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Polymerization of Acrylonitrile Initiated by 1,4-Dimethyl-1,4-bis(p-nitrophenyl)-2-tetrazene

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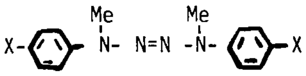
ABSTRACT

The polymerization of acrylonitrile (AN) initiated by 1,4-dimethyl-1,4-bis(p-nitrophenyl)-2-tetrazene (Ie) was studied in dimethylformamide (DMF) at high temperature. The polymerization proceeds by a radical mechanism. The rate of polymerization is proportional to $[\mathrm{Ie}]^{0.64}$ and $[\mathrm{AN}]^{1.36}$. The overall activation energy for the polymerization is 21.5 kcal/mole within the temperature range of 115-130°C. The chain transfer of Ie was also undertaken over the temperature range of 120-135°C. The activation parameters for the decomposition of Ie

at 120°C are $k_d = 2.78 \times 10^{-6}$ sec^{-1}, $\Delta H^\ddagger = 40.8$ kcal/mole, and $\Delta S^\ddagger = 19.5$ cal/mole-deg, respectively.

INTRODUCTION

Information about the reaction of reactive radicals with an unpaired electron at the nitrogen atom (e. g., an aminyl radical) with simple olefins is insufficient. Dimethyl aminyl radicals derived from thermal or photochemical decomposition of 1,1,4,4-tetramethyl-2-tetrazene (TMT) have been found to add to α-methylstyrene [1-3]. Piperidinyl radicals derived from 1,1:4,4-bis(pentamethylene)-2-tetrazene (BPT) also form the products of addition to α-methylstyrene [4]. In the case of radical polymerization, several 2-tetrazenes such as TMT [2, 5-9], BPT [4], and 1,4-dimethyl-1,4-dicarbomethoxy-2-tetrazene [10] are effective initiators for the polymerization of vinyl monomers (e. g., acrylonitrile, methy methacrylate, styrene, and ethylene). At the same time, the initiating species was suggested to be a substituted aminylradical derived from thermal or photochemical decomposition of a 2-tetrazene. On the other hand, aromatic 2-tetrazenes act as inhibitors or retarders in the polymerization of vinyl monomer [11, 12]. 1,1,4,4-Tetraphenyl-2-tetrazene inhibits the radical polymerization of styrene [12], while 1,4-dimethyl-1,4-diphenyl-2-tetrazene and 1,4-diphenyl-1,4-dibenzyl-2-tetrazene retard the polymerization of styrene initiated by azobisisobutylonitrile (AIBN). In addition 1,4-dimethyl-1,4-diaryl-2-tetrazenes (I) act as chain-transfer agents in the polymerization of acrylonitrile [13].



I

	a	b	c	d	e
X =	OCH_3	CH_3	H	Cl	NO_2

In the course of the study on the radical-induced decomposition of I, it Ie was found to act as an effective initiator for the polymerization of acrylonitrile at high temperature. In connection with our study on reactivities of nitrogen radicals, the present paper is concerned mainly with a detailed study on the initiating properties of Ie for the polymerization of acrylonitrile.

EXPERIMENTAL

Materials

Ie was prepared by oxidation of N-methyl-4-nitrophenylhydrazine with lead dioxide in 1,2-dimethoxyethane, according to the method of Nelsen [14], mp 239-240°C dec. (lit. [15] mp, 239°C dec.). Acrylonitrile and dimethylformamide (DMF) were purified by standard methods and distilled twice under reduced pressure in an atmosphere of nitrogen before use.

Polymerization

The polymerization procedures were the same as those described in a previous paper [10]. The rate of polymerization was calculated by subtracting the weight of thermal polymerization from that of overall dry polymer obtained. The intrinsic viscosities of polyacrylonitrile were determined in DMF at 30°C by using an Ubbelohde viscometer. The number-average molecular weight of the polymer was calculated from the intrinsic viscosity according to the equation [16]:

$$[\eta] = 3.92 \times 10^{-4} M_n^{0.75} \tag{1}$$

Thermal Decomposition

A known amount of Ie 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 contents of the tube were characterized by UV measurements.

