basis of the assumption that the TMTD radicals (RS·) are abstracting hydrogen from the alfa-CH_2 groups or that they are added to the double bonds of the rubber molecules and C—C crosslinks are formed. Because it was found that thiuram vulcanizates contain sulfidic crosslinks, too, and because of the impossibility of direct identification of the presence of RS· radicals in the vulcanization system and also for various considerations of the behavior of organic sulfur compounds in the conditions of polymerization of vinyl monomers,[1–3] Bateman et al.[4] considered that TMTD is not thermally decomposed even up to temperatures of 140°, which leads to the forming of the "polar" mechanism of vulcanization.

Our results obtained during the detailed study of the influence of TMTD on the polymerization of vinyl monomers unambiguously proved that TMTD is decomposed already at 60–80° to radicals and initiates the polymerization of reactive monomers.[5,6] The formed polymers contain bound fragments of TMTD and are able also to initiate under convenient conditions the polymerization.[7]

This paper deals with the influence of TMTD on the polymerization of styrene in the presence of natural rubber.

EXPERIMENTAL

Styrene was purified by removing the inhibitor with 10% sodium hydroxide solution and washing with distilled water; after drying, it was distilled in nitrogen.

For grafting, natural rubber (white crepe) masticated for 5 min on laboratory rolls was used.

Tetramethylthiuram disulfide was purified by precipitation with methanol from chloroform solution and by twice-repeated recrystallization from chloroform.

The kinetic of styrene polymerization in the presence of rubber was studied by the dilatometric method. It was carried out with the help an "overturn" dilatometer type, where Hg was used as measuring liquid.

The samples for determination of the amount of unbonded (free) rubber were prepared by the gravimetric method in a seal tube. For determination of the amount of unbonded rubber in mixtures after the polymerization, the method of fractional precipitation was used. Benzene as solvent and a mixture of acetone-methanol in a ratio 9:1 by volume was used as precipitant.

RESULTS AND DISCUSSION

The influence of TMTD on the polymerization of styrene in the presence of natural rubber at 80°, 95°, 115°, and 130° was studied. The TMTD concentration was changed over the range 9×10^{-4} to 1×10^{-1} mole/kg of mixture. In all cases, the concentration of —OOH groups (2.64×10^{-4} mole/kg) and the molar ration of rubber to monomer ($X = 0.0763$) were constant. The polymerization was carried out up to 10% conversion. The conversion curves were linear.

The dependences of the polymerization rate (R_p) on the square root of TMTD concentrations are given in Figure 1. From Figure 1 it is evident that with the increase in TMTD concentration the rates are increasing and are going through a maximum. With increase in temperature, the maximum is shifted to the lower TMTD concentrations.

When the dependence $R_p = f([TMTD]^{1/2})$ in the system styrene–rubber–TMTD is compared with that in the styrene–TMTD system,[8] it can be seen that in the system without rubber the polymerization rates are higher under the same conditions than in the system with rubber and are not going through a maximum.

Further, we also studied the changes of the content of "free" rubber in the polymer mixtures after 10% conversion of styrene in the dependence on the TMTD concentration at 80°, 95°, 115°, and 130°C. The results are given in Table I.

From Table I, it is evident that TMTD influences very significantly the composition of the mixture during the polymerization of styrene in the presence of natural rubber. From the analysis of these results, it is evident that TMTD has a substantial influence on the polymerization course of styrene in the presence of natural rubber. The low content of "free" rubber in mixtures prepared in the absence of TMTD proves that a substantial part of rubber participates in the reactions taking place in the polymerization, at which a modified copolymer (rubber–styrene) is formed. If TMTD in the system is present, the content of

TABLE I
Influence of TMTD Concentration on "Free" (Unbound)
Rubber at Various Temperatures

