[Contribution of the Frick Chemical Laboratory, Princeton University]

Organic Disulfides as Initiators of Polymerization: Tetramethylthiuram Disulfide

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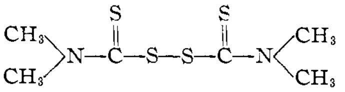
The compound tetramethylthiuram disulfide (TMTD) has been used as a polymerization initiator with methyl methacrylate and styrene monomers at 70°. TMTD is surprisingly only somewhat less reactive as an initiator than benzoyl peroxide at 70°. $R_i'/[\text{cat}]$ is 5.45×10^{-6} sec.$^{-1}$ for TMTD in methyl methacrylate and 3.34×10^{-6} sec.$^{-1}$ in styrene at low catalyst concentrations. The chain transfer to catalyst constant, $C_{\text{tr. cat}}$, has been evaluated as 0.0115 in methyl methacrylate and 0.0136 in styrene. TMTD appears to have the interesting property that it acts as a retarder as well as an initiator, this effect being very marked at high concentrations.

Introduction

The compound tetramethylthiuram disulfide (TMTD)



was studied as the initial member of a series to investigate the properties of organic disulfides as initiators of polymerization. It is used extensively in the rubber industry as an accelerator and has also been found capable of vulcanizing rubber without the presence of sulfur.

It was originally thought that this compound would be most useful as an initiator at temperatures above 100° since it is used in vulcanization at temperatures in the neighborhood of 125°. It was soon found that TMTD as an initiator for styrene or methyl methacrylate was much too reactive to use at such elevated temperatures and thus it has been studied at 70° in these familiar monomers.

Experimental

The TMTD used was commercial "Thiurad" obtained from the Monsanto Chemical Company and recrystallized as follows: three times from boiling $CHCl_3$; once from boiling $CHCl_3$, initiating the precipitation of TMTD by dropwise addition of ethanol and then allowing to cool, and finally once from cold $CHCl_3$, precipitating with ethanol. The purpose of the final conditions was twofold: (1) to prevent the formation of decomposition products on heating the material, (2) ethanol is listed as a solvent for tetramethylthiuram monosulfide which has been mentioned as an inhibitor in vulcanization by TMTD. An experiment in which % conversion was studied as a function of time gave an induction period of 10 minutes with a catalyst concentration of 0.0415 g./100 ml. after the third recrystallization using methyl methacrylate as the monomer. After the fifth recrystallization the apparent induction period was cut to two minutes. This was felt to represent the amount of time taken to warm the 10-ml. sample from room temperature to 70° in an oil-bath.

The methyl methacrylate was purified by extracting twice with 5% NaOH solution, washing four times with distilled water, drying for at least four hours over anhydrous Na_2CO_3 and finally distilling at 100 mm. under nitrogen, taking roughly the middle 60%.

The styrene was purified by distillation from copper pellets at 20 mm. under nitrogen and taking the middle 60%.

The sample solutions of monomer and TMTD were prepared using normal precautions as to accuracy and cleanliness and 10-ml. aliquots transferred to thin walled glass tubes, where they were degassed using three cycles of freezing, evacuation and thawing. The evacuated tubes were finally sealed off and polymerized for the desired length of time at 70° (±0.5°) in an oil-bath. The rate of polymerization was calculated from the time of polymerization and the per cent. conversion to polymer obtained by precipitating the contents of the tube in a large excess of methanol, collecting it on a sintered glass filter and weighing after drying for 2 days at 60° in a vacuum oven. The per cent. conversion was about 2% in most cases and below 7% in all cases.

In those cases in which molecular weights were required, they were obtained from the intrinsic viscosities of the polymers in benzene at 30° using the relationship of Mayo, Gregg and Matheson[1] for unfractionated styrene.

$$\bar{P}_n = 1605 \times [\eta]^{1.37}$$

Since some of the data used in arriving at this equation were obtained from polymers prepared in the presence of CCl_4 the transfer activity of TMTD should not affect the accuracy of the $\bar{P}_n$'s obtained by use of the above equation.

For methyl methacrylate the equation of Tobolsky and Baysal[2] for unfractionated polymer was used.

$$\bar{P}_n = 315 \times [\eta]^{1.25}$$

The intrinsic viscosities here were run in $CHCl_3$ at 25°.