UV Measurements

The rate of the thermal decomposition of Ie in DMF was determined by spectrophotometry, measuring the rate of disappearance of the absorptions of Ie at 443 nm. The first-order decomposition rate constants, k_d, were calculated from Eq. (2):

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

where D_0 and D_t represent the absorbances at zero time and time t, respectively.

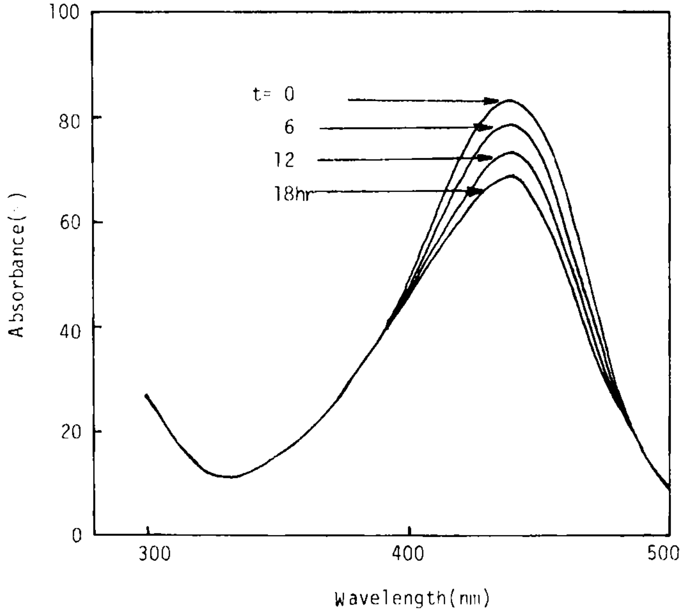


FIG. 1. UV spectra taken during the course of the decomposition of Ie in DMF at 120°C.

RESULTS AND DISCUSSION

Thermal Decomposition of Ie

The thermal decomposition of Ie was carried out at 120, 125, 130, and 135°C. As a typical example, the spectral changes with time t during the thermal decomposition of Ie in DMF at 120°C are shown in Fig. 1. The changes of absorption vs. concentration of Ie at 443 nm followed Beer's law quite well. For the decomposition of Ie at different temperatures, the plots of $\ln(D_0/D_t)$ vs. time according to Eq. (2) gave good straight lines, as shown in Fig. 2. From this, it can be seen that the rate of decomposition follows a 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 as shown in Fig. 3. It corresponds to Eq. (3):

$$k_d = 5.40 \times 10^{16} \exp\{-40/RT\} \sec^{-1} \text{ (for 120-135°C)} \qquad (3)$$