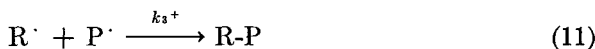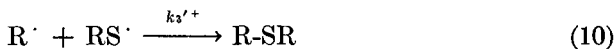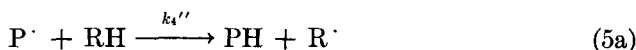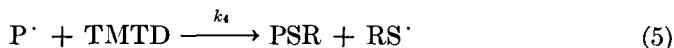| [TMTD], (mole/kg) × 10²	Unbound rubber, %			
	80°C	95°C	115°C	130°C
0	...	5.9	4.5	3.0
2.17	78.5	74.8	75.0	...
4.33	87.3	83.2	80.3	77.2
8.67	95.9	90.7	83.9	83.1
13.00	97.0	91.0	87.0	85.1
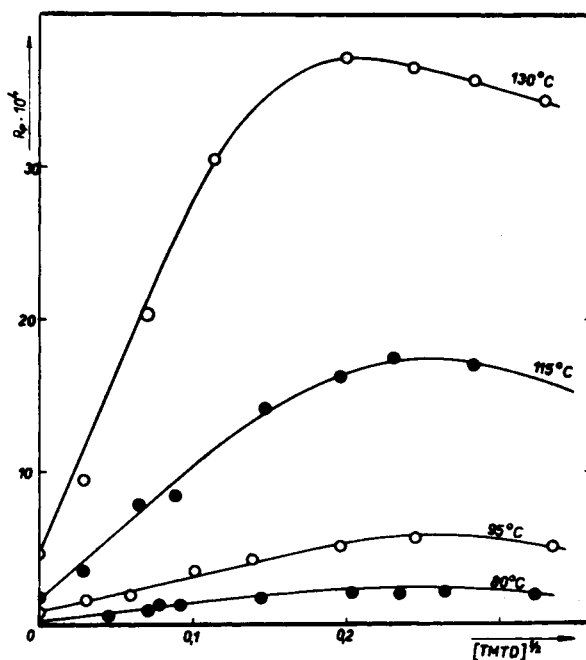
Fig. 1. Dependence of R_p on $[TMTD]^{1/2}$ at various temperatures.

"free" rubber is considerably increased, the rubber is therefore involved in the reactions of the polymer (polystyrene) radicals in a substantially smaller manner. From the mentioned results, it is evident that the main role, which takes place during the ploymerization of styrene in the presence of natural rubber and TMTD, is the homopolymerization of styrene, particularly at higher TMTD concentrations and at lower temperatures.

On the basis of the similar course of the dependence of $R_p = f([TMTD]^{1/2})$ in the systems styrene–rubber–TMTD and styrene–TMTD, it is possible to assume that in both systems similar reactions take place. In the system which contains also natural rubber, it is possible that, apart from the reactions where radicals from TMTD are involved, also reactions where rubber and rubber radicals (R·) produced during the transfer take place. The rubber radicals take part especially in the termination reactions and only to a negligible degree in reinitiation, because these are less reactive than RS· radicals or polymer radicals P·.

On the basis of the mentioned assumptions, it is possible to propose the following reaction scheme for the styrene polymerization in the presence of rubber and TMTD:

