Inhibition Effect of 1, 1, 4, 4-Tetraphenyl-2-tetrazene in the Radical Polymerization of Vinyl Acetate

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ABSTRACT

1,1,4,4-Tetraphenyl-2-tetrazene (TPT) inhibits the polymerization of vinyl acetate (VAc) initiated by 2,2'-azoisobutylonitrile. The induction period is proportional to the concentration of TPT. The ratio of the rate constants of propagation and termination reactions, $k_p^2/2k_t$, were estimated from the consumption rate of TPT. The chain transfer constant of TPT in the radical polymerization of VAc was also calculated.

INTRODUCTION

The reactivity of neutral aminyl radicals derived from 2-tetrazene is reduced by the effect of substituents of N^1 and N^4 on the decompositic

of 2-tetrazene [1, 2]. It has been reported that 1,4-dimethyl-1,4-diphenyl-2-tetrazene and its 4,4'-substituted derivatives act as chain transfer agents in the radical polymerization of acrylonitrile [3]. Some of them enhance the polymerization rate and others retard it. This result is consistent with that of the effect of substituents on thermal decomposition [2, 4]. This indicates that the reactivities of the aminyl radical depend on the stability of 2-tetrazene. The reactive radicals derived from 1,1,4,4-tetramethyl-2-tetrazene can initiate the polymerization of several vinyl monomers [5-9], while relatively stable radicals such as diphenylaminyl radical inhibit the polymerization [10]. Thermal decomposition of 1,1,4,4-tetraphenyl-2-tetrazene occurs easily to form two diphenyl aminyl radicals with nitrogen [11]. The diphenylaminyl radical is suggested to be stabilized by resonance of its odd electron with the π-system of the phenyl groups [4]. Accordingly, it reacts mostly with the reactive radicals such as the initiating species and the growing radicals, rather than adding to olefins or abstracting hydrogen atoms [12, 13]. Recently it has been reported that TPT acts as an effective inhibitor for the polymerization of styrene [10] and methyl methacrylate [14]. In these cases, TPT cannot sharply depress polymerization because polystylyl and polymethyl methacrylate radicals are somewhat stabilized by delocalization of growing radicals with the side groups [15]. The effect of TPT on the polymerization of unconjugated vinyl monomers such as vinyl acetate (VAc) could be expected to lead to interesting results. As expected, the authors have found that the polymerization of VAc initiated by 2,2'-azobisisobutylonitrile (AIBN) is completely depressed during the inhibition period by the addition of TPT.

The present paper is mainly concerned with a detailed study of the effect of TPT on the polymerization of VAc initiated by AIBN in order to clarify the essential nature of the diphenylaminyl radical and TPT.

EXPERIMENTAL

Materials

TPT, mp 123.5°C dec. (Ref. 16, mp 123°C dec.) was prepared by oxidation of 1,1-diphenylhydrazine with manganese dioxide. VAc was purified in the usual manner and redistilled under a stream of nitrogen just before use.

Thermal Decomposition Procedure

A known amount of TPT in VAc was placed in an ampule which was cooled in a Dry Ice/methanol bath and sealed. The ampule was
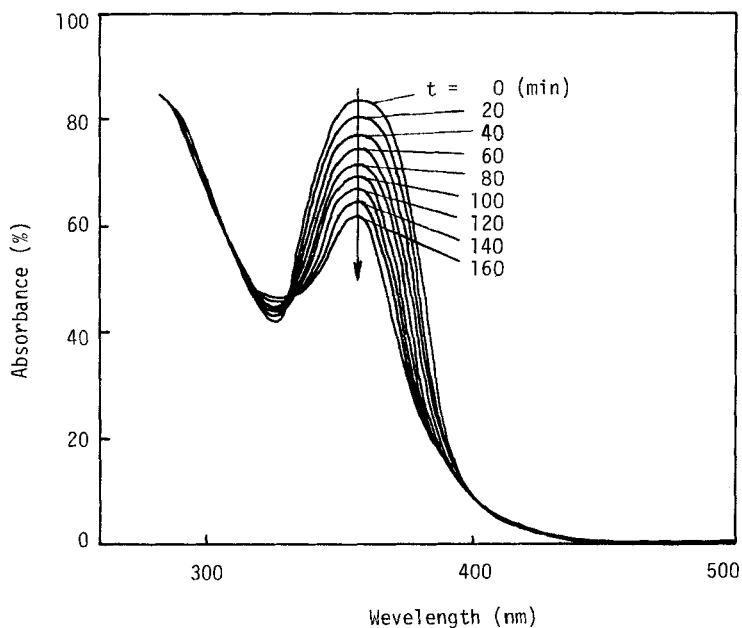
FIG. 1. UV spectra for the decomposition of TPT in VAc at 45°C.

shaken in a thermostat maintained at a definite temperature. After thermal decomposition for a given time, the content of the tube was determined by UV measurements.

