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# Polymerization of Styrene Initiated by 1,4-Dimethyl-1,4-bis(p-anisyl)-2-tetrazene

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# Polymerization of Styrene Initiated by 1,4-Dimethyl-1,4-bis(p-anisyl)-2-tetrazene

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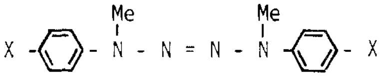
## ABSTRACT

The polymerization of styrene (St) initiated by 1,4-dimethyl-1,4-bis(p-anisyl)-2-tetrazene (1a) was studied kinetically in benzene. The polymerization proceeds through a radical mechanism. The rate of polymerization is proportional to $[\underline{1a}]^{0.5}$ and $[\mathrm{St}]^{1.0}$. The overall activation energy for the polymerization is found to be 81.2 kJ/mol within the temperature range of 65 to 80°C. The activation parameters for the decomposition of 1a at 70°C are $k_d = 1.88 \times 10^{-5}\ \mathrm{s}^{-1}$, $\Delta H^{\ddagger} = 133.1$ kJ/mol, and $\Delta S^{\ddagger} = 29.9$ J/mol·deg.

## INTRODUCTION

It is known that tetraalkyl-2-tetrazenes, especially the tetramethyl derivatives, can initiate the radical polymerization of vinyl monomers [1-7], while aralkyl-2-tetrazenes are generally not as much initiators as inhibitors or/and retarders in polymerization [8, 9]. For instance, 1,1,4,4-tetraphenyl-2-tetrazene, which is a source of diphenylamino radicals, has been used as an effective inhibitor for the radical polymerization of styrene [8]. It has been also found that a series of 1,4-dimethyl-1,4-bis(p-substituted phenyl)-2-tetrazenes (1) act as chain-transfer agents in the radical polymerization of acrylonitrile [9].



| 1: | a | b | c | d | e |
|---|---|---|---|---|---|
| X: | OMe | Me | H | Cl | $NO_2$ |

A plot of the chain-transfer constants vs $\sigma$-values of substituents (X) gives a straight line with a negative $\rho$. It was also found that 1c-e enhanced the polymerization of acrylonitrile, 1b affected it little, whereas 1a retarded it. It seems that the reactivity of the anilino radicals depends on the substituents attached at the nitrogen atoms [9].

On the other hand, Nelsen et al. [10, 11] have shown the N-tert-butyl-p-substituted anilino radical is a member of Walter's "class S" radicals based on measuring the spin densities of the odd electron on the nitrogen atoms. Accordingly, both electron donor and acceptor substituents make the unpaired electron delocalize and cause a decrease in the spin density of the nitrogens.

In a previous paper [12] it was found that an arylamino radical with an electron-acceptor group, that is, N-methyl-p-nitrophenylamino radicals derived from 1e, can initiate the radical polymerization of acrylonitrile in N,N-dimethylformamide at rather high reaction temperatures. In connection with the facts mentioned above, 1a will initiate polymerization only if suitable conditions are chosen. The present paper is mainly concerned with a kinetic study of the polymerization of styrene initiated by 1a, which produces an arylamino radical with an electron-acceptor group.

## EXPERIMENTAL

### Materials

1a was prepared by oxidation of N-methyl-N-p-anisylhydrazine with freshly sublimed quinone in absolute ethanol, according to the method of Nelsen and Heath [13], mp 152-153°C dec. (Ref. 13, mp 152°C dec.), UV (in benzene) 452 nm (log $\epsilon$ 4.56), 319 nm (log $\epsilon$ 4.53). Styrene was purified as follows. After an inhibitor was removed by sodium thiosulfate aqueous solution, the styrene was dried over barium oxide and distilled twice under reduced pressure just before use. Benzene was washed sequentially with sulfuric acid, water, alkaline solution, and water. After being dried over calcium chloride, benzene was distilled from a sodium wire.

### Polymerization

A benzene solution containing the required amounts of styrene and 1a in a tube was degassed by the freeze-thaw technique using a Dry-Ice/methanol bath and sealed in vacuo. The sealed tube was shaken in a thermostat maintained at a definite temperature. After polymerization for a given time, the content of the tube was poured into a large amount of methanol to precipitate the polymer. The rate of polymerization was calculated by subtracting the weight of thermal polymerization products from that of the overall dry polymer obtained. The intrinsic viscosities of polystyrene were determined in benzene at 30°C by using an Ubbelohode viscometer. The number-average molecular weight of the polymer was calculated from the intrinsic viscosity [14]:

$$P_n = 1.77 \times 10^3 \, [\eta]^{1.40} \qquad (1)$$

### Thermal Decomposition

A known amount of 1a in benzene was placed in a glass tube which was cooled in a Dry-Ice/methanol bath and sealed. The sealed tube was shaken in a thermostat maintained at a definite temperature. After decomposition for a given time, the content of the tube was determined by UV measurements.