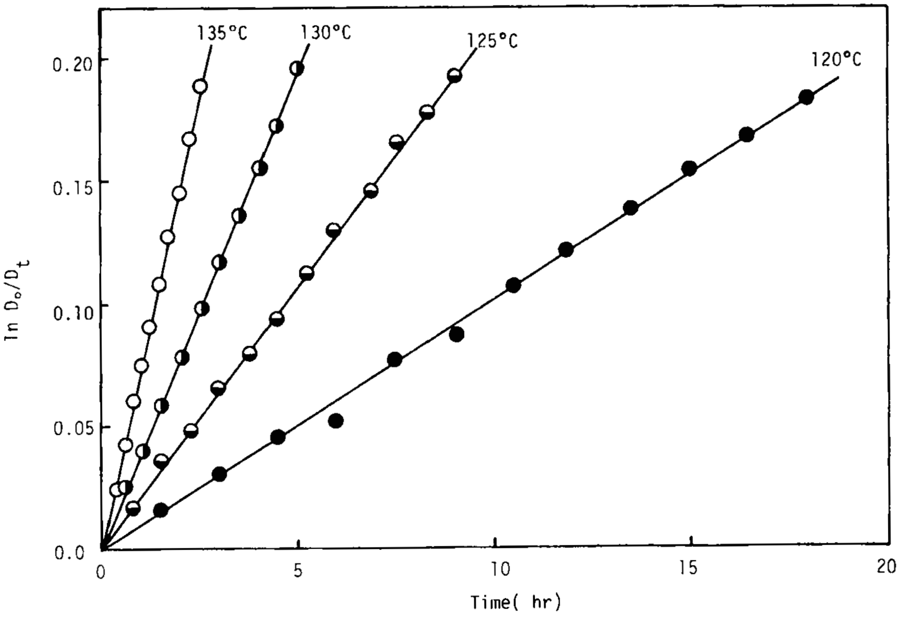


FIG. 2. Plots according to Eq. (2) for decomposition of Ie in DMF at various temperatures.

TABLE 1. First-Order Rate Constant k_d for the Thermal Decomposition of Ie at Various Temperatures

Temperature (°C)	$k_d \times 10^5$ (sec^{-1})
120	0.278
125	0.603
130	1.02
135	1.97

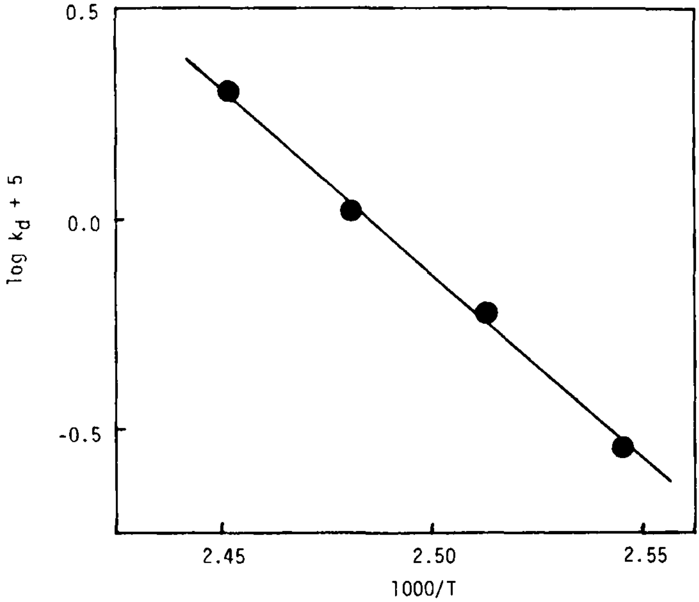


FIG. 3. Arrhenius plot for the decomposition of Ie.

The enthalpy of the activation was obtained from the equation,

$$\Delta H^{\ddagger} = E_a - RT$$

and the entropy of activation $\Delta S^{\ddagger}$ from the Eyring equation,

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

At 120°C, $\Delta H^{\ddagger} = 40.8$ kcal/mole, $\Delta S^{\ddagger} = 19.5$ cal/mole deg, and $\Delta G^{\ddagger} = 33.2$ kcal/mole.

Overall Activation Energy for the Polymerization of Acrylonitrile by Ie

It has been reported that nitro compounds do not inhibit the radical polymerization of acrylonitrile [17]. Thus, we chose acrylonitrile as the vinyl monomer to determine the catalytic activity of Ie for the