Results and Discussion

A. Rate Measurements.

—The equation

$$R_p^2 = R_{p,th}^2 + B_1[\text{cat}] \qquad (1)$$

where R_p is the total rate of polymerization, $R_{p,th}$ is the rate of thermal polymerization, B_I is an experimental constant and [cat] is catalyst concentration, has been verified for a large number of cases, although exceptions to this rule are not unknown.[3] Polymerization data from Table I are given in Fig. 1 as a plot of R_p^2 *vs.* [cat] in accord-

Table I

Vinyl Polymerization Initiated by TMTD Experimental Results

A. Methyl methacrylate, 70°			B. Styrene, 70°		
[cat] $\times 10^3$, mole/l.	R_p, $\times 10^5$, mole/l. sec.	$1/\bar{P}_n$ $\times 10^5$	[cat] $\times 10^2$, moles/l.	R_p $\times 10^5$, moles/l. sec.	$1/\bar{P}_n$ $\times 10^3$
0.082	2.21	5.83	0.0952	1.87	0.401
.149	2.87	6.46	.238	2.51	0.570
.248	3.50	8.59	.595	3.63	1.07
.411	4.15	10.90	1.32	5.29	2.02
1.23	5.63	...	1.49	5.10	1.81
1.24	6.09	...	3.30	6.92	3.94
1.47	5.97	24.60	8.25	8.50	9.90
2.06	6.44	...			
2.46	6.59	32.2			
3.69	6.84	54.0			
3.72	6.88	...			
6.14	7.01	69.9			
9.28	6.70	...			
23.2	5.52	...			
38.7	4.18	...			

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(1) F. R. Mayo, R. A. Gregg and M. S. Matheson, This Journal, **73**, 1691 (1951).

(2) B. Baysal and A. V. Tobolsky, *J. Polymer Sci.*, **9**, 171 (1952).

(3) (a) R. N. Haward and W. Simpson, *Trans. Faraday Soc.*, **47**, 212 (1951); (b) G. V. Schulz, *Z. Elektrochem.*, **47**, 265 (1941).

ance with this equation for methyl methacrylate monomer and TMTD catalyst at 70°. Figure 2 gives the experimental results from Table I in the same type of plot for styrene monomer. In both cases the deviation of R_p^2 *vs.* [cat] from linearity becomes quite marked at rather low catalyst concentrations. In the case of methyl methacrylate a maximum R_p of 7×10^{-5} mole/l. sec. is observed at a catalyst concentration of 5.5×10^{-3} mole/l. A maximum in the R_p^2 *vs.* [cat] curve was not observed with styrene, but this may be due to the fact that sufficiently high TMTD concentrations could not be used because of the limitation imposed by solubility in the monomer.

For polymerizations which obey the rate equation 1 the rate of initiation of polymer radicals R_i' can be obtained from equation 2[4]

$$R_i' = \frac{2A'}{[M]^2}[R_p^2 - R_{p,th}^2] \qquad (2)$$

where

$$A' = \frac{k_{tc} + 2k_{td}}{k_p^2}$$

k_{tc} = rate constant for termination of polymer radicals by combination

k_{td} = rate constant for termination of polymer radicals by disproportionation

k_p = rate constant for the propagation step in the polymerization

Equations 1 and 2 are valid for the case in which the *only* ways in which polymer radicals are deactivated are by combination and disproportionation. This condition is very probably true for the TMTD data in the nearly linear portions of the R_p^2 *vs.* [cat] curves in Figs. 1 and 2 which obtain at very low concentrations. At higher TMTD concentration neither equation 1 nor 2 is valid, since an additional mode of termination is no doubt operative. Presumably this involves some interaction between the growing polymer radicals and the TMTD molecules.

In view of these considerations a straight line was drawn tangent to the initial portion of the R_p^2 *versus* [cat] curve in Fig. 1. This represents an extension of the linear region of the R_p^2 *versus* [cat] curve. It is presumed that equation 2 is valid for this fictitious line and yields the true rate of initiation of polymer radicals. The value of R_i'/[cat] obtained in this manner has been tabulated in Table II, column 3.

TABLE II

COMPARISON OF RATES OF FORMATION OF RADICALS BY TMTD FROM POLYMERIZATION DATA AND AS DETERMINED WITH DPPH

A. Methyl methacrylate, 70°

[cat], mole/l.	$\frac{R_{DPPH}}{[cat]} \times 10^6$	$\frac{R'_i \times 10^6}{[cat]}$	$\frac{2A'(R_p^2 - R_{p,th}^2)}{[M]^2[cat]}$
3.33×10^{-4}	5.44	5.4	3.92×10^{-6}
1.66×10^{-3}	5.21	5.4	2.62×10^{-6}
4.16×10^{-3}	5.94	5.4	1.33×10^{-6}
1.04×10^{-2}	6.51[a]	5.4	4.73×10^{-7}

[a] The rapid disappearance of the DPPH color prevented an accurate determination at this catalyst concentration.

