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A NOTE ON THE EFFECTS OF TETRAMETHYLTHIURAM MONOSULPHIDE ON RADICAL POLYMERIZATIONS

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Abstract—A report is given of effects of tetramethylthiuram monosulphide (TMTM) upon the polymerization of styrene at 80°; it can act as both an initiator and a retarder and there is great sensitivity to light. Experiments with ^{14}C-TMTM show that transfer to initiator is important. Attempts were made to measure the rate of dissociation of TMTM spectrophotometrically and by isotope dilution analysis. At room temperature in benzene solution, there are exchange reactions between TMTM and the corresponding disulphide.

MANY OF the problems connected with the effects of tetraethylthiuram disulphide (TETD) upon radical polymerizations have been solved by careful application of tracer techniques.(1, 2) The techniques were used to determine the initiator fragments incorporated in polymers prepared in the presence of the disulphide and also to identify these fragments. It was then possible to discriminate between various reaction schemes(3, 4) which satisfy the observed kinetic behaviour during polymerization.

Procedures of the same types have also been applied to systems involving a related compound, viz. tetramethylthiuram monosulphide (TMTM). A preliminary account of the study is given here for styrene; very similar results were found for methyl methacrylate. One significant result of studies involving ^{14}C-TMTM has been quoted already.(2)

EXPERIMENTAL

Procedures for polymerization, recovery and purification of polymers and assay of labelled materials were similar to those described previously.(1, 2) For polymerizations under "dark" conditions, the bulbs of the dilatometers were covered with masking tape.

TMTM was prepared by treatment of tetramethylthiuram disulphide with potassium cyanide; the disulphide was prepared from dimethylamine and carbon disulphide using oxidation by iodine. The scale of working involved 2·8 g of dimethylamine, containing 0·1 mc of carbon-14 in the appropriate cases.

The TMTM was recrystallized repeatedly from ethanol. Overall yields, based on dimethylamine, were about 40 per cent. The specific activity of the labelled product was about 12 μc/g.

RESULTS AND DISCUSSION

TMTM acts as a sensitizer for the polymerization of styrene at 80° but, as in the case of TETD, anomalies of two types are observed. The systems are very sensitive even to diffuse daylight; further, at high concentrations, both substances evidently act as retarders (see Fig. 1). The effect of light was not examined for the case of methyl methacrylate but, for that monomer also, the retarding effect was clear.

The rate of polymerization for a particular system was not reproducible. For styrene at 4·1 moles l.$^{-1}$ in benzene under "dark" conditions at 80°, the observed rates of

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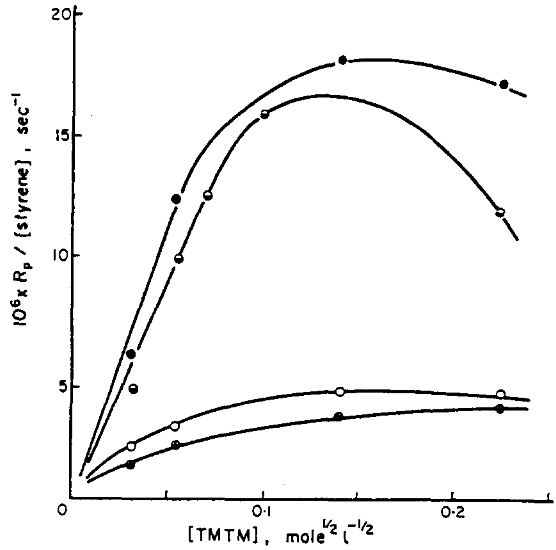

FIG. 1. Effect of tetramethylthiuram monosulphide on rate of polymerization of styrene at 80°. ● —(styrene) = 8·2 mole l^{-1}; polymerization in light. ◒ —(styrene) = 4·1 mole l^{-1}; diluent = benzene; polymerization in light. ○ —(styrene) = 8·2 mole l^{-1}; polymerization in dark. ⊕ —(styrene) = 4·1 mole l^{-1}; diluent = benzene; polymerization in dark.

