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## Polymerization of Acrylonitrile Initiated by the System Tetramethyl-2-tetrazene and p-Toluenesulfonic Acid

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### ABSTRACT

The polymerization of acrylonitrile (AN) initiated by tetramethyl-2-tetrazene (TMT) and p-toluenesulfonic acid (TSA) in dimethylformamide (DMF) was studied. The polymerization was confirmed to proceed through a radical mechanism. The initial rate of polymerization  $R_p$  was expressed by the equation:  $R_p = k[\text{TMT}]^{0.6} [\text{TSA}]^{0.46} [\text{AN}]^{1.35}$ . The overall activation energy for the polymerization was estimated as 20.7 kcal/mole. In the absence of monomer, the reaction of TMT with TSA was also studied kinetically by measuring the evolution of nitrogen. From these results and ESR measurement of the TMT/TSA system, a possible initiation mechanism is proposed.

### INTRODUCTION

TMT has been used as an initiator for the radical polymerization of ethylene [1-3], AN [4, 5], styrene (St) [6] at high temperature.

The previous papers have shown that the rate of polymerization of AN initiated by TMT is accelerated and the polymerization temperature is dropped by the addition of electrophilic reagents, such as acid anhydrides [4], haloacetic acids [7, 8], p-substituted benzyl chlorides [9, 10], and pyruvic acid [11]. The dimethylaminy radicals are at first generated by the reaction of TMT with the above electrophilic reagents, followed by formation of several basic products and tetramethylhydrazine radical cations which are detected by ESR spectroscopy. It was postulated that the initiating species is a dimethylaminy radical derived from the catalytic decomposition of TMT. During the work to extend previous studies on vinyl polymerization using tetrazenes as initiator, the author has found that the system of TMT and TSA acts as an effective initiator for the polymerization of vinyl monomers. In this paper, the radical polymerization of AN was carried out under homogeneous conditions with TMT/TSA as initiating system. In order to elucidate the detailed mechanism of initiation for the polymerization, the reaction of TMT with TSA in DMF was also studied kinetically and by ESR.

## EXPERIMENTAL

### Materials

The preparation of TMT was by the same procedure described in a previous paper [12]. TSA, benzenesulfonic acid (BSA), p-toluenesulfonyl chloride (TSC), and benzenesulfonyl chloride (BSC) were purified in the usual manner. DMF, AN, St, and methyl methacrylate (MMA) were purified in the usual manner and redistilled under a stream of nitrogen just before use.

### Polymerization

The polymerization procedure was the same as that described previously [7]. The copolymerization products from MMA and St were analyzed by elemental analysis for carbon and hydrogen. The intrinsic viscosity (dl/g) of polyacrylonitrile was determined in DMF at 30°C by using an Ubbelohde viscometer. The number-average molecular weight of the polymer was evaluated by Houtz's equation [13]:

$$[\eta] = 1.75 \times 10^{-3} \bar{M}_n^{0.66} \text{ dl/g}$$

### Kinetics

The kinetic apparatus consisted of a reaction vessel and an Ishii type dilatometer connected by glass tubes. The apparatus was kept isothermal to  $\pm 0.02^\circ\text{C}$ . The amount of nitrogen was measured by a volumetric method according to Overberger et al. [14, 15].

### ESR Measurement

The ESR measurement was carried out with a JES-ME instrument (Jeol Co.) equipped with 100-Hz modulation. The ESR spectra were rapidly measured at room temperature by the addition of TMT to a solution of TSA or TSC in DMF.

### Isolation of Basic Products

A mixture of 5.8 g (0.05 mole) of TMT and 8.2 g (0.05 mole) of TSC in 100 ml of tetrahydrofuran was allowed to stand for 5 days at room temperature. The oil liberated was separated and washed with 2 N hydrochloric acid. The oily material gradually became solid. Recrystallization of the solid from water/ethanol gave N,N-dimethylsulfonamide as yellow plates in 2.3 g yield, mp  $86^\circ\text{C}$  (lit. [16] mp  $86-87^\circ\text{C}$ ). The tetrahydrofuran layer combined with the above hydrochloric acid layer was used for washing. After removal of the solvent, hydrochloric acid salts of basic products were obtained in 3.5 g yield, and then made basic to give the tetramethylhydrazine, bp  $70-72^\circ\text{C}$ ,  $n_d$  1.402 (lit. [17] bp  $71-72^\circ\text{C}$ ,  $n_d$  1.40138) in 0.3 g yield.

Volatile dimethylamine was separated in a trap containing a 2 N hydrochloric acid; the dimethylamine HCl salt was mp  $170-171^\circ\text{C}$ . The reaction of TMT with TSA was also carried out in tetrahydrofuran. Tetramethylhydrazine and dimethylamine were obtained.

