European Polymer Journal, Vol. 14, pp. 1067 to 1069
© Pergamon Press Ltd 1978. Printed in Great Britain

0014-3057/78/1201-1067$02.00/0

# POLYMERIZATION OF METHYLMETHACRYLATE IN PRESENCE OF TETRAMETHYLTHIURAMDISULPHIDE

E. Štaudner, G. Kyselá, J. Beniska and D. Mikolaj
Chemical Faculty of the Slovak Technical University, Bratislava, Czechoslovakia

(*Received* 25 *March* 1975; *revised* 10 *January* 1978)

**Abstract**—The effect of TMTD on the polymerization of methyl methacrylate was studied. The plot of $R_p$ vs $[\mathrm{TMTD}]^{1/2}$ shows a maximum ascribed to participation of TMTD-radicals in cross ($\mathrm{P}^{\cdot} + \mathrm{RS}^{\cdot}$) and mutual-termination ($\mathrm{RS}^{\cdot} + \mathrm{RS}^{\cdot}$). The total polymerization rate is then well expressed by a derived relation. Study of the influence of TMTD on the molecular weight of polymethylmethacrylate allows characterization of the transfer process.

The polymerization of styrene is initiated by tetramethylthiuramdisulphide (TMTD) [1–4] but the dependence of $R_p$ on $[\mathrm{TMTD}]^{1/2}$ is not linear. The deviation has been explained by participation of TMTD-radicals in cross-termination ($\mathrm{P}^{\cdot} + \mathrm{RS}^{\cdot}$). For the polymerization of methyl methacrylate (MMA), plots of $R_p$ on $[\mathrm{TMTD}]^{1/2}$ show maxima, attributed to the participation of TMTD-radicals in cross- and mutual-termination ($\mathrm{RS}^{\cdot} + \mathrm{RS}^{\cdot}$); it has also been assumed that there is transfer to TMTD. This paper presents results on the influence of TMTD on the polymerization of methyl methacrylate and on the molecular weight of the resulting polymer; the mechanism is discussed.

## EXPERIMENTAL

MMA was purified by vacuum distillation under $N_2$, by partial polymerization (prepolymerization) in the presence of a small amount of dibenzoylperoxide and by repeated vacuum distillation. TMTD was purified by precipitation and repeated crystallization from $\mathrm{CHCl_3}$. Procedures were described previously [1,2]. Polymerizations were followed dilatometrically up to 5–10%; conversion curves were linear [5]. Samples for molecular weight determination were prepared by a gravimetric method (conversion 5%). The molecular weights ($\overline{\mathrm{M}}$) of the samples were determined viscometrically with an Ubbelohde viscometer using toluene as solvent at 25 ± 0.1°. Molecular weights were calculated using the relation [7]:

$$[\eta] = 7.1 \times 10^{-5} \times \overline{\mathrm{M}}^{0.73}.$$

## RESULTS AND DISCUSSION

It has been shown [3,5,6] that the polymerizations of styrene and MMA in the presence of TMTD satisfy the relation:

$$R_p = \frac{(R_{pt_0}^2 + R_{pi_0}^2)^{1/2}}{\left(1 + 2B^* \dfrac{[\mathrm{TMTD}]}{[\mathrm{M}]} + C^* \dfrac{[\mathrm{TMTD}]^2}{[\mathrm{M}]^2}\right)^{1/2}} \tag{1}$$

$B^*$ and $C^*$ are complex constants:

$$B^* = \frac{k'_3 k'_4}{k_3 k'_1} \quad \text{and} \quad C^* = \frac{k''_3 k_4^2}{k_3 k_1'^2} \tag{2}$$

where $k_3$, $k'_3$ and $k''_3$ refer to mutual termination of polymer radicals, interaction of polymer radicals and TMTD-radicals ($\mathrm{RS}^{\cdot}$) and mutual-termination of $\mathrm{RS}^{\cdot}$ radicals respectively; $k_4$ is the transfer rate constant of polymer radicals to TMTD; $k'_1$ is the initiation rate constant for the addition of $\mathrm{RS}^{\cdot}$ radicals to monomer; $R_{pt_0}$ and $R_{pi_0}$ are "theoretical" rates of thermal and induced polymerization for cases where termination involves only polymer radicals. [TMTD] and [M] are concentrations of TMTD and monomer.