polymerization in successive experiments with one batch of TMTM at $2·0 \times 10^{-2}$ moles l^{-1} sec^{-1} were $1·45 \times 10^{-5}$, $1·47 \times 10^{-5}$ and $1·39 \times 10^{-5}$ moles/l^{-1} sec^{-1}. Similar experiments with another batch gave $1·04 \times 10^{-5}$ and $1·03 \times 10^{-5}$ mole/l^{-1} sec^{-1} although no differences were found between the purities of the two samples of TMTM. The rate of polymerization under particular conditions was affected by the presence of oxygen and by the length of the interval between making up a reaction mixture and performing the polymerization at 80°.

Experiments with unlabelled polymers and ^{14}C-TMTM showed that complete removal of the labelled material could readily be achieved by reprecipitation of the polymer. It was then shown, by using labelled additive during the polymerization, that labelled fragments of the monosulphide became chemically combined in the polymer during its formation. Rates of incorporation were calculated from the observed rates of polymerization and the specific activities of the monosulphide and the derived polymers;(5) they were not reproducible.

The mixed initiator technique(6) was applied to examine the possibility of transfer to initiator during polymerization under "dark" conditions. Experiments with ^{14}C-*azobis*-cyclohexylnitrile (ACHM) showed that the rate of incorporation of fragments of that initiator was depressed by the presence of TMTM in the reaction mixture (see Fig. 2). This finding suggests that the monosulphide captures radicals which would otherwise initiate polymerization. Figure 3 refers to experiments involving ^{14}C-TMTM with unlabelled ACHN or unlabelled tetramethylthiuram disulphide (TMTD) and provides clear evidence that fragments of TMTM are incorporated in polymer by processes other than initiation; further, the intercept on the axis suggests that the true rate of initiation for the particular sample of TMTM at $1·0 \times 10^{-2}$ moles l^{-1} at 80° was about 5×10^{-8} moles l^{-1} sec^{-1}.

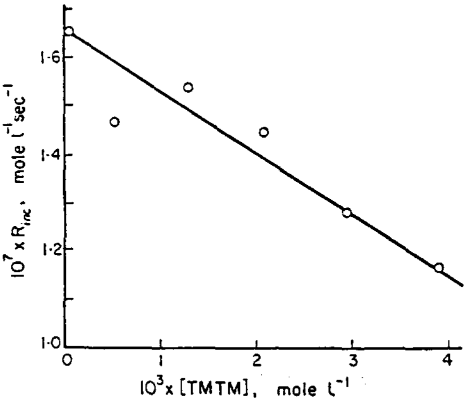

FIG. 2. Effect of tetramethylthiuram monosulphide upon rate of incorporation into polystyrene of fragments derived from *azobis*-cyclohexylnitrile. (azonitrile) = 0·010 mole l^{-1}; (styrene) = 4·1 mole l^{-1}; diluent = benzene; polymerization in dark at 80°.

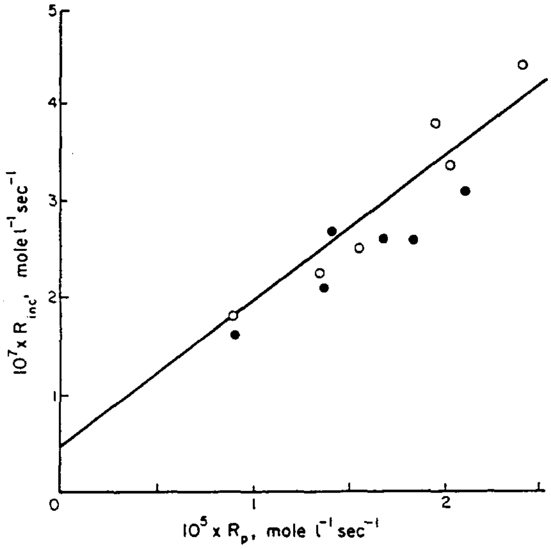

FIG. 3. Effects of added initiators upon rate of incorporation into polystyrene of fragments derived from tetramethylthiuram monosulphide. (TMTM) = 0·010 mole l^{-1}; (styrene) = 4·1 mole l^{-1}; diluent = benzene; polymerization in dark at 80°. ○—*azobis*-cyclohexyl nitrile present; ●—tetramethylthiuram disulphide present.