### UV Measurement

The rate of thermal decomposition of 1a in benzene was determined by spectrophotometry, measuring the rate of disappearance

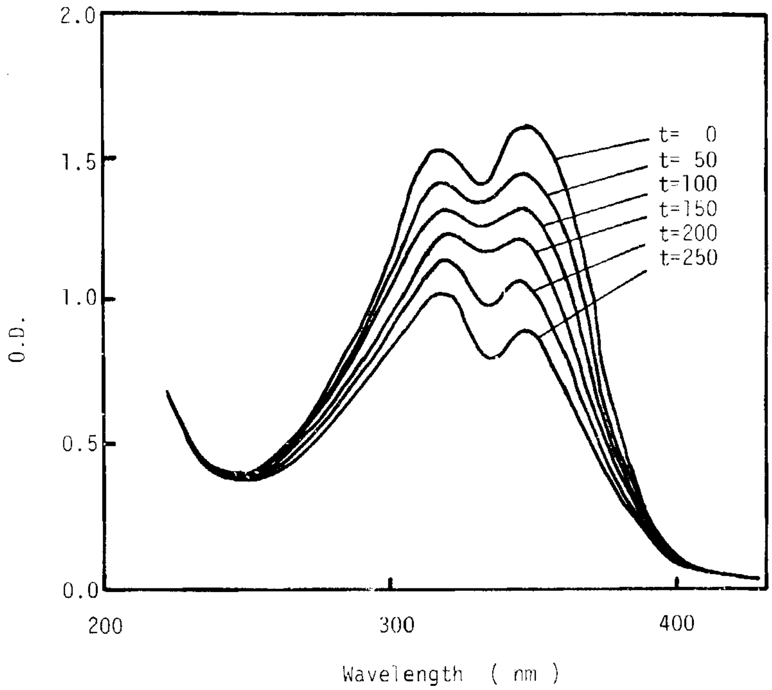


FIG. 1. UV spectra taken during the course of decomposition of 1a in benzene at 70°C. t is in minutes.

of the absorption at 352 nm of 1a. The first-order decomposition rate constants, $k_d$, were calculated from

$$k_d = t^{-1} \times \ln (D_0/D_t) \qquad (2)$$

where $D_0$ and $D_t$ represent the absorbances at times 0 and t, respectively.

## RESULTS AND DISCUSSION

### Thermal Decomposition of 1a

The thermal decomposition of 1a was accomplished over the temperature range of 65 to 85°C. As a typical example, the spectral change with time t during the decomposition of 1a in benzene at 70°C

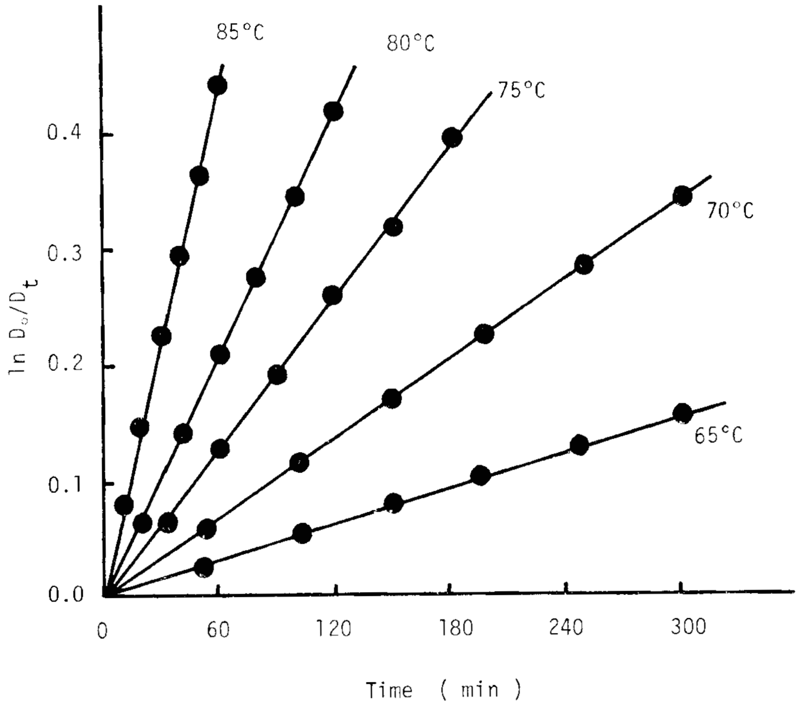


FIG. 2. Plots according to Eq. (1) when la was decomposed in benzene at various temperatures.