Rearranging (1) leads to:

$$\left(\frac{R_{pt_0}^2 + R_{pi_0}^2}{R_p^2} - 1\right)\frac{[\mathrm{M}]}{[\mathrm{TMTD}]} = 2B^* + C^* \frac{[\mathrm{TMTD}]}{[\mathrm{M}]} \tag{3}$$

It is possible to estimate the complex constants $B^*$ and $C^*$. The values of $B^*$ are not very accurate and are little changed by temperature; $B^* = 450 \pm 100$. The estimated values for $C^* \times 10^{-6}$ are 3.10, 1.78, 1.45, 0.99, 0.80, 0.61 and 0.44 for 60, 70, 80, 90, 95, 105 and 115° respectively.

The estimated values for $B^*$ and $C^*$ allow calculation of the "theoretical" dependence of $R_p$ on $[\mathrm{TMTD}]^{1/2}$ for the various temperatures, as illustrated in Fig. 1 (solid lines). There is very good agreement of experimental and calculated values except for the highest concentrations of TMTD. Dotted lines correspond to termination only by polymer radicals. The deviation from the simple reaction scheme occurs at rather low concentrations of TMTD and the dependences of $R_p$ on $[\mathrm{TMTD}]^{1/2}$ pass through maxima. With rising temperature, the maximum is shifted to higher concentrations of TMTD.

The explanation of these facts is that, during the polymerization of the less reactive MMA, there is not only cross ($\mathrm{P}^{\cdot} + \mathrm{RS}^{\cdot}$) but also mutual-termination ($\mathrm{RS}^{\cdot} + \mathrm{RS}^{\cdot}$), i.e. for this case polymerization rate is described by the complete Eqn. (1) unlike the case of styrene [3].

Radicals are produced from TMTD by thermal decomposition as well as in transfer reactions involving TMTD. Evaluation of the effect of the transfer

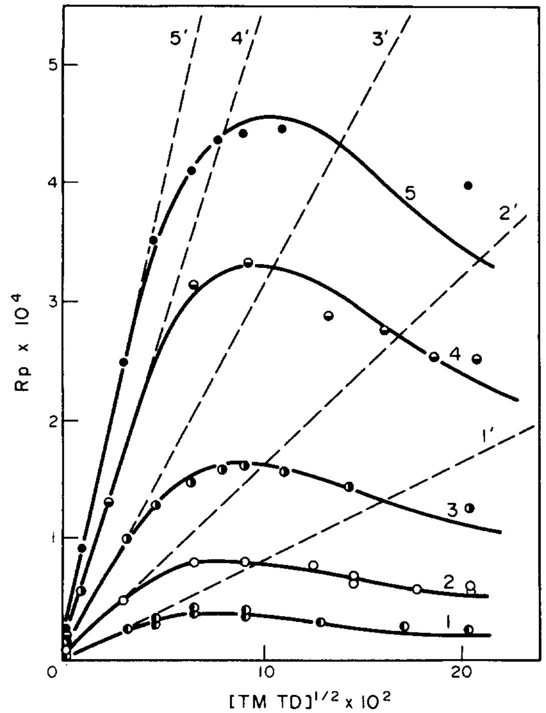

Fig. 1. Dependences of $R_p$ on $[\text{TMTD}]^{1/2}$ at various temperatures: 1,1' = 60°, 2,2' = 70°, 3,3' = 80°, 4,4' = 90°, 5,5' = 95°. 1, 2, 3, 4, 5 refer to theoretical dependences calculated from Eqn (1); 1', 2', 3', 4', 5' refer to "simple" reaction scheme. Points are experimental values.

reaction (by transfer constants $C_T$) on the course of polymerization of MMA allowed interpretation of the influence of TMTD on the molecular weight of polymethylmethacrylate produced at 80, 90, 105 and 115°.

For estimation of transfer constants ($C_T$), a modified relation was used [3]:

$$\Delta = \frac{1}{\bar{X}} - \frac{\delta^2 R_p}{[\text{M}]^2}\left(1 + B^* \frac{[\text{TMTD}]}{[\text{M}]}\right)$$
$$= C_m + C_T \frac{[\text{TMTD}]}{[\text{M}]}. \qquad (4)$$

The dependences of $\Delta$ on [TMTD]/[M] for various temperatures are illustrated in Figs. 2 and 3. The values obtained for $C_T$ are 0.53, 0.63, 0.65, 0.67 and 0.76 for 80, 90, 95, 105 and 115° respectively. From the estimated values $C_T$ and the known values of $k_2$ [8], the rate constant $k_4$ ($1\ \text{mole}^{-1}\ s^{-1}$) was calculated as 430, 600, 690, 900 and 1200 for 80, 90, 95, 105 and 115° respectively. The transfer constants $C_T$ are lower but the rate constants $k_4$ are higher than those for styrene [3]. The values of $C_T$ are about two orders higher than the transfer constants $C_T$ given by Ferington and Tobolsky [9] because their values for $C_T$ were calculated incorrectly.