## RESULTS AND DISCUSSION

### Effect of Sulfonic Acid Derivatives

In order to examine the catalytic activity of benzenesulfonic acid derivatives, the polymerization of AN initiated by TMT was carried out in the presence of various sulfonic acid derivatives, such as TSA, BSA, TSC, and BSC. Figure 1 shows the time-conversion curves,

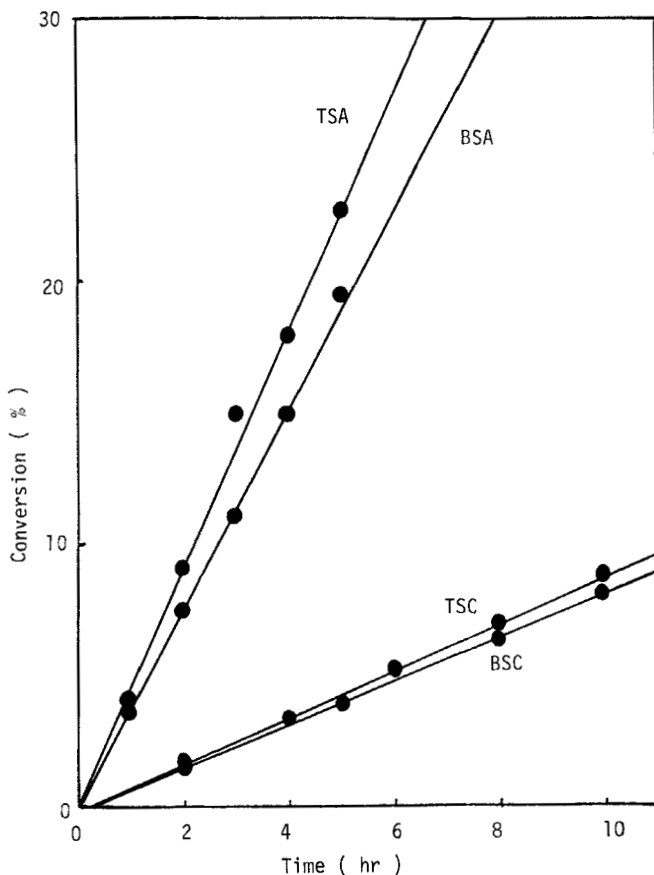


FIG. 1. Polymerization of AN initiated by TMT in the presence of benzenesulfonic acid derivatives in DMF at 45°C.  $[AN] = 4.56$  mole/liter;  $[TMT] = 0.02$  mole/liter;  $[TSA] = [BSA] = [TSC] = [BSC] = 0.004$  mole/liter.

from which it can be seen that the catalytic activity decreases in the order  $TSA > BSA > TSC > BSC$ . In this case, polymerization of AN was not initiated by TMT alone. TSA considerably accelerated catalytic decomposition of TMT. Thus the polymerization of AN initiated by TMT/TSA was investigated in some detail.

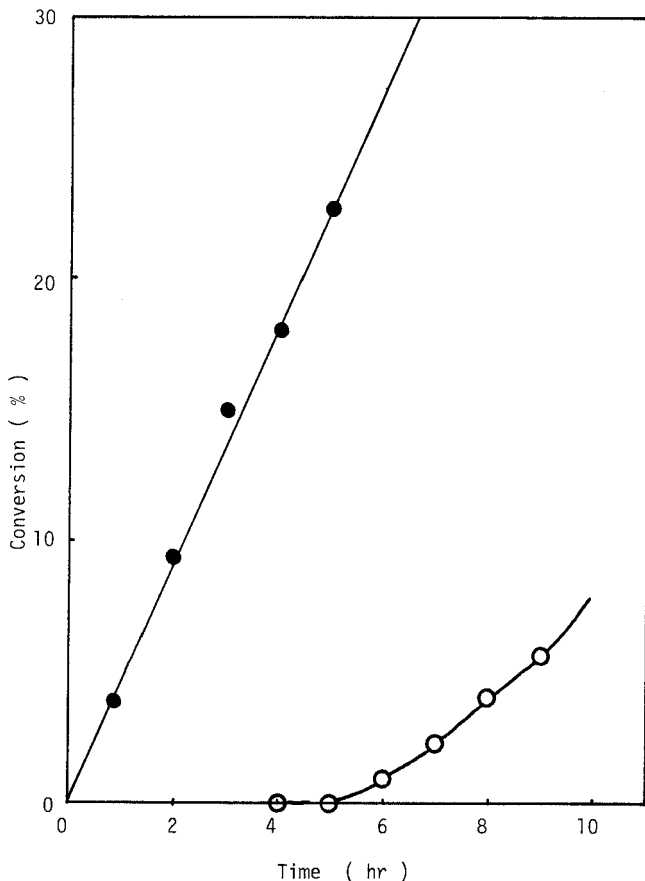


FIG. 2. Effect of p-quinone on the polymerization of AN initiated by the TMT/TSA system: (●) without p-quinone; (○) [p-quinone] =  $1.5 \times 10^{-4}$  mole/liter. [AN] = 4.56 mole/liter; [TMT] = 0.02 mole/liter; [TSA] = 0.004 mole/liter; at 45°C, in DMF.