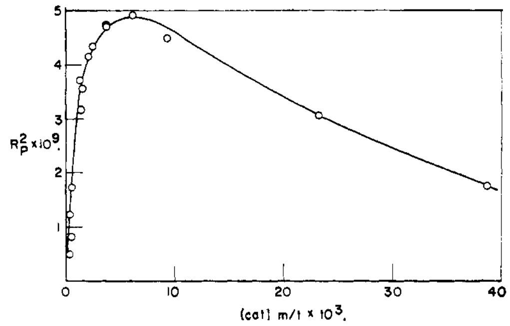

Fig. 1.—Rate of polymerization of methyl methacrylate with TMTD at 70°.

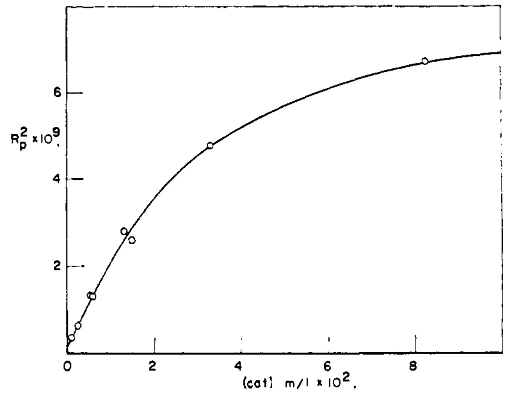

Fig. 2.—Rate of polymerization of styrene with TMTD at 70°.

Further information on the cleavage of TMTD was obtained by the use of the stable free radical diphenylpicrylhydrazyl (DPPH). One can follow the production of radicals in solutions of TMTD in methyl methacrylate by observing the rate of fading of the characteristic violet color of the DPPH with a photometer.[5] This was done for the same concentrations as used in the polymerization experiments. This data is tabulated as R_{dpph}/[cat] in column 2 of Table II. It shows good agreement with column 3 of Table II.

In contrast, the extent of deviation of equation 2 from the true rate of initiation of polymer radicals may be seen by comparing columns 2 and 3 with column 4 of Table II. In column 4 the value of R_p used in equation 2 was the actual experimental value.

The fact that columns 2 and 3 in Table II are nearly identical indicates quite well that the curves shown in Figs. 1 and 2 are not due to irregularities in the production of radicals by the catalyst.

For comparison it may be noted that the value of R_i'/[cat] for benzoyl peroxide in methyl methacrylate at 70° is 2.91×10^{-5}.

B. TMTD as a Retarder with Azo-I Catalyst.—The behavior of TMTD as a retarder was examined by working at 30° and using 2-azobisisobutyronitrile (Azo-I) as a catalyst. It was assumed that at this temperature the rate of initiation due to TMTD was negligible and that the rate of production of radicals by the Azo-I was not affected by the presence of the TMTD. The mono-

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(4) A. V. Tobolsky and B. Baysal, *J. Polymer Sci.*, **11**, 471 (1953).

(5) C. E. H. Bawn and S. F. Mellish, *Trans. Faraday Soc.*, **47**, 1216 (1951).

mer used was methyl methacrylate. A plot of % conversion against time of polymerization was constructed by using several tubes at a given Azo-I concentration. From these experiments it was found that TMTD did not act as an inhibitor but rather as a retarder. A straight line was obtained up to 6% conversion at an Azo-I concentration of 2.12×10^{-2} mole/l. and a TMTD concentration of 2.19×10^{-2} mole/l. From this line the observed R_p was 5.82×10^{-6} mole/l. sec. while a similar run with no TMTD present gave an R_p of 25.3×10^{-6}.

Retardation may be considered as due to the action of the TMTD molecule itself or as due to some decomposition product of the TMTD. TMTD is known to break down on heating to CS_2, S_8 and tetramethylthiourea.[6] Of these S_8 has been found to be an inhibitor of polymerization in styrene by Schulz[7] and CS_2 has been shown by us to have practically no effect. If the retarding action is due to the decomposition products the plot of conversion against time using TMTD as the initiator should be curved downward indicating greater retardation as conversion increases. This was not found to be the case (Fig. 3), the conversion *versus* time curve being quite linear.