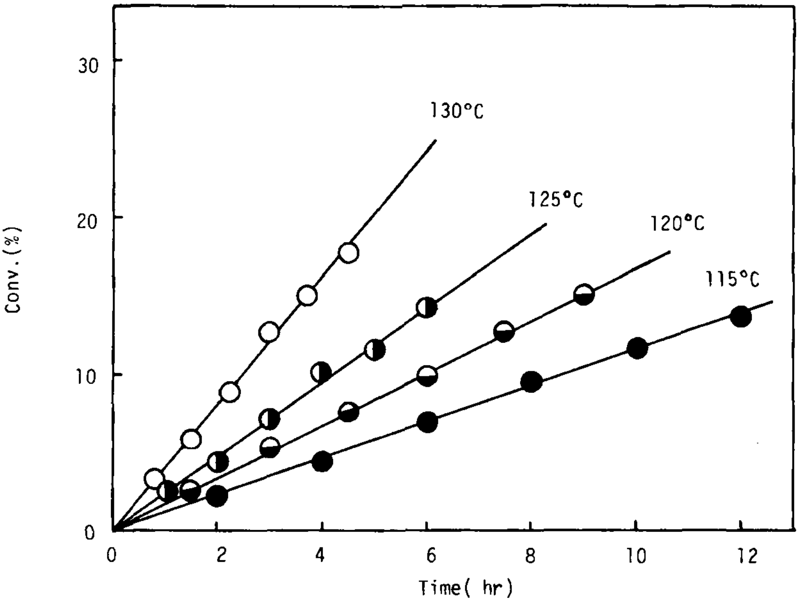


FIG. 4. Time-conversion curves in the polymerization of acrylonitrile (AN) initiated by Ie in DMF at various temperatures. [AN] = 4.55 mole/liter; [Ie] = 0.01 mole/liter.

polymerization. There is no serious difficulty in using acrylonitrile in the application of activity test to Ie, as discussed below. In this paper, kinetics will be discussed on the basis of the rate of polymerization which is free from thermal polymerization of acrylonitrile. The homogeneous polymerization of acrylonitrile initiated by Ie was carried out in DMF, at temperatures varying over the range of 115 to 130°C. Figure 4 shows the time-conversion curves of the polymerization of acrylonitrile, from which it can be seen that Ie begins to show the catalytic activity for the polymerization at relatively higher temperature. The plot of the polymerization rate R_p, was obtained from the slope in Fig. 4. R_p vs. $1/T$ gave a linear relationship, as shown in Fig. 5. The overall activation energy of the polymerization was estimated to be 21.5 kcal/mole.

Effect of p-Quinone

p-Quinone inhibited the polymerization of acrylonitrile initiated by Ie, as shown in Fig. 6. It indicates that the polymerization proceeded by a radical mechanism.

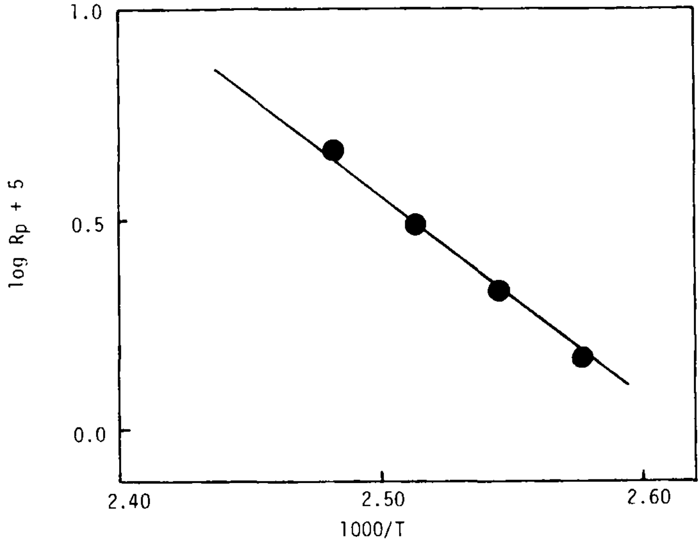


FIG. 5. Arrhenius plot for the polymerization of acrylonitrile initiated by Ie.

Kinetics of Polymerization

The polymerization of acrylonitrile initiated by Ie was studied kinetically. The polymerization was at first carried out in bulk at 120°C with varying concentrations of Ie. The polymerization was also carried out in DMF with varying concentrations of acrylonitrile and with the concentration of Ie constant. The results are summarized in Table 2. The relationship between R_p and the initial concentration of Ie is shown in Fig. 7. The rate was proportional to the 0.64 power of the concentration of Ie. As shown in Fig. 8, the rate was proportional to the 1.36 power of the acrylonitrile concentration.