### Confirmation of a Radical Mechanism

p-Quinone inhibited the polymerization of AN as shown in Fig. 2. The copolymerization of MMA with St initiated by TMT/TSA system was also carried out in DMF. The results obtained are shown in Fig. 3, which verifies a radical mechanism.

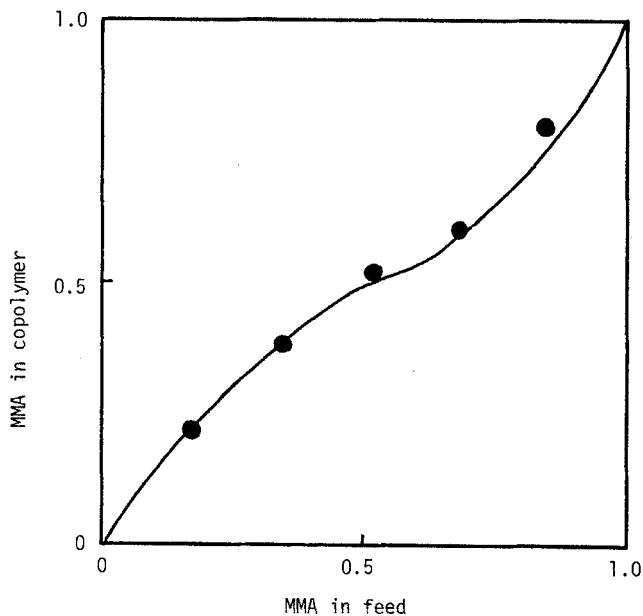


FIG. 3. Composition curve for the copolymerization of St and MMA initiated by the TMT/TSA system in DMF at 45°C for 4 hr. [TMT] = 0.02 mole/liter; [TSA] = 0.004 mole/liter.

### Effect of TSA

The polymerization of AN initiated by TMT/TSA system was carried out at 45°C by varying the TSA concentration with the concentration of TMT constant. As can be seen from Fig. 4, maximum conversion of AN was obtained at TSA concentration of  $4 \times 10^{-4}$  mole/liter. A reason for the depression in the polymerization rate with increasing TSA concentration could be that TSA acts vigorously as a chain-transfer agent (mentioned below and see Fig. 10). On the other hand, the binary system of TMT and TSC gave the maximum conversion of AN at a TSC concentration of  $2 \times 10^{-4}$  mole/liter. A cause for the fall in the rate with increasing TSC concentration could be that depressed the polymerization because of the inhibition effect of liberated chloride anions.

The polymerization of AN initiated by the TMT/TSA system was also carried out by varying the concentration of TSA below about  $4 \times 10^{-3}$  mole/liter. The rates of polymerization  $R_p$  were calculated

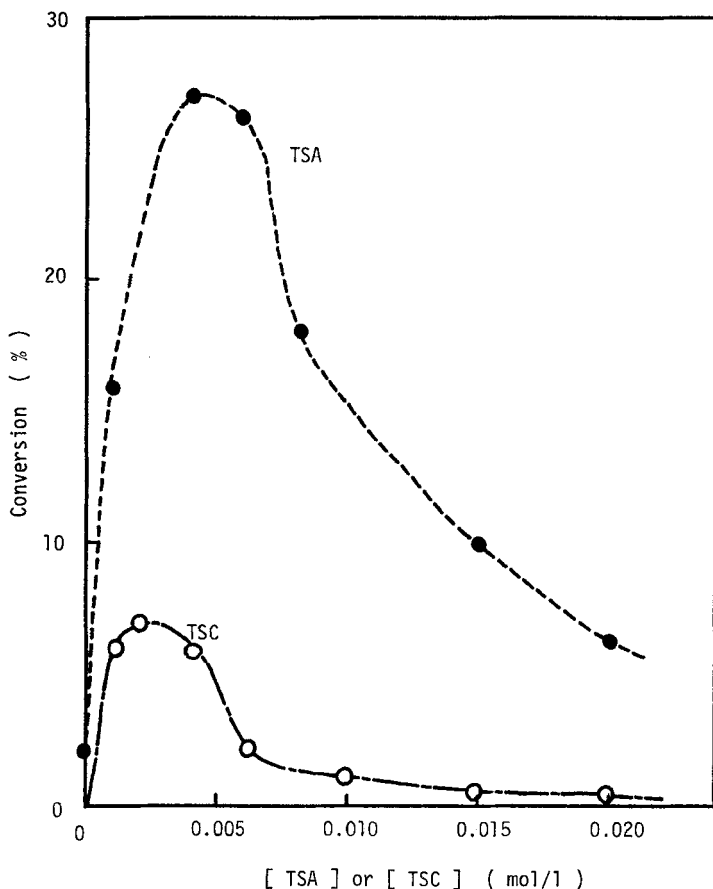


FIG. 4. Effect of TSA on the polymerization of AN initiated by TMT in DMF at 45°C for 6 hr.  $[AN] = 4.56$  mole/liter  $[TMT] = 0.02$  mole/liter;  $[TSA]$  was varied.

from the slope of the time-conversion curves, which were linear function up to 10 hr. The conversion were within 15% in all experiments. As can be seen from Fig. 5,  $R_p$  was proportional to the 0.46 power of the TSA concentration. Since the reaction order of TSA is smaller than 0.5, it is indicated that the initiating radicals and propagating radicals react with TSA.