is shown in Fig. 1. The changes of absorption at $\lambda_{max}$ (352 nm) vs the concentration of la followed Beer's law quite well. As can be seen from the plots of ln $(D_0/D_t)$ vs time according to Eq. (2) at different temperatures (Fig. 2), the rate of decomposition followed first-order kinetics. The rate constants are summarized in Table 1. The Arrhenius plot of the data in Table 1 yielded a good straight line. The enthalpy of activation and the entropy of activation were calculated from

$$\Delta H^{\ddagger} = E_a + RT \tag{3}$$

$$k_d = (\kappa T/h) \exp(-\Delta H^{\ddagger}/RT) \exp(\Delta S^{\ddagger}/R) \tag{4}$$

From applying the data to Eqs. (3) and (4), $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ at 70°C were estimated to be 133.1 kJ/mol and 29.9 J/mol·deg, while in the case of le the activation parameters were estimated in N,N-dimethylformamide

TABLE 1. First-Order Rate Constants, $k_d$, for the Decomposition of 1a at Various Temperatures

| Temperature: (°C): | 65 | 70 | 75 | 80 | 85 |
|---|---|---|---|---|---|
| $k_d \times 10^5$ ($s^{-1}$): | 0.903 | 1.88 | 3.57 | 5.97 | 12.2 |

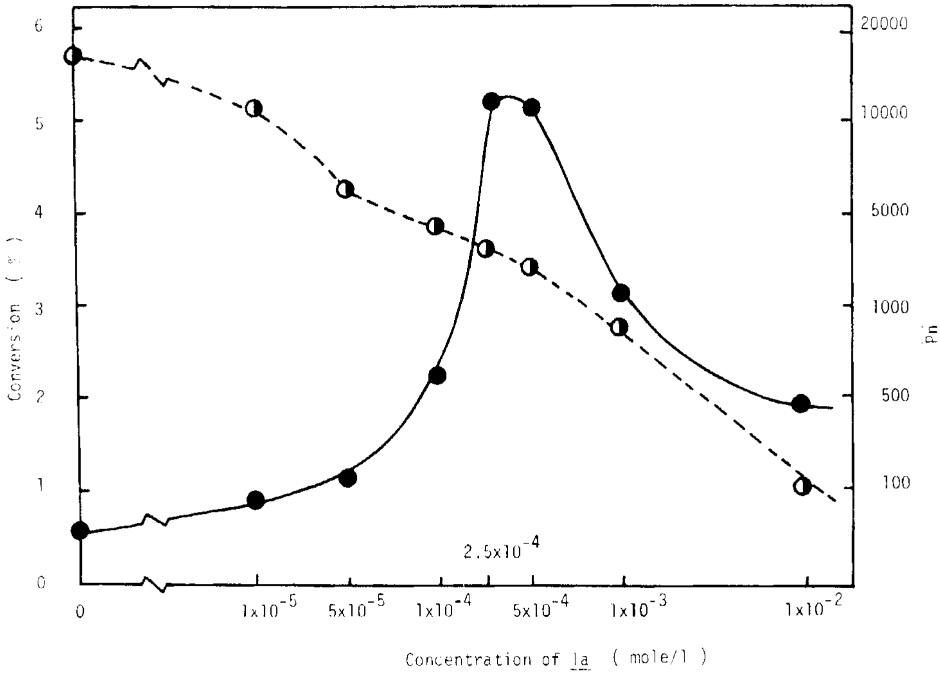


FIG. 3. Polymerization of styrene in the presence of 1a in benzene at 65°C for 6 h. [1a] was varied, [St] = 4.33 mol/L. Solid line: Conversion. Dashed line: $P_n$.

at 120°C as $\Delta H^‡ = 170.8$ kJ/mol and $\Delta S^‡ = 81.6$ J/mol·deg [12]. 1a decomposes easier than any other 2-tetrazenes in 1 since the relative decomposition rate of 1 in toluene [13] and acetonitrile [15] gives a negative $\rho$ in Hammett correlation with $\sigma$. Nelsen et al. suggested that the stability of the odd electron on the nitrogen radical is not very important in the rate-determining step of the decomposition of 1, but all of the rate decrease may be caused by the $\Delta S^‡$ term [13].