Therefore, the initial rate of polymerization of acrylonitrile catalyzed by Ie can be expressed by Eq. (4):

$$R_p = k\,[\mathrm{Ie}]^{0.64}\,[\mathrm{Acrylonitrile}]^{1.36} \qquad (4)$$

The higher order dependence on Ie concentration may be explained by the participation of the polyacrylonitrile growing radicals in

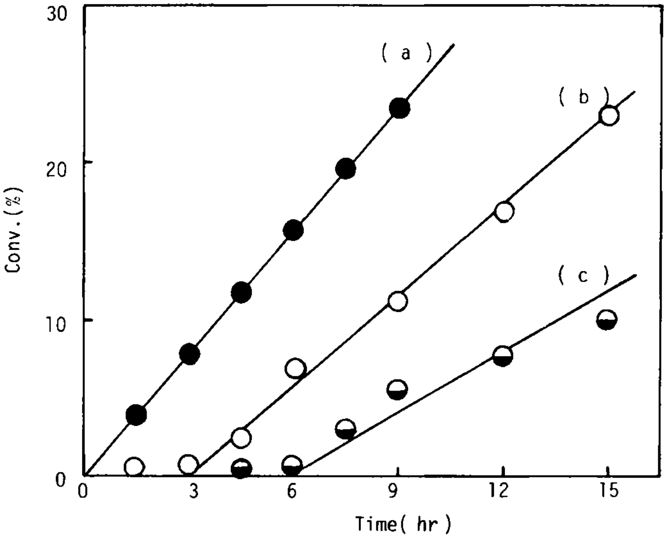


FIG. 6. Effect of p-quinone on the polymerization of acrylonitrile (AN) initiated by Ie in DMF: (a) [p-quinone] = 0, (b) [p-quinone] = 1×10^{-4}, (c) [p-quinone] = 1×10^{-3} mole/liter. The conversion was calculated from the whole dry polymer obtained.

TABLE 2. Kinetic Data for the Polymerization of Acrylonitrile (AN) Initiated by Ie in DMF at 120°C

[AN] (mole/liter)	[Ie] (mole/liter)	$R_p \times 10^5$ (mole/liter-sec)	P_n *[a]
1.52	0.01	0.455	94
2.28	0.01	0.751	125
3.04	0.01	1.21	186
3.79	0.01	1.57	305
4.55	0.0025	0.640	420
4.55	0.005	1.43	362
4.55	0.01	2.32	326
4.55	0.02	4.33	262

[a] Polymerization for 12 hr.

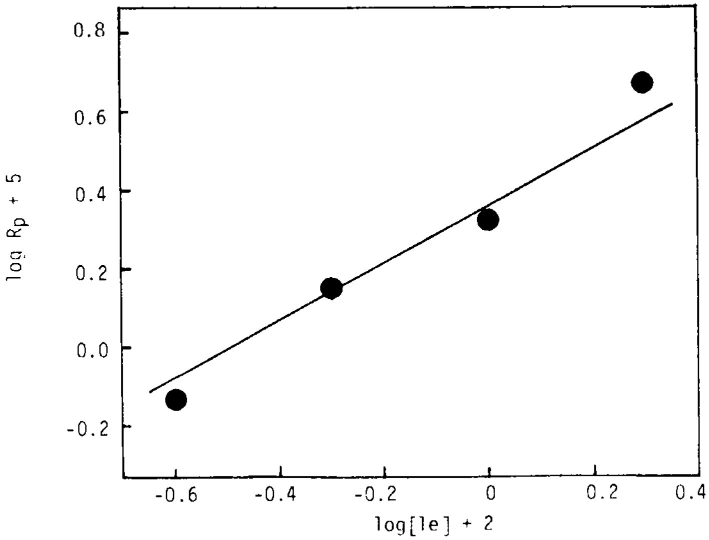


FIG. 7. R_p vs. [Ie] in the polymerization of acrylonitrile (AN) in DMF at 120°C. [AN] = 4.55 mole/liter [Ie] was varied.