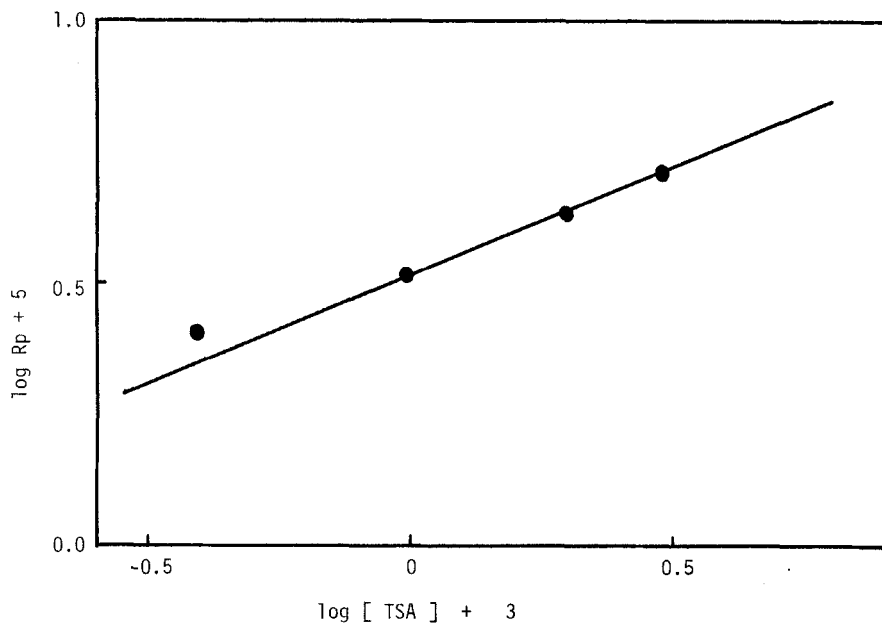


FIG. 5. Relationship between  $\log R_p$  and  $\log [TSA]$  for the polymerization of AN in DMF at 45°C.  $[AN]_p = 4.56$  mole/liter;  $[TMT] = 0.02$  mole/liter;  $[TSA]$  was varied.

#### Effect of TMT

The polymerization was carried out in DMF, at varying concentrations of TSA, and constant concentration of AN and TSA. As seen in Fig. 6,  $R_p$  is proportional to the 0.6 power of the concentration of TMT in the range  $0.4$  to  $2.0 \times 10^{-2}$  mole/liter.

#### Effect of AN

Furthermore, the polymerization was carried out in DMF at varying AN concentrations and constant concentrations of TMT and TSA.  $R_p$  is proportional to the 1.35 power of the concentration of AN as shown in Fig. 7. Therefore, the initial rate of polymerization of AN catalyzed by the TMT/TSA system can be expressed by

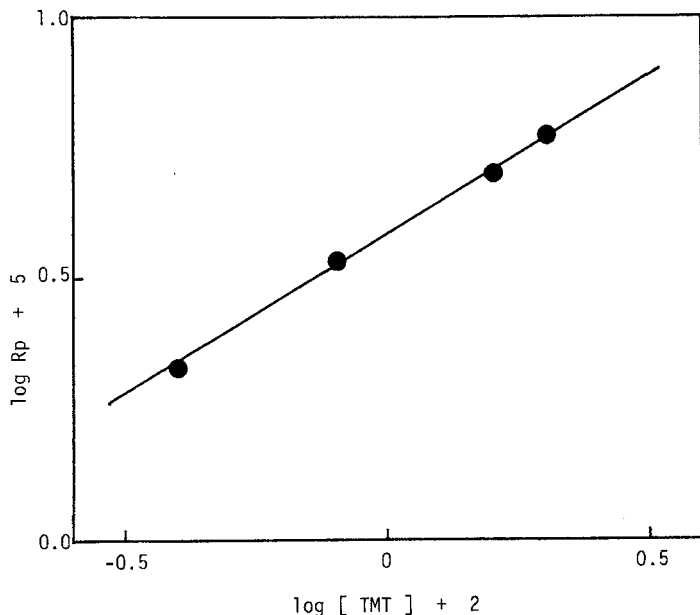


FIG. 6. Relationship between  $\log R_p$  and  $\log [TMT]$  for the polymerization of AN in DMF at 45°C.  $[AN] = 4.56$  mole/liter;  $[TSA] = 0.004$  mole/liter;  $[TMT]$  was varied.

$$R_p = k [TMT]^{0.6} [TSA]^{0.46} [AN]^{1.35}$$

The same kinetic behavior was obtained in the polymerization of AN initiated by the system consisting of TMF and some electrophilic reagents [4, 7-11]. The higher-order dependence on AN concentration may be explained by the participation of relatively unreactive radicals produced from DMF by chain transfer, as has been described previously [5, 18]. This explanation is supported by the evidence the chain-transfer constant of DMF ( $C_{DMF}$ ) is large, having values of  $1.0 \times 10^{-3}$ , as reported by Thomas et al. [19] or  $1.28 \times 10^{-3}$  as we reported previously [5].