Attempts were made to measure the rate of decomposition of TMTM in solution at 80° using a spectrophotometric technique and also isotope dilution analysis to determine the residual monosulphide. The former technique was made difficult because the monosulphide and its decomposition products have very similar absorption spectra; from the initial slope of the log (peak height) vs. time curve, it was deduced that k_d is roughly 10^{-5} sec^{-1}. The isotope dilution analyses were inconclusive because of exchange reactions involving TMTM.

Mixtures of ^{14}C-TMTM and unlabelled TMTD were dissolved in methanol; the disulphide was immediately separated by preferential crystallization and purified by recrystallization. No activity could be detected in the recovered TMTD showing that the mono- and disulphides could be separated. If, however, similar mixtures were kept in benzene solution at room temperature before separation of the components, the recovered disulphide was radioactive. The transfer of activity to the disulphide under "light" conditions was much more pronounced than under "dark" conditions. After about 48 hr in "light", exchange was over 50 per cent complete; for "dark" conditions, the proportion was less than 5 per cent. The possibility of exchange reactions of this type was first demonstrated by Lecher.⁽⁷⁾

It is concluded that TMTM behaves in a complex manner in polymerizing systems. Many features of its behaviour are unresolved but it is clear that it would probably be useful to use tracer techniques in further studies.

In many respects, the effects upon radical polymerizations of tetramethylthiuram monosulphide are very similar to those produced by tetraethylthiuram disulphide. It is concluded that primary radical termination is probably of great significance for both substances. It has been shown already⁽²⁾ that polymers prepared in the presence of the monosulphide contain two distinct types of end-group derived from the additive; they are presumed to be $(CH_3)_2$ N.CS. and $(CH_3)_2$ N.CS.S.

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Résumé—Cette étude a pour sujet les effets du monosulfure de tetraméthylthiurame (TMTM) sur la polymérisation du styrène à 80°. Cet additif peut agir à la fois comme amorceur et comme inhibiteur; la sensibilité à la lumière est grande. Des expériences effectuées avec le TMTM$-{}^{14}$C mettent en évidence un important transfert à l'amorceur. Des essais ont été effectués dans le but de mesurer la vitesse de dissociation du TMTM par spectrophotométrie et par analyse de dilution isotopique. A température ordinaire et en solution dans le benzène, des réactions d'échange ont lieu entre le TMTM et le disulfure correspondant.

Sommario—Viene dato un resoconto degli effetti del tetrametiltiuram monosolfuro (TMTM) sulla polimerizzazione dello stirene a 80°; esso può agire sia come iniziatore e come ritardatore e c'è una grande sensibilità alla luce. Gli esperimenti con ^{14}C-TMTM mostrano che il trasferimento all'iniziatore è importante. Sono stati fatti tentativi di misurare le velocità di dissociazione del TMTM tramite spettrofotometria e analisis a diluizione isotopica. A temperatura ambiente in soluzione di benzene, avvengono reazioni di scambio tra TMTM e il disolfuro corrispondente.

Zusammenfassung—Es wird über den Einfluß von Tetramethylthiurammonosulfid (TMTM) auf die Polymerisation von Styrol bei 80° berichtet. TMTM kann sowohl als Initiator als auch als Retardierungsmittel wirken und es besteht eine erhebliche Lichtempfindlichkeit. Experimente mit ^{14}C-TMTM zeigen, daß die Übertragung zum Initiator eine wichtige Rolle spielt. Es wurde versucht, die Dissoziationsgeschwindigkeit von TMTM spektrophotometrisch und durch die Isotopenverdünnungsanalyse zu messen. Bei Zimmertemperatur in Bezollösung finden Austauschreaktionen zwischen TMTM und dem entsprechenden Disulfid statt.