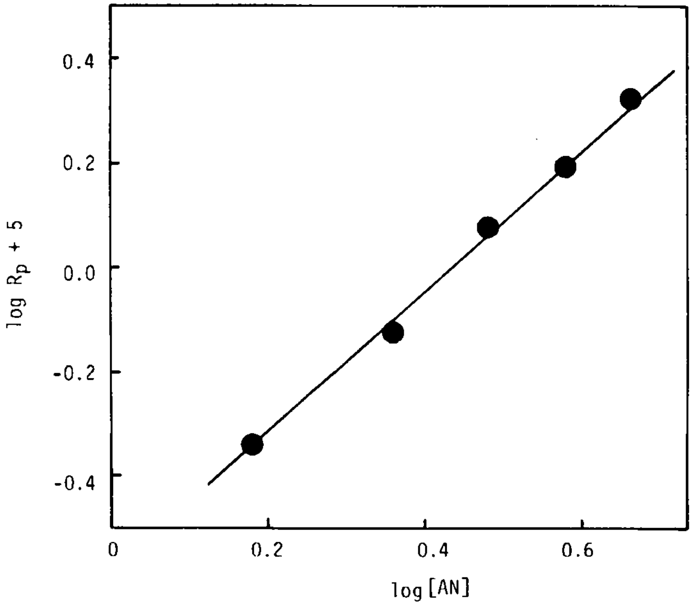


FIG. 8. R_p vs. [AN] in the polymerization of acrylonitrile (AN) in DMF at 120°C. [Ie] = 0.01 mole/liter, [AN] was varied.

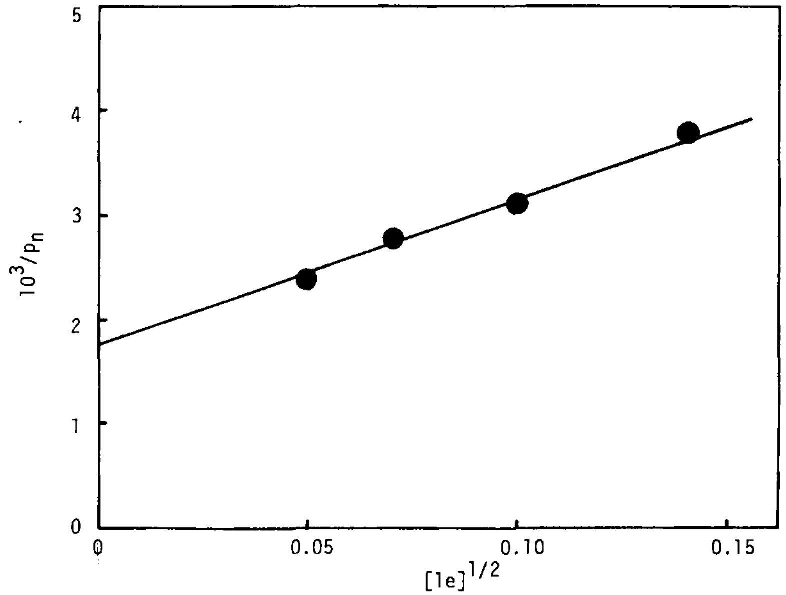


FIG. 9. Plot according to Eq. (5).

chain-transfer to Ie. Thomas et al. [18] and other authors [16, 19, 20] have reported that DMF is an effective chain-transfer agent which is due to the resonance stabilization of the radical formed by transfer. Accordingly, the higher order dependence on monomer concentration may be explained by the participation of the relatively unreactive radicals produced from DMF by chain-transfer. The chain-transfer constant of DMF, C_{DMF}, for the polymerization of acrylonitrile initiated by Ie was evaluated by applying Thomas' equation [18]:

$$1/P_n = \text{Const.}\,[\text{Ie}]^{0.5} + C_{DMF}\,[\text{DMF}]/[\text{Acrylonitrile}] \qquad (5)$$

The plot of $1/P_n$ against $[\text{Ie}]^{0.5}$ gave a straight line, as shown in Fig. 9. From the intercept obtained, C_{DMF} was estimated to be 0.897×10^{-3}. This value is consistent with that reported in our previous papers [10, 21] and by Thomas et al. [17].