#### Overall Activation Energy

The polymerization of AN initiated by the TMT/TSA system was carried out at varying temperatures between 30 and 50°C. The results

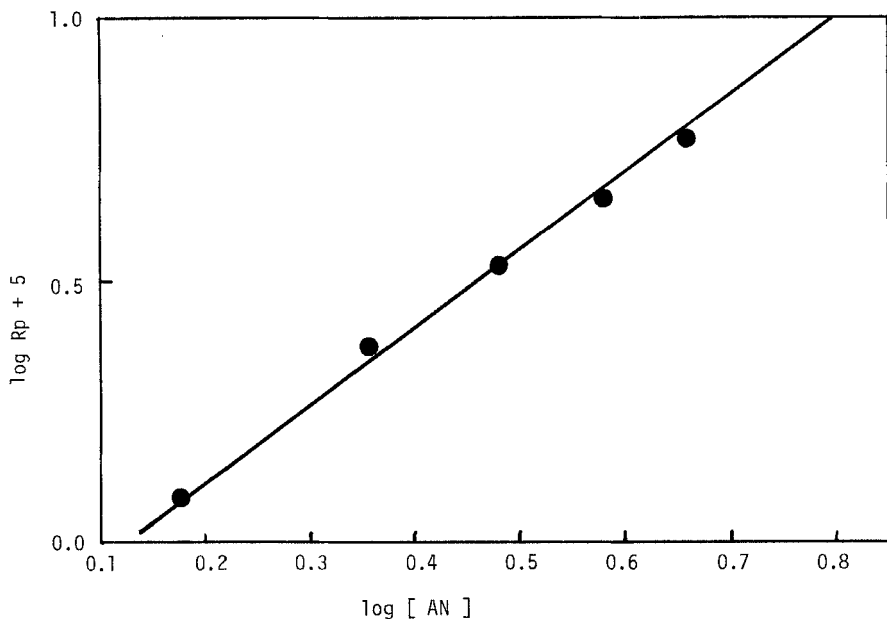


FIG. 7. Relationship between  $\log R_p$  and  $\log [AN]$  for the polymerization of AN in DMF at  $45^\circ\text{C}$ .  $[TMT] = 0.02$  mole/liter;  $[TSA] = 0.004$  mole/liter;  $[AN]$  was varied.

are shown in Fig. 8. From the slopes of the lines,  $R_p$  was calculated. The Arrhenius plot of  $\log R_p$  against  $1/T$  yielded an estimated overall activation energy of 20.7 kcal/mole, (Fig. 9).

#### Degree of Polymerization of the Polymers

The degree of polymerization of  $P_n$  of the resulting polyacrylonitrile was generally low, as shown in Fig. 10.

#### Reaction Kinetics

In order to clarify the initiation mechanism of the polymerization of AN initiated by the TMT/TSA system, the kinetics of the reaction

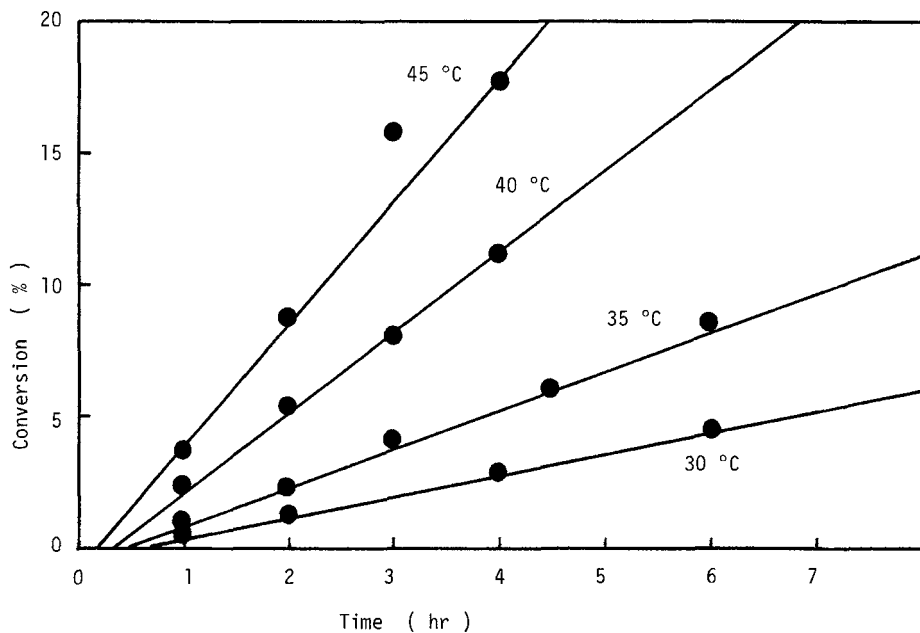


FIG. 8. Conversion vs. time in the polymerization of AN initiated by the TMT/TSA system in DMF at various temperatures.  $[AN] = 4.56$  mole/liter;  $[TMT] = 0.02$  mole/liter;  $[TSA] = 0.004$  mole/liter.

between TMT with TSA in DMF in the absence of AN was made by measuring the amount of nitrogen evolved from the reaction, as described in the Experimental section.