UV Measurements

UV spectra were obtained with a Shimadzu double beam spectrophotometer UV-200S. The rate of decomposition of TPT was determined by spectrophotometry which measured the rate of disappearance of absorption at 355 nm. The change of absorbance vs concentration followed Beer's law quite well in VAc.

The first-order decomposition rate constants, k_d, were calculated from

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

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

FIG. 2. Plots according to Eq. (1) when TPT was decomposed in VAc at various temperatures.
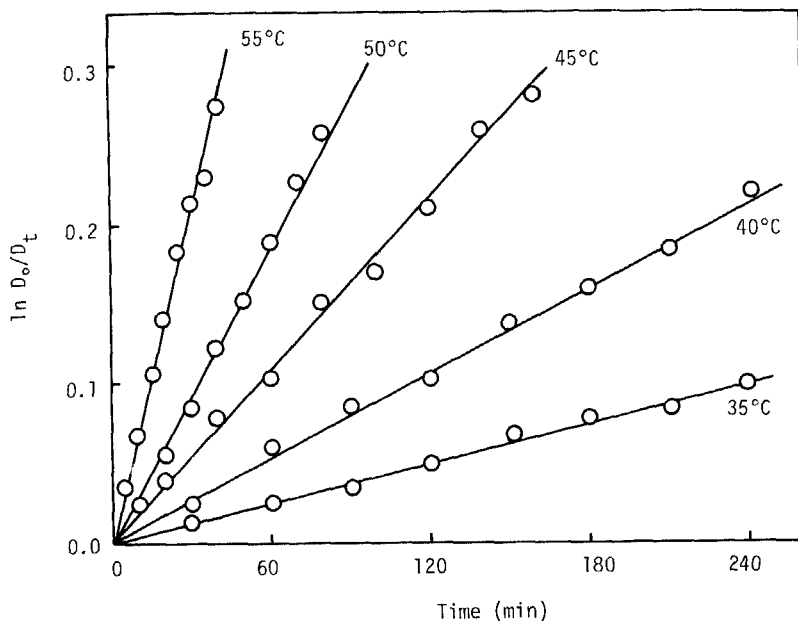
Polymerization Procedures

VAc, AIBN, and TPT were placed in an ampule. The ampule was flushed with nitrogen, frozen, evacuated at 0.01 mmHg, and sealed. The sealed tube was shaken in a thermostat maintained at a definite temperature $\pm 0.02°C$. After the polymerization, the contents of the ampule were poured into a large amount of diethyl ether in order to precipitate the polymer. The number-average degree of polymerization (p_n) was estimated from the intrinsic viscosity $[\eta]$ of its benzene solution determined at 30°C by using Nakajima's equation [17]:

$$[\eta] = 56.3 \times 10^{-5} M^{0.62} \tag{2}$$

RESULTS AND DISCUSSION

Thermal Decomposition of TPT

Thermal decomposition of TPT was carried out in VAc at various temperatures. Typical spectral changes with time t during the thermal

TABLE 1. First-Order Rate Constants, k_d, for the Decomposition of TPT in VAc at Various Temperatures

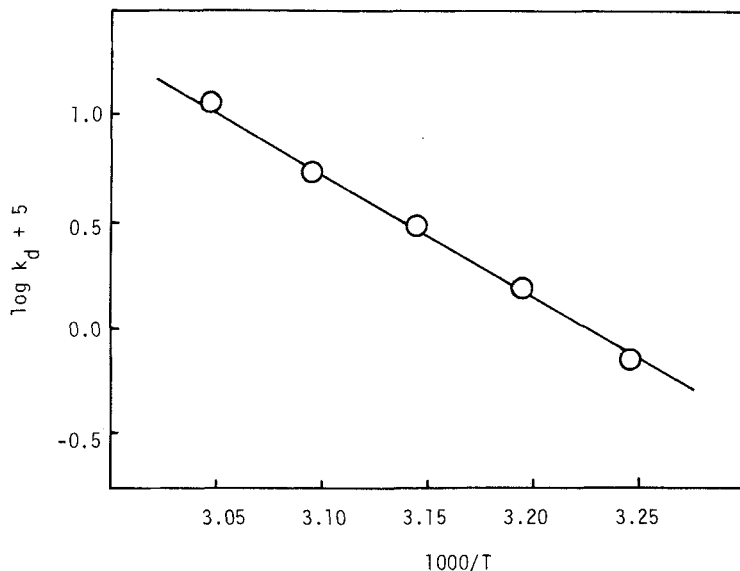| Temperature ($^\circ$C)	35	40	45	50	55
$10^5 k_d$ (sec^{-1})	0.685	1.48	3.00	5.30	11.7

FIG. 3. Arrhenius plot for the decomposition of TPT in VAc.

decomposition of TPT at 45°C are shown in Fig. 1. Similar spectral changes were observed with the other temperatures. Plots of Eq. (1) are shown in Fig. 2. The decomposition rates follow first-order kinetics. The first-order rate constants, k_d, are listed in Table 1.