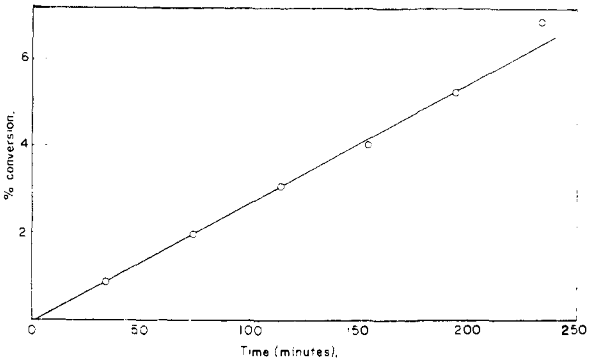

Fig. 3.—Methyl methacrylate polymerized with TMTD. % conversion *vs.* time at 70°.

C. Chain Transfer Activity of TMTD.—The chain transfer activity of TMTD was studied with the help of equation 3

$$\frac{1}{\bar{P}_n} = C_{tr,M} + \frac{A'R_p}{[M]^2} + C_{tr,cat}\frac{[cat]}{[M]} \qquad (3)$$

where

$\bar{P}_n$ = no. av. degree of polymn. of polymer obtained by viscosity measurements

$C_{tr,X}$ = chain transfer to X constant

$= \frac{k_{tr,X}}{k_p}$, $k_{tr,X}$ = rate constant for the transfer step

A plot of $1/\bar{P}_n$ *vs.* R_p was constructed for both methyl methacrylate and styrene using polymer representing the entire range of catalyst concentrations given in Figs. 1 and 2. A' for methyl methacrylate was taken as 44[8,9] and for styrene as 494.[10] In both cases marked curvature of the plot was obtained indicating that $C_{tr,cat}$ was appreciable. Accordingly equation 3 was transformed to

$$\frac{1}{\bar{P}_n} - \frac{A'R_p}{[M]^2} = \Delta = C_{tr,M} + C_{tr,cat}\frac{[cat]}{[M]} \qquad (4)$$

and the graphs of Δ *vs.* [cat] constructed. As may be seen in Figs. 4 and 5, the plot was nicely linear over the entire range. The values of the constants are given in Table III.

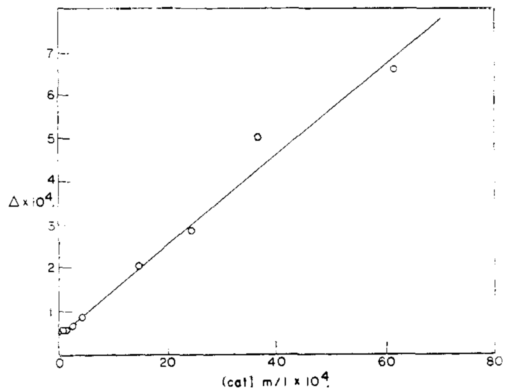

Fig. 4.—$1/\bar{P}_n - A'R_p/[M]^2 = \Delta$ *vs.* catalyst concentration for methyl methacrylate polymerized with TMTD at 70°.

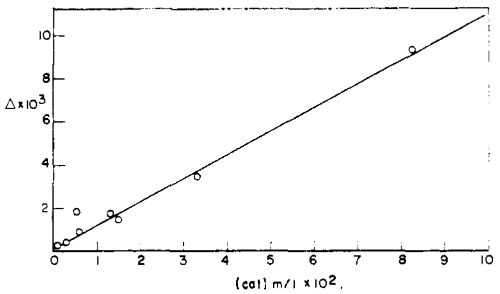

Fig. 5.—Δ *vs.* catalyst concentration for styrene polymerized with TMTD at 70°.

TABLE III

TRANSFER CONSTANTS AT 70° —TMTD CATALYST

Monomer	$C_{tr,M}$	$C_{tr,cat}$
Methyl methacrylate	4.5×10^{-5}	1.15×10^{-2}
Styrene	6×10^{-5}	1.36×10^{-2}

Equation 3 was derived from the case in which no retarder is present. When it was rearranged as in 4, a good straight line was obtained by plotting Δ *vs.* [cat]. However when the full kinetic picture describing Fig. 1 is available it may be necessary to modify equation 3 somewhat. In the case when retarder is present (or when catalyst is acting as retarder) $C_{tr,cat}$ must be regarded as representing the combined effects of transfer with catalyst and retardation by the catalyst or its offspring.

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(6) J. v. Braun and K. Weissbach, *Ber.*, **63**, 2836 (1930).

(7) G. V. Schulz, *Makromol. Chem.*, **1**, 94 (1947).

(8) G. V. Schulz and G. Haborth, *ibid.*, **1**, 106 (1947).

(9) M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, THIS JOURNAL, **71**, 497 (1949).

(10) J. A. Offenbach and A. V. Tobolsky, *J. Polymer Sci.*, in press.