In order to determine the rate dependence, the reaction of TMT at a fixed concentration of TSA and that of TSA at a fixed concentration of TMT were followed. From the plots of  $\log [N_2]$  vs.  $\log [C]$ , the slopes are found to be 1.1 and 0.87 for the TMT and TSA, respectively, as shown in Fig. 11. The reaction is first-order with respect to TMT and is considered to be first-order in TSA. Therefore the reaction proceeds by a bimolecular second-order reaction.

Accordingly, the second-order constants ( $k_2$ ) were estimated graphically for the reaction from the following rate expression:

$$k_2 = (1/t) \{x/[a(a - x)]\}$$

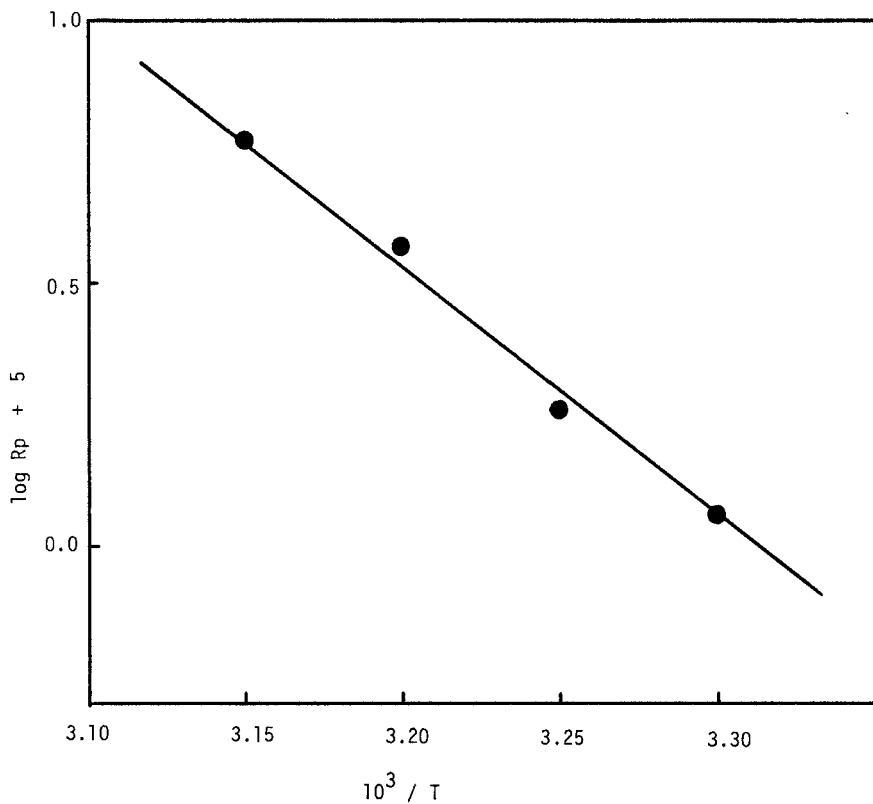


FIG. 9. Relationship between  $\log R_p$  and  $1/T$ .

where  $t$ ,  $x$ , and  $a$  represent the time, the amount of nitrogen formed at time  $t$ , and the initial concentration of TMT and TSA, respectively.

The kinetics of the reaction were followed over the temperature range 30-60°C. For equimolar initial concentrations of TMT and TSA, the plots of  $x/[a(a-x)]$  versus time gave good straight lines, as shown in Fig. 12. An Arrhenius plot of  $\log k_2$  afforded a good straight line as shown in Fig. 13, which gave 27.5 kcal/mole for the energy of activation. The enthalpy of activation ( $\Delta H^\ddagger$ ) was obtained from the equation