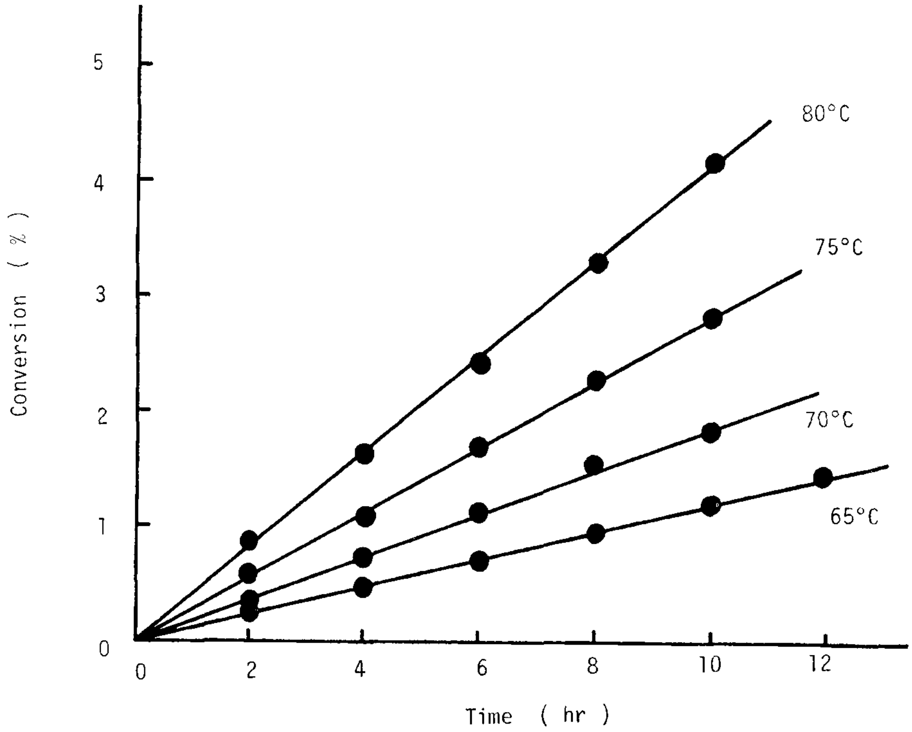


FIG. 4. Time-conversion curves in the polymerization of styrene (St) initiated by 1a in benzene at various temperatures. [St] = 2.60 mol/L, [1a] = 2.5 × $10^{-4}$ mol/L.

## Polymerization of Styrene in the Presence of 1a

In order to test the initiating ability of 1a, the polymerization of styrene was carried out in bulk at 65°C for 8 h with varying concentrations of 1a. As can be seen from Fig. 3, the rate increases with the concentration of 1a up to about 2.5 × $10^{-4}$ mol/L, but above a limiting concentration of 1a the polymerization is depressed while the number-average molecular weight of polystyrene keeps on decreasing with the concentration of 1a. It is suggested that 1a acts as both initiator and retarder; that is, 1a shows catalytic activity for polymerization only at low concentrations. Henceforth in this article, the polymerization of styrene was carried out below a concentration of 2.5 × $10^{-4}$ mol/L of 1a.

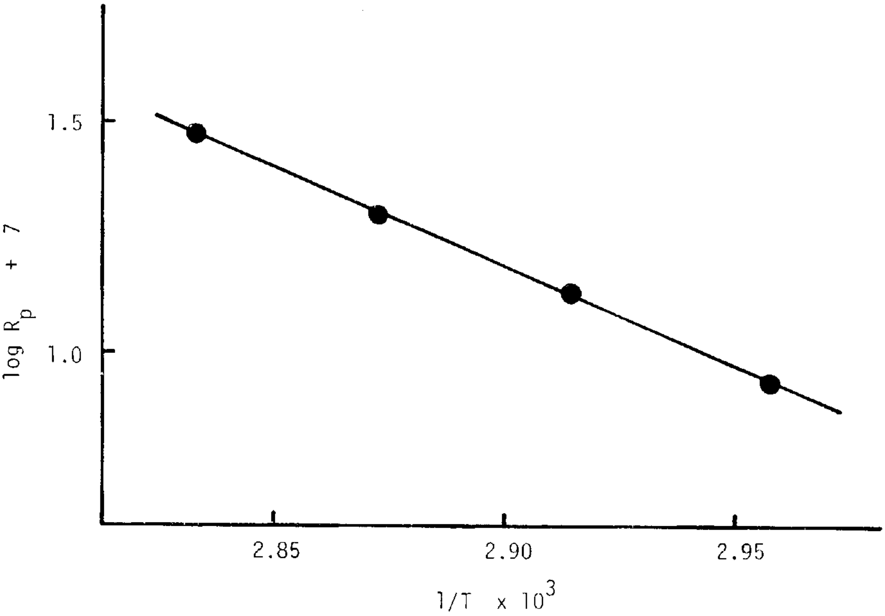


FIG. 5. Arrhenius plot for the polymerization of styrene initiated by 1a.