From the dependence of $\log k_4$ on $T^{-1}$, the activation energy of transfer ($E_4$) is found to be $34.3\ \text{kJ mole}^{-1}$. The complex constant $B^*$ does not change (or changes very little) with temperature [5], therefore the effective activation energy $E_{B^*}$ is very small. From Eqn. (2) for $E_{B^*}$

$$E_{B^*} = E'_3 + E_4 - E_3 - E'_1 = 0.$$

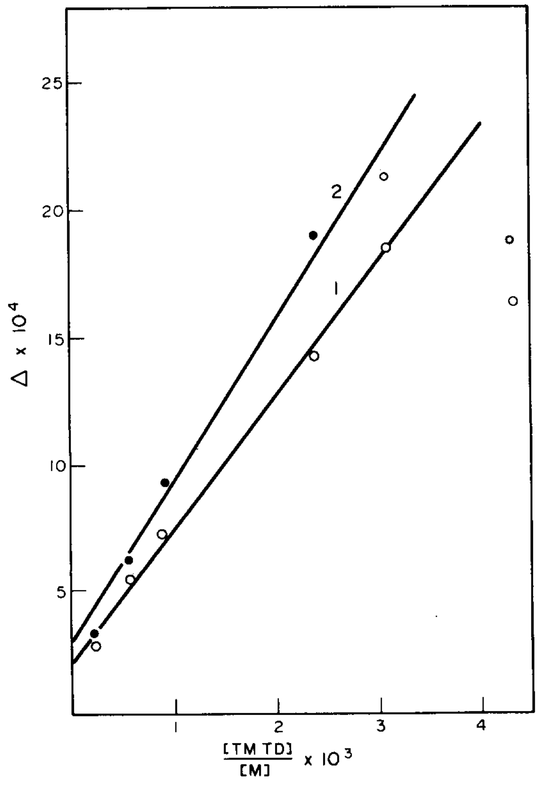

Fig. 2. Dependences of $\Delta$ on [TMTD]/[M], 1-80°, 2-90°.

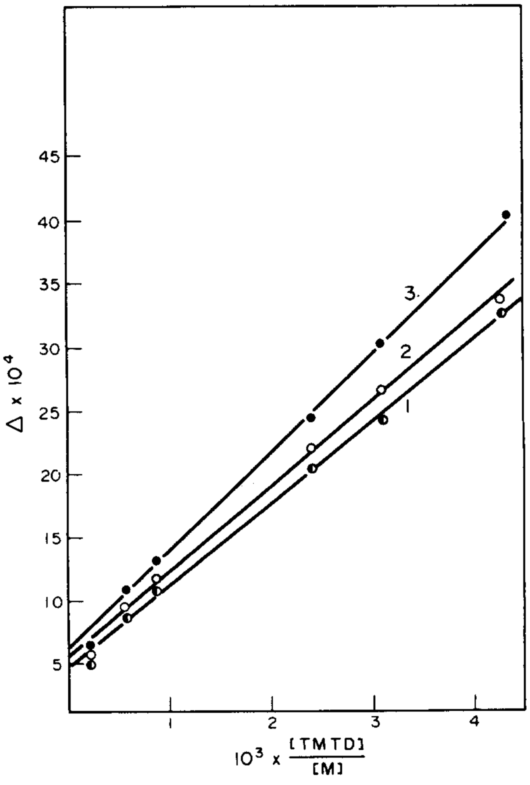

Fig. 3. Dependences of $\Delta$ on [TMTD]/[M], 1-95°, 2-105°, 3-115°.