$$\text{Ther. init.} \xrightarrow{k_1} P \cdot \tag{1}$$

$$\text{TMTD} \xrightarrow{k_d} 2RS \cdot \tag{2}$$

$$RS \cdot + M \xrightarrow{k_1'} P \cdot \tag{3}$$

$$P \cdot + M \xrightarrow{k_2} P \cdot \tag{4}$$

$$P \cdot + \text{TMTD} \xrightarrow{k_4} PSR + RS \cdot \tag{5}$$

$$P \cdot + RH \xrightarrow{k_4''} PH + R \cdot \tag{5a}$$

$$RS \cdot + RH \xrightarrow{k_4'} R \cdot + RSH \tag{6}$$

$$R \cdot + M \xrightarrow{k_1''} P \cdot \tag{7}$$

$$P \cdot + P \cdot \xrightarrow{k_3} P\text{-}P \tag{8}$$

$$P \cdot + RS \cdot \xrightarrow{k_3'} P\text{-}SR \tag{9}$$

$$R \cdot + RS \cdot \xrightarrow{k_3'^+} R\text{-}SR \tag{10}$$

$$R \cdot + P \cdot \xrightarrow{k_3^+} R\text{-}P \tag{11}$$

$$R \cdot + R \cdot \xrightarrow{k_3''} R\text{-}R \tag{12}$$

As mentioned before, the results of the separation of the mixtures after the polymerization in the system styrene–rubber–TMTD showed that only a small amount of grafted polymer (high content of "free" rubber) is formed, and therefore it is possible to neglect reactions (7) and (11). The absence of gel in the polymer mixture enables also to neglect reaction (12). The higher mobility and reactivity of the $RS \cdot$ radicals results in the fact that these radicals will participate in a higher degree in termination reactions, too.

On the basis of the mentioned reaction scheme, when neglecting reactions (5a), (7), (11), and (12), and also the small concentration of —OOH groups in comparison with TMTD, it is possible to derive the relation

$$\left(\frac{R_{p0}^2 - R_p^2}{R_p^2 - R_{pt}^2}\right)\frac{[M]}{[RH]} = 2\frac{k_4'}{k_1'} + 2\frac{k_4 k_4' k_2}{k_3 k_1'}\frac{R_p[TMTD][M]}{R_p^2 - R_{pt}^2}$$

where $R_{p0} = (R_{pt}^2 + R_{pt}^2)^{1/2}$; R_p, R_{pi}, and R_{pt} are total, initial, and thermal polymerization rates, respectively; and [RH], [TMTD], and [M] are concentrations of rubber, thiuram, and monomer, respectively. This relation corresponds to an equation for a straight line,

$$Y = A + BX$$

where

$$A = 2\frac{k_4'}{k_1'} \text{ and } B = \text{tg } \alpha = 2\frac{k_4 k_4' k_2}{k_3 k_1'}.$$

TABLE II
Values k_4'/k_1', tg α, and k_4 Determined with the Aid of Values A and B

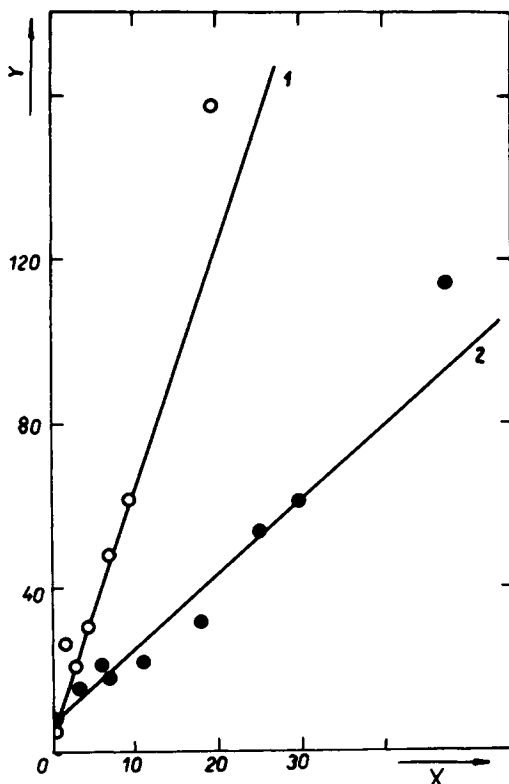| Temp., °C	k_4'/k_1'	tg α $\times 10^2$	k_4, l. mole^{-1} s^{-1}
80	. . .	1.79	49
95	3.5	5.99	77
115	4.0	23.30	254
130	5.0	80.00	394

Fig. 2. Dependence of Y on X at (1) 95°C; (2) 80°C.

The course of the dependence $Y = A + BX$ for the individual temperatures of the polymerization is illustrated in Figures 2 and 3.