## Overall Activation Energy for the Polymerization of Styrene Initiated by 1a

Since 1a shows initiating ability, the homogeneous polymerization of styrene initiated by 1a was carried out in benzene at temperatures varying over the range of 65 to 80°C. Figure 4 shows the time-conversion curves of the polymerization of styrene initiated by 1a. The Arrhenius plot of log $R_p$ vs 1/T gave a good straight line, as shown in Fig. 5. The overall activation energy was estimated to be 81.2 kJ/mol.

## Kinetics of Polymerization

The polymerization of styrene initiated by 1a was studied kinetically. Polymerization was carried out in benzene or in bulk at 65°C with varying concentrations of 1a from $0.5 \times 10^{-4}$ to $2.5 \times 10^{-4}$ mol/L. Polymerization was also carried out in benzene with varying concentrations of styrene (from 0.87 to 2.60 mol/L) with the concentration of 1a constant. The results are summarized in Table 2. The

TABLE 2. Kinetic Data for the Polymerization of Styrene (St) Initiated by 1a in Benzene at 65°C

| [St] (mol/L) | [1a] (mol/L) | $R_p \times 10^7$ (mol/L·s) | $P_n$[a] |
|---|---|---|---|
| 0.870 | 1.00 | 1.70 | |
| 1.30 | 1.00 | 2.57 | |
| 1.73 | 1.00 | 3.47 | |
| 2.16 | 1.00 | 4.37 | |
| 2.60 | 1.00 | 5.39 | |
| 2.60 | 0.500 | 3.85 | |
| 2.60 | 1.50 | 6.73 | |
| 2.60 | 2.00 | 7.60 | |
| 2.60 | 2.50 | 8.75 | |
| 8.66[b] | 0.500 | 4.62 | 10,020 |
| 8.66[b] | 1.00 | 7.20 | 8,240 |
| 8.66[b] | 1.50 | 8.60 | 6,960 |
| 8.66[b] | 2.00 | 9.58 | 5,750 |
| 8.66[b] | 2.50 | 10.8 | 4,640 |

[a] The polymer used was obtained from polymerization for 6 h.
[b] Polymerization was carried out neat.

relationship between $R_p$ and the concentration of 1a is shown in Fig. 6. The rate was proportional to the 0.5 power of the concentration of 1a below $2.5 \times 10^{-4}$ mol/L. As shown in Fig. 7, the rate was proportional to the 1.00 power of the styrene concentration. Therefore, the initial rate of polymerization of styrene by 1a can be expressed by

$$R_p = k[1a]^{0.5}[\text{styrene}]^{1.00} \tag{5}$$

A plot of $R_p$ and $1/p_n$ (Fig. 8) does not give a straight line, partly because 1a may be easily decomposed to give an anilino radical by polystyryl-radical-induced decomposition and partly because the anilino radicals may couple with the growing radicals.

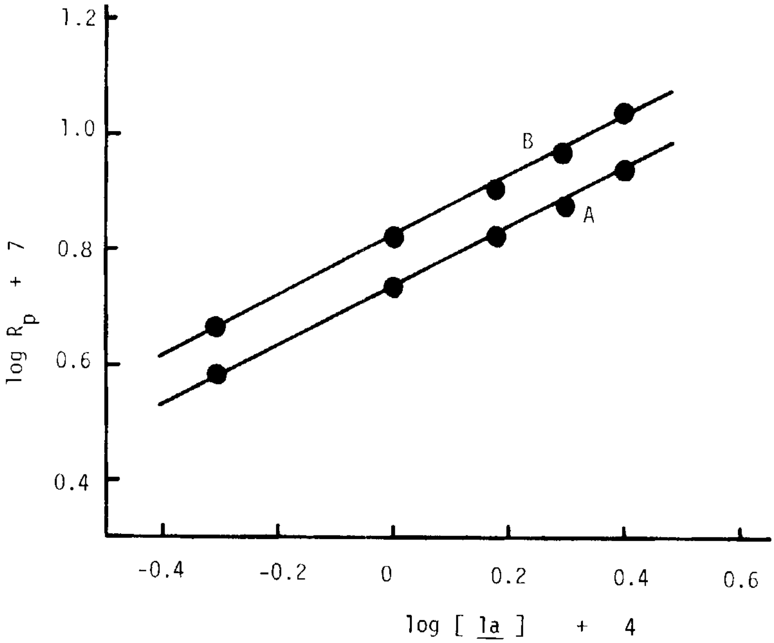


FIG. 6. $R_p$ vs [1a] in the polymerization of styrene in benzene (A) and neat (B) at 65°C. A: [St] = 2.60 mol/L, [1a] was varied. B: [St] = 8.66 mol/L, [1a] was varied.