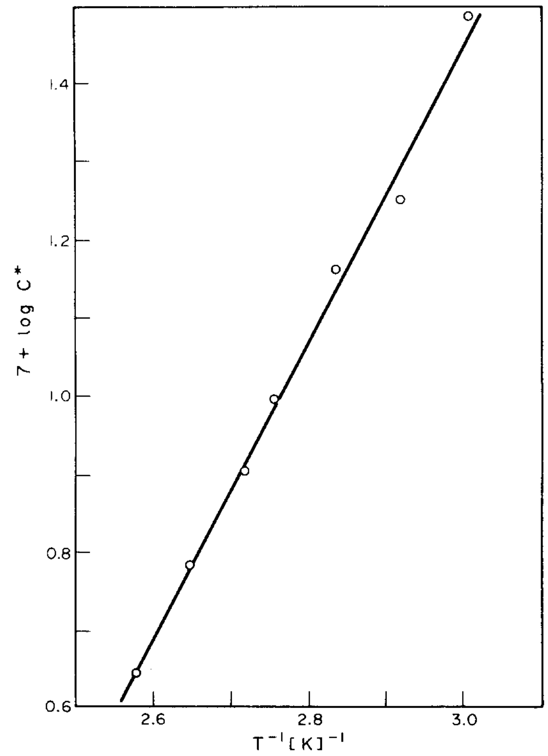

Fig. 4. Dependence of log $C^*$ on $1/T$.

Provided that $E'_3$ is approximately equal to $E_3$, we can evaluate the activation energy $E'_1$ of reinitiation or addition of RS$^\cdot$ to the monomer and

$$E'_1 = E_4 = 34.3 \pm 4\,\mathrm{kJ\,mole}^{-1}.$$

The activation energy $E'_1$ can also be evaluated from the effective activation energy $E_{C^*}$, determined from the dependence of $\log C^*$ on $T^{-1}$ (see Fig. 4), i.e. $E_{C^*} = -33.4\,\mathrm{kJ\,mole}^{-1}$. From relation (2)

$$E_{C^*} = E''_3 + 2E_4 - E_3 - 2E'_1 = -33.4.$$

Provided again that $E''_3 = E_3$

$$E'_1 = E_4 + 16.7 = 51.0\,\mathrm{kJ\,mole}^{-1}.$$

This difference can be due either to inaccurate determination of complex constants $B^*$ or to $E'_3$ not being equal to $E_3$ but being greater than $E_3$, i.e. that cross-termination ($P^\cdot + RS^\cdot$) has a higher activation energy than other termination reactions as a consequence of steric hindrance.

The values of $E'_1$, however, are in both cases higher than in the case of styrene [3] and they are also higher than the activation energy for propagation ($E_2$). It follows that RS$^\cdot$ radicals are less reactive towards MMA and they will be more involved in cross- and mutual-termination reactions than in initiation.

RS$^\cdot$ radicals can also react with TMTD, leading to a further reaction not considered in the kinetic analysis, viz. an induced decomposition of TMTD and formation of the less reactive $RS_2^\cdot$ radicals. These radicals will be mainly or exclusively involved in termination with $P^\cdot$ radicals giving a relatively reactive product

$$\left(P^\cdot + RS_2^\cdot \xrightarrow{k_3^*} PSSR\right)$$

these products can decay producing more reactive PS$^\cdot$ and RS$^\cdot$ radicals [10] which can also take part in initiation; in this way the polymerization rate and molecular weight of polymer are higher than those corresponding to relations (1) or (4) respectively.

From kinetic analysis and the experimental results, it is evident that TMTD-radicals can be formed by thermal decay as well as by transfer of $P^\cdot$ radicals with TMTD. RS$^\cdot$ radicals take part in initiation but, even at low concentration of TMTD, they also participate in cross- and mutual-termination.

## REFERENCES

1. E. Štaudner, J. Beniska and G. Znamenáková, *Chemické Zvesti* **20,** 18 (1966).
2. J. Beniska and E. Štaudner, *J. Polym. Sci.* **C16,** 1301 (1967).
3. E. Štaudner and J. Beniska, *Europ. Polym. J.* Supplement, 537 (1969).
4. J. Beniska, *Vysokomolek. soedin.* **13,** 1970 (1971).
5. E. Štaudner, J. Beniska and G. Kyselá, *Zborník prác CHTF SVŠT, Bratislava,* 113 (1968).
6. E. Štaudner, J. Beniska and G. Kyselá, *Zborník prác CHTF SVŠT, Bratislava* (1973). In press.
7. Cjan-Žeň-Juaň, *Opredelenie molekularnych vesov polimerov I.I.L.,* Moskva (1962).
8. Ch. A. Bagdasarjan, *Teoria radikaľnoj polimerizaciji, I.A.N. ZSSR,* Moskva (1955).
9. T. E. Ferington and A. V. Tobolsky, *J. Am. chem. Soc.* **77,** 4510 (1955).
10. E. Štaudner, J. Beniska and D. Bakoš, *Zborník prác CHTF SVŠT, Bratislava,* 145 (1971).