Table II shows the calculated values k_4'/k_1' and tg α and the values k_4 determined with the help of the values A and B and the known values of k_2 and k_3 for styrene.[9]

From the dependence of log $(k_4'/k_1') = f(T^{-1})$ and from the known value[5] for E_1', it is possible to estimate the value $E_4' = 8.8$ kcal/mole. It is possible to calculate the value E_4' also from the relation for B where $E_B = E_4 + E_4' + E_2 - E_3 - E_1'$ is valid. The determined value $E_B = 20.2 \pm 2$ kcal/mole and the other values are known from the literature.[5,9] Then, $E_4' = 8.5$ kcal/mole. The values E_4' determined from the constants A and B are in very good agreement.
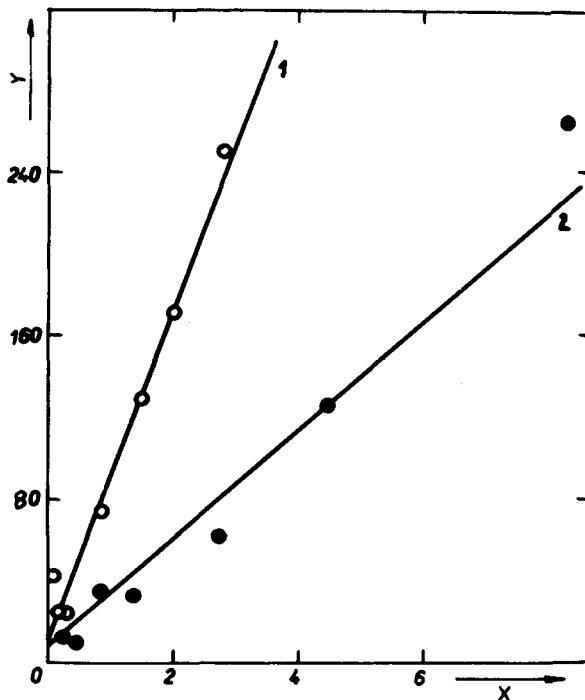
Fig. 3. Dependence of Y on X at (1) 130°C; (2) 115°C.

With the help of the determined values of A (k_4'/k_1') and B (tg α) also the transfer rate constants k_4 of the transfer of P⋅ radicals on TMTD can be calculated. These values compare with the estimated rate constants of transfer k_4 in the system styrene–TMTD.[5] The difference can be explained by the presence of rubber and by the simplifications which were made, and therefore the derived relation expresses only approximately the process which takes place during the polymerization of styrene in the presence of natural rubber.

On the basis of the experimental results and the kinetic analysis, it can be concluded that TMTD is decomposed to the free radicals RS⋅ in the presence of rubber, too. The radicals of TMTD react with rubber, and rubber radicals are formed. The former are less reactive and less mobile and therefore react predominantly with RS⋅ radicals.

Because of the dependence of the reactivity of polymeric matrix on the concentration of TMTD, also RS_x⋅ radicals can be formed (where $x \geqslant 1$) in consequence of an induced decomposition of TMTD. Then rubber contains bound fragments of TMTD (rubber–S_xR), which can be further decomposed to radicals.[10] The sulfur crosslinks are formed in consequence of the recombination reactions of the different rubber–sulfur radicals.

References

1. T. Otsu, *J. Polym. Sci.*, **21**, 559 (1956).
2. A. J. Kern, *J. Amer. Chem. Soc.*, **77**, 1382 (1958).
3. T. E. Ferington and A. V. Tobolsky, *J. Amer. Chem. Soc.*, **77**, 4510 (1955).
4. L. Bateman, *The Chemistry and Physics of Rubber-like Substances,* Wiley, New York, 1963, chap. 15.

5. E. Štaudner and J. Beniska, *Eur. Polym. J.*, Suppl., 573 (1969).

6. E. Štaudner, J. Beniska, and G. Kyselá, *Zborník Prác CHTF SVTL*, Bratislava, 1968, p. 113.

7. E. Štaudner, J. Beniska, and D. Bakoš, *Zborník Prác CHTF SVTL*, Bratislava, 1968, pp. 145, 151.

8. J. Beniska and E. Štaudner, *J. Polym. Sci., C*, **16**, 1301 (1967).

9. Ch. Walling, *Svobodnyje Radikaly v Rostvore*, I.I.L., Moscow, 1960, p. 78.

10. J. Beniska, 3. Mezinárodní Gumárenské Symposium, Gottwaldov, ČSSR, 1971, No. 3, p. 8.