$$\Delta H^\ddagger = E_a$$

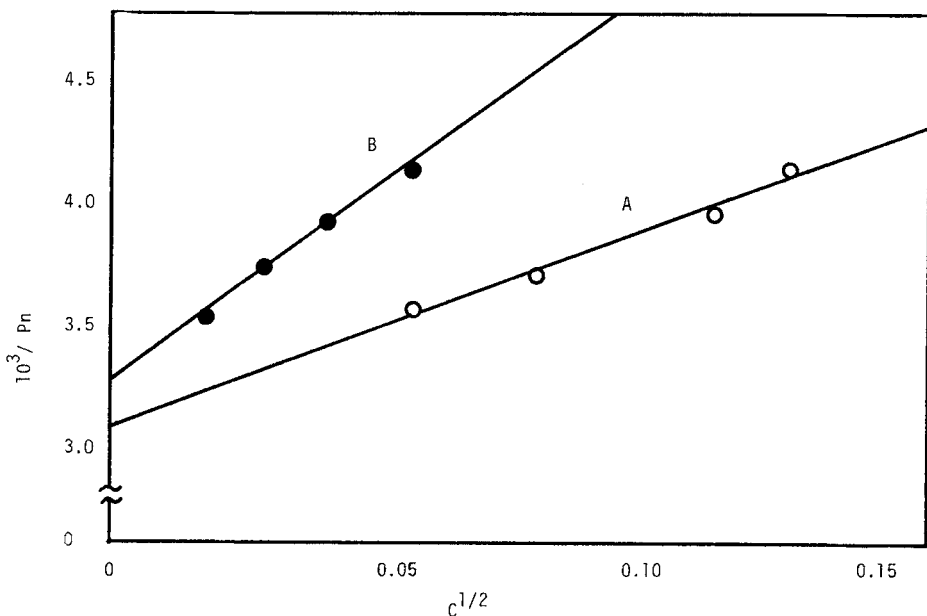


FIG. 10. Relationship between  $1/P_n$  vs.  $[TMT]^{1/2}$  or  $[TSA]^{1/2}$ , respectively, where  $c$  is the initiator concentration: (A)  $c = [TMT]$  was varied,  $[TSA] = 0.004$  mole/liter;  $[AN] = 4.56$  mole/liter; (B)  $c = [TSA]$  was varied,  $[TMT] = 0.02$  mole/liter;  $[AN] = 4.56$  mole/liter.

and the entropy of activation ( $\Delta S^\ddagger$ ) from the Eyring equation,

$$k_2 = kT/h \exp \{ \Delta H^\ddagger / RT \} \exp \{ \Delta S^\ddagger / R \}$$

The free energy of activation ( $\Delta G^\ddagger$ ) calculated from the equation

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$$

At  $45^\circ\text{C}$ ,  $\Delta H^\ddagger = 27.5$  kcal/mole,  $\Delta S^\ddagger = -7.79$  cal-mole/deg,  $\Delta G^\ddagger = 29.9$  kcal/mole. The negative entropy of activation reflects a high degree of activation, and this value is consistent with a reaction of neutral molecules via polarized transition state to form an ion intermediate.

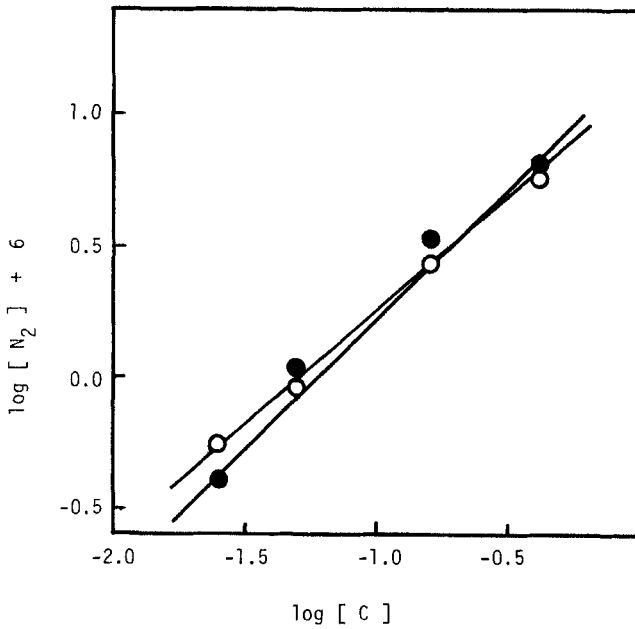


FIG. 11. Plot of  $\log [N_2]$  vs.  $\log [c]$  in DMF at  $30^\circ\text{C}$ : (●)  $c = [\text{TMT}]$  was varied,  $[\text{TSA}] = 0.1$  mole/liter; (○)  $c = [\text{TSA}]$  was varied,  $[\text{TMT}] = 0.1$  mole/liter.

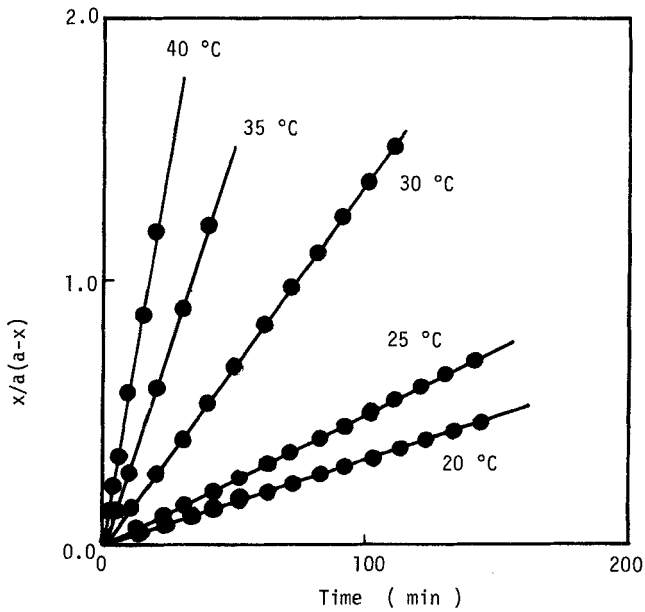


FIG. 12. Second-order plots for the reaction of TMT with TSA in DMF at various temperatures,  $[TMT] = [TSA] = 0.1$  mole/liter.