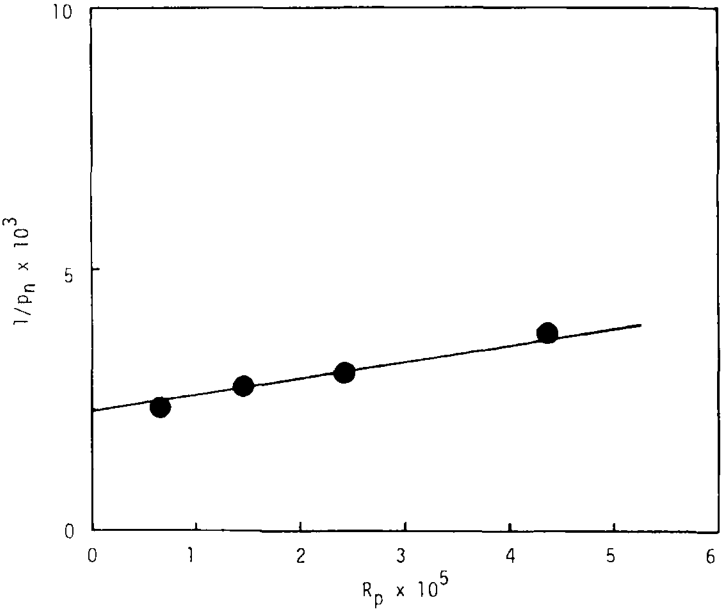


FIG. 10. Relationship between $1/P_n$ and R_p.

Chain-Transfer Constant, C_T, for Ie

Recently it was found that I acts as a chain-transfer agent in the polymerization of acrylonitrile initiated by AIBN [13]. At the same time Ic-Ie enhanced the polymerization rate; Ib affected it only slightly; whereas Ia retarded it. These results are attributed to the fact that the reactivity of the aminyl radicals derived from I increases with electron-withdrawing groups in the 1,4-position of I. The C_T values of I in the polymerization of acrylonitrile gave a fairly good straight line when Otsu and Yamamoto's equation [22], $\rho = -0.5$, $\gamma = 2.6$ was applied. This warranted the estimation of the chain transfer constant for Ie in the polymerization of acrylonitrile initiated by Ie. C_T was calculated by Tobolsky's equation [23]:

$$1/P_n = C_{AN} + C_T\,[\mathrm{Ie}]/[\mathrm{AN}] + C_{DMF}\,[\mathrm{DMF}]/[\mathrm{AN}] + AR_p \qquad (6)$$

where AN represents acrylonitrile.