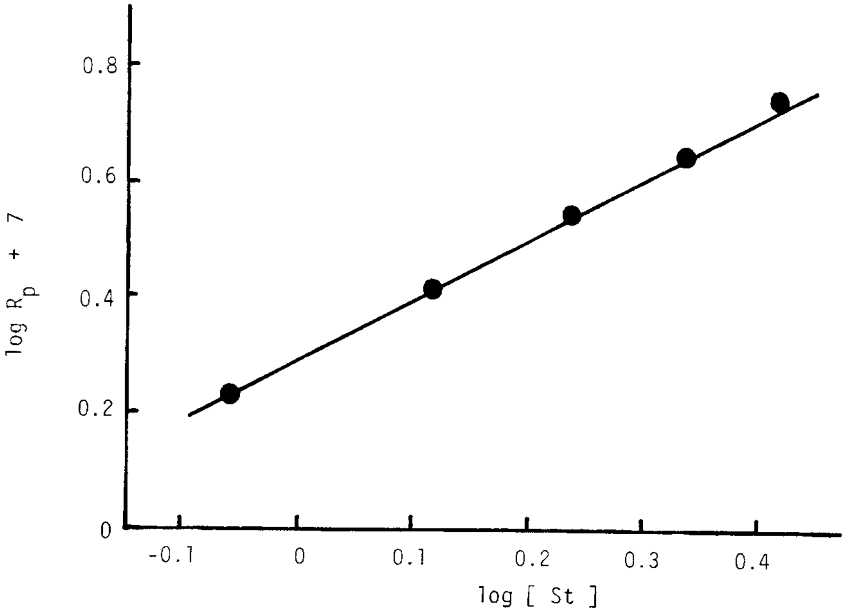


FIG. 7. $R_p$ vs [St] in the polymerization of styrene in benzene at 65° C. [1a] = $1 \times 10^{-4}$ mol/L, [St] was varied.

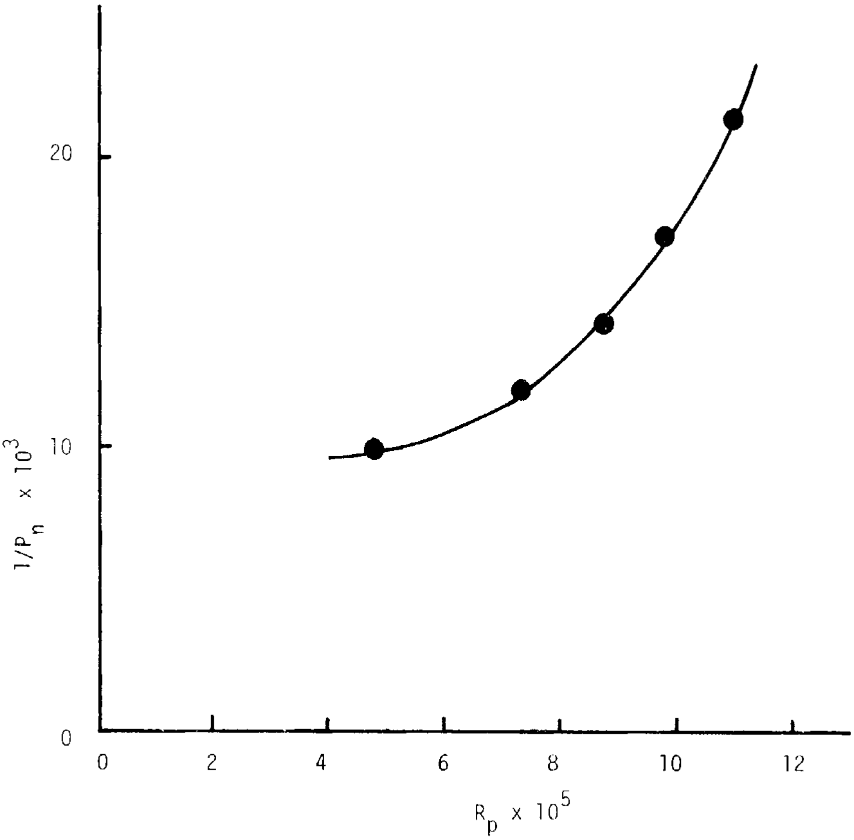


FIG. 8. Relationship between $1/P_n$ and $R_p$ in the polymerization of neat styrene at 65°C for 6 h. [St] = 8.66 mol/L, [1a] was varied.