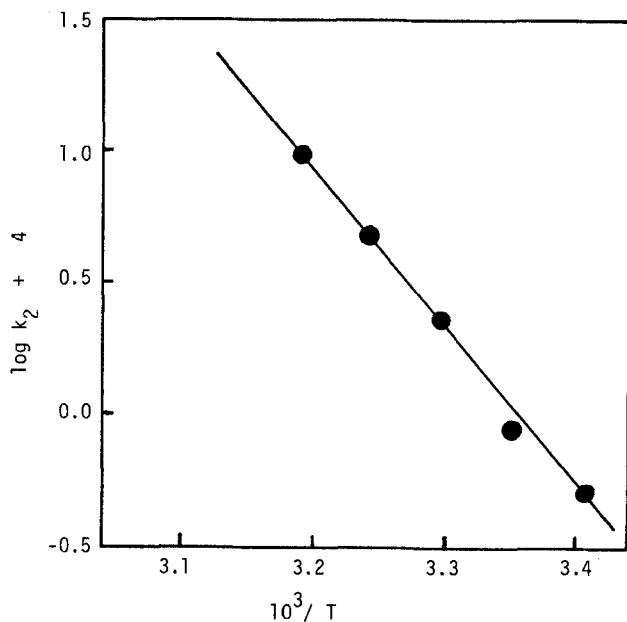


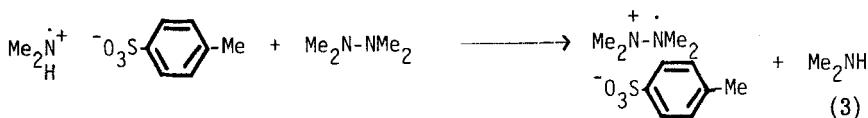
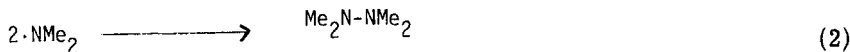
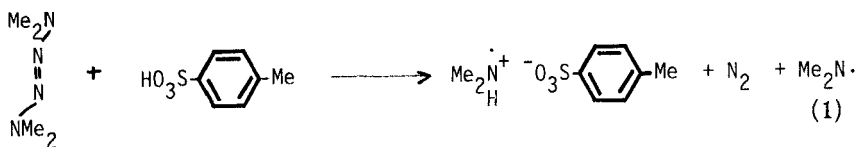
FIG. 13. Arrhenius plot for the reaction of TMT with TSA.

### Detection of ESR Signal

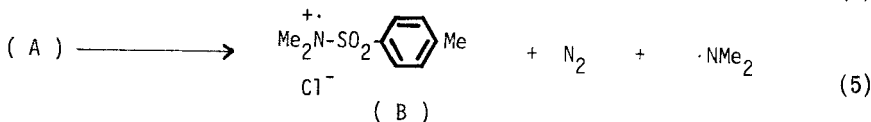
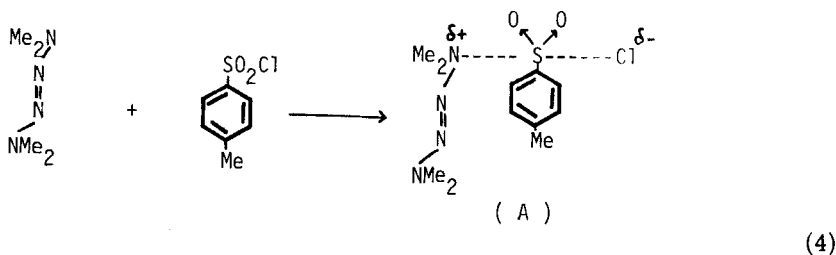
To gain more information about the radical species in the polymerization of AN initiated by the TMT/TSA and TMT/TSC system, the ESR spectrum was taken in the absence of AN in DMF at room temperature. In either case, the ESR spectrum gave the splittings for two equivalent nitrogens ( $a_{\text{H}} = 13.6$  gauss) and twelve equivalent hydrogens (12.4 gauss). Accordingly, the spectrum was identified as that of the tetramethylhydrazine radical cation observed on the reaction of TMT with several electrophilic reagents [20, 21].

### Initiation Mechanism

In the case of the binary system of TMT and TSA, the mechanism of the initiation proposed to account for the observation reported here is summarized in Eqs. (1)-(3).



On the other hand, the decomposition of TMT in the presence of TSC is believed to proceed by a nucleophilic attack of the dimethylamino nitrogen of TMT at the sulfur atom of TSC [Eqs. (4)-(7)]. This is supported by the present data and the earlier results of others [20, 21].



In combination with previous [9-12] and present results, it is confirmed that the dimethylaminyl radical induced the polymerization of AN.

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