The value of A was estimated as 31.0 from the slope of the linear

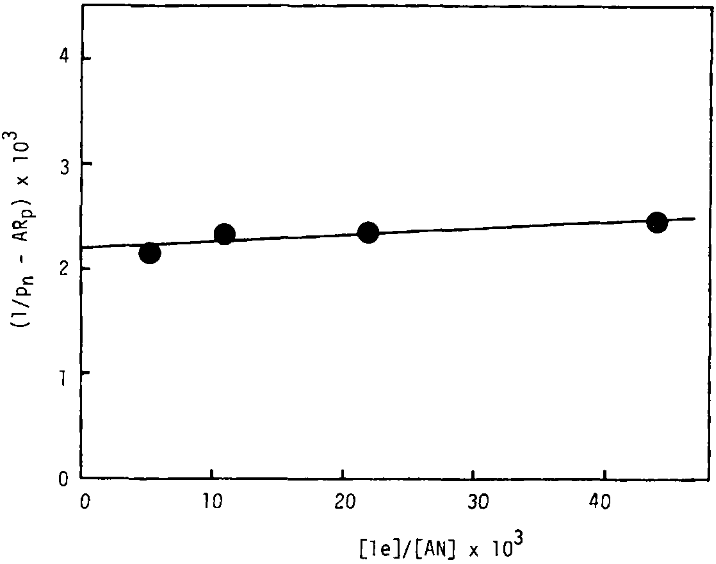


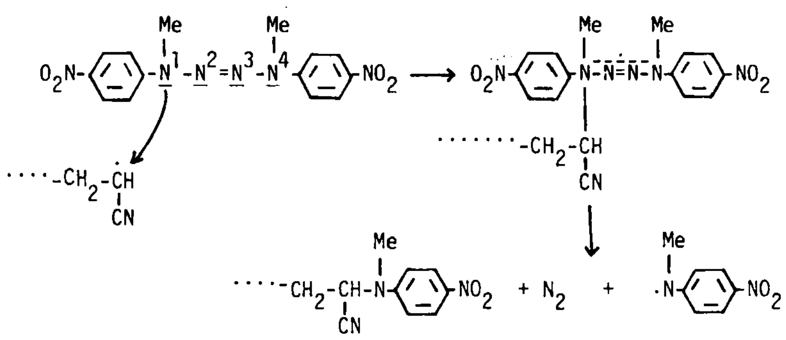
FIG. 11. Relationship between $1/P_n$-AR_p and [Ie]/[AN].

relationship between the reciprocal of P_n and R_p, as shown in Fig. 10. The chain-transfer constant of the initiator was evaluated to be 6.25 × 10^{-3} from the slope of the ($1/P_n$ - AR_p) vs. [Ie]/[AN] plot, as shown in Fig. 11.

From ρ and γ values for C_T of I mentioned above, the chain transfer reaction involves an electrophilic attack of a polyacrylonitrile radical on the N^1 of Ie in the transition state. Accordingly a mechanism of the chain transfer reaction is summarized as shown in Eq. (7).

Detection of Initiating Species

In order to detect the N-methyl-4-nitroanilinyl groups in polymer ends, UV spectra of polymer obtained from the polymerization of acrylonitrile initiated by Ie were measured in DMF (Fig. 12). The homopolyacrylonitrile (P_n = 262) used was free from unreacted Ie and other basic products derived from Ie, which were isolated by Soxhlet extraction with acetone for 40 hr.



(7)

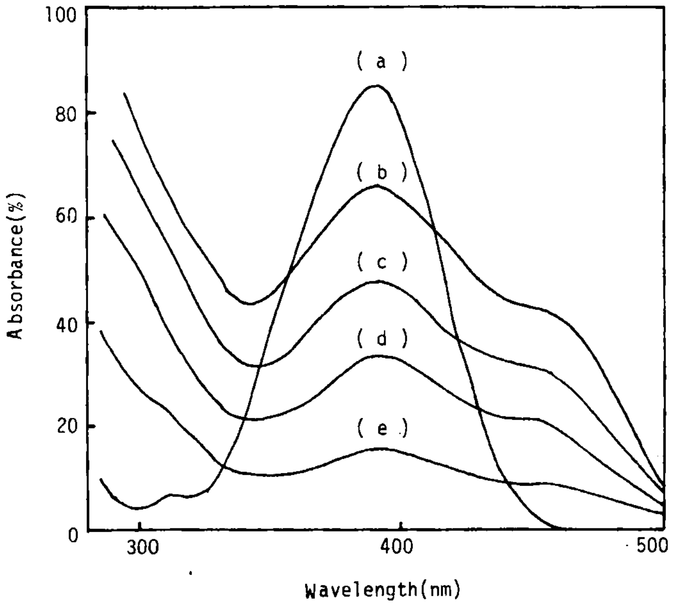


FIG. 12. UV spectra (in DMF solution) of polyacrylonitrile (PAN) initiated by Ie: (a) N-methyl-4-nitroaniline, 3.47 × 10^{-5} mole/liter; (b) [PAN] = 0.066 g/liter; (c) [PAN] = 0.050 g/liter; (d) [PAN] = 0.033 g/liter; (e) [PAN] = 0.016 g/liter.

There is no absorption of polyacrylonitrile in the wavelength region from 350 to 500 nm in DMF, while N-methyl-4-nitroaniline has an absorption maximum at 390 nm in DMF. As can be seen from Fig. 12, it is indicated that N-methyl-4-nitroanilinyl groups are presumably incorporated as endgroups in the polymers. Though chain-transfer reaction of the polyacrylonitrile growing radical to Ie surely occurs in the polymerization, it appears that N-methyl-4-nitroanilinyl radicals derived from Ie are responsible for the main part of the initiation of the polymerization.

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