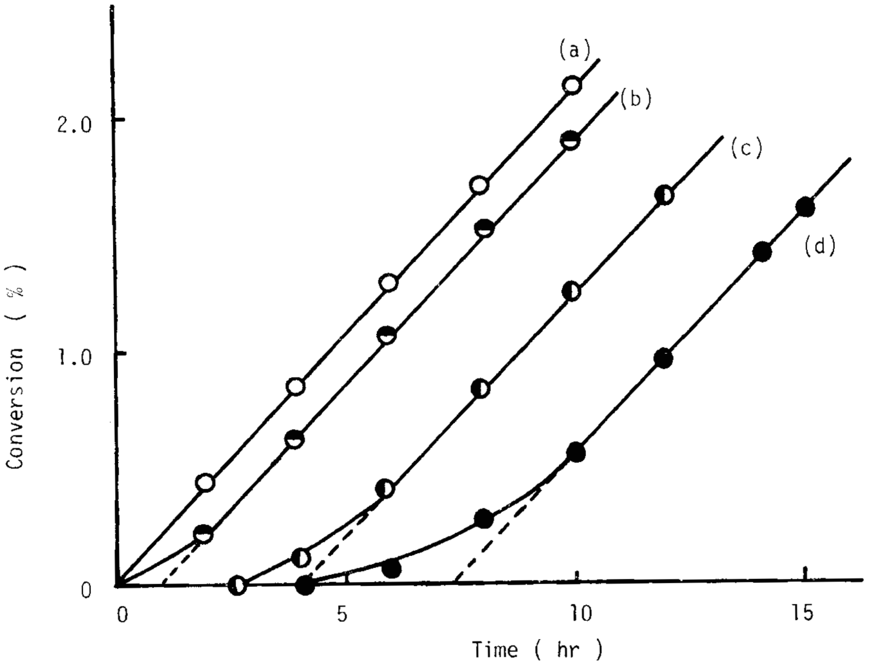


FIG. 9. Effect of p-quinone on the polymerization of styrene initiated by 1a in benzene at 65°C. In this figure the conversion was calculated from the whole dry polymer obtained. [St] = 2.60 mol/L, [1a] = $1 \times 10^{-4}$ mol/L, [p-quinone] = 0, $0.5 \times 10^{-5}$, $1.5 \times 10^{-5}$, and $3.0 \times 10^{-5}$ mol/L for a, b, c, and d, respectively.

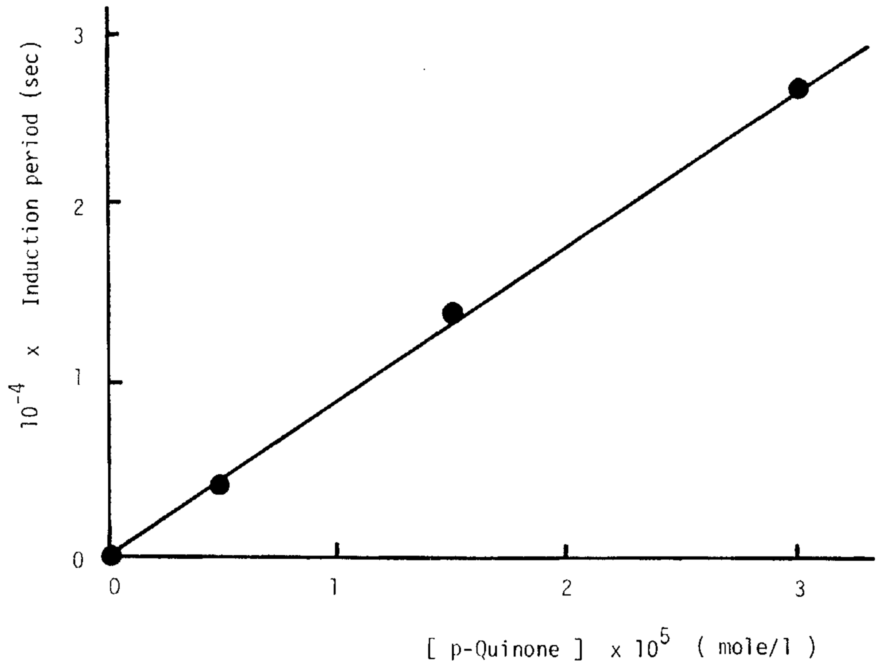


FIG. 10. Relationship between induction period and [p-quinone].

## Effect of p-Quinone

In order to clarify the initiating ability of 1a, the polymerization of styrene catalyzed by 1a was carried out in the present of various amount of p-quinone in benzene as shown in Fig. 9. p-Quinone inhibited the polymerization. This indicates that the polymerization proceeds through a radical mechanism. The relationship between the concentration of p-quinone and the induction period is a linear function (Fig. 10) from which slope the rate of initiation of polymerization ($R_i$) was obtained to be 1.11 × $10^{-7}$ mol/L·s. The ratio of the rate constants of propagation and termination, $k_p^2/k_t$, was estimated according to Eq. (6) [16]:

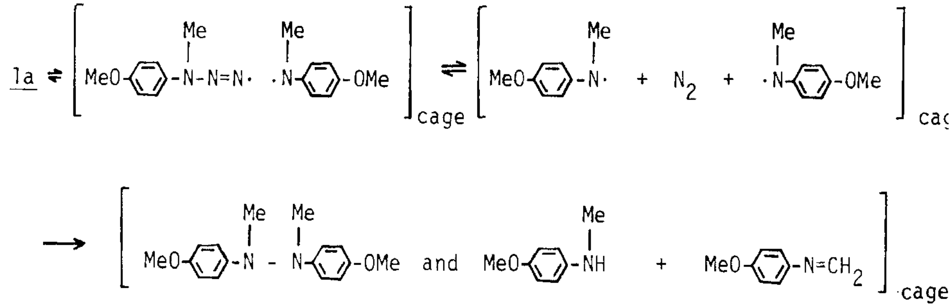
$$k_p^2/k_t = R_p^2/(R_i[M]^2) \tag{6}$$

The value of $k_p^2/k_t$ was calculated as 3.18 × $10^{-4}$ L/mol·s. The efficiency of the initiator, f, was calculated by Eq. (7) [17]:

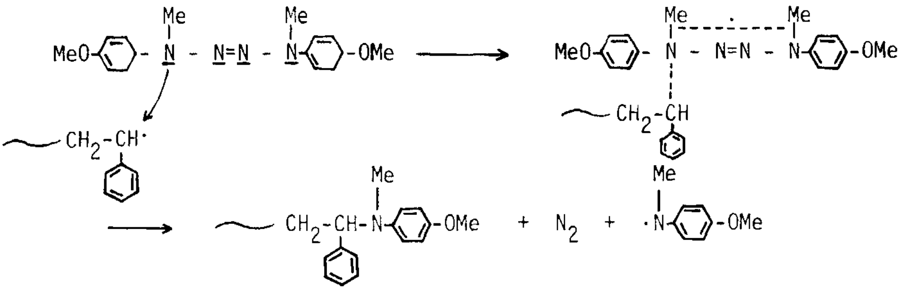
$$f = R_i/(2k_d[I]) \tag{7}$$

where I represents the initiator. f is found to be 0.296, which is rather small as compared with the case of 1e (f = 0.832) [12].

The odd electron of the anilino radicals derived from 1e is expected to be in the most delocalized molecular orbitals, and that of the anilino radical from 1a is also delocalized. An explanation could be that in the case of 1a the following reaction may occur in a solvent cage in preference to addition to monomer out of the cage. The coupling reaction of the geminate N-methyl-p-nitroanilino radicals in the cage is, however, hardly possible because of the highly cationic character of the radicals.



Another reason could be that 1a is easily attacked by the growing polystyryl radicals to give relatively low molecular weight products. The polystyryl-radical-induced decomposition of 1a might occur as follows:



Although the exact behavior of 1a is somewhat indistinct in the polymerization system, 1a obviously acts as an initiator as well as an inhibitor or retarder, depending on its concentration.

There have been some disputes about whether or not a nitrogen radical can add to simple alkenes [6, 18-20]. Michejda and Campbell found that the neutral dialkylamino radical (dimethylamino radical) adds electrophilically to simple olefins, while a complex amino radical is revealed to add nucleophilically to vinyl monomers [18]. The aralkylamino radicals derived from 1a can add to an olefin when they exist at low concentrations in the reaction system, while the radicals react predominantly with the original radicals or the propagating radicals to inhibit the propagation reaction when they are present at a higher concentration. At the same time, the resonance stabilization of the radical plays an important role in the addition to olefins, as discussed in a previous paper [21].

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