The Arrhenius plot of the above data give a good straight line (Fig. 3) which gave 27.5 kcal/mole for the energy of activation.

The enthalpy of activation was obtained from the equation

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

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

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

At 45°C, $\Delta H^{\ddagger} = 28.1$ kcal/mole, $\Delta S^{\ddagger} = 14.8$ cal/mole · deg.

In a previous paper it was found that $\Delta H^{\ddagger}$ is more favorable for the more polar solvent in the decomposition of TPT in various aprotic solvents [14]. This result suggests that the transition state for decomposition has a higher polarity than the ground state. It is also indicated that TPT does not decomposes by a one-step mechanism. The activation parameters for the decomposition of TPT in VAc are in agreement with the values obtained in various aprotic solvents [14]. The following mechanism of decomposition is proposed to account for the previous results [14, 18] and the present data:
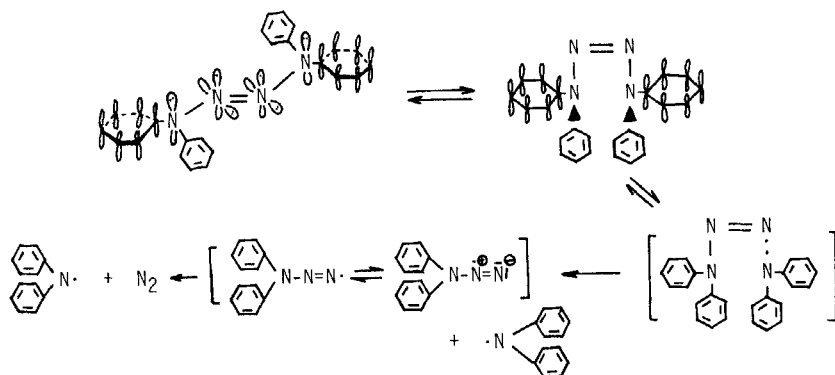
Effect of TPT on the Polymerization of VAc

In order to clarify the effect of TPT on the rate of radical polymerization of unconjugated monomer, the bulk polymerization of VAc was carried out in the presence of TPT at $60°$C, varying the concentration of TPT from 0.75×10^{-3} to 1.25×10^{-3} mole/L, and keeping the concentration of AIBN constant (2.5×10^{-3} mole/L). TPT acts as an effective inhibitor for the polymerization of VAc, as shown in Fig. 4.

The polymerization of VAc was completely depressed during the induction period by the addition of TPT. The polymerization rate after the inhibition period was almost equal to the normal rate as observed in the absence of TPT. The situation is not similar to the case of polymerization of conjugated monomers such as styrene [10] and methyl methacrylate [14]. In the latter cases there was a slight retardation effect after the addition of TPT.

The polymerization of VAc was also carried out in the presence of TPT with varying concentrations of AIBN.

In order to see the effect of TPT on the polymerization of VAc, the relationship between the concentration of TPT and the induction period at various concentrations of AIBN is shown in Fig. 5.

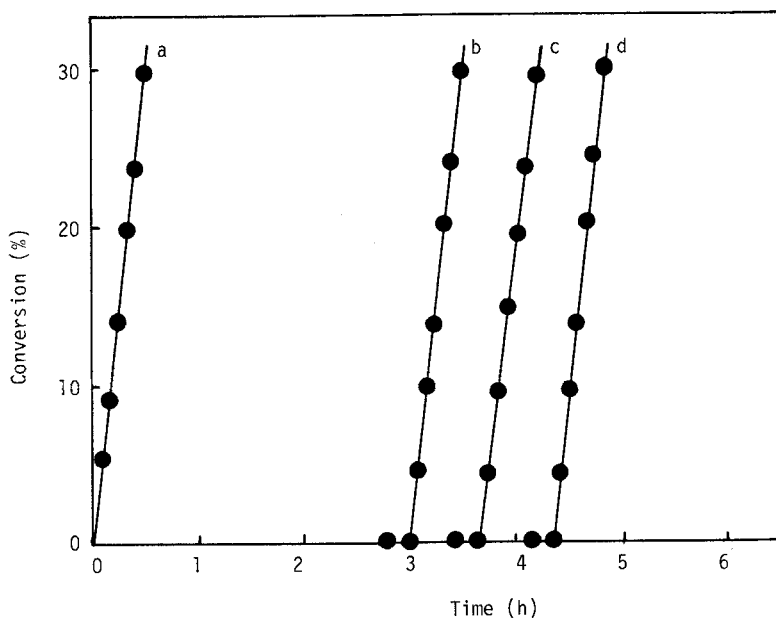As it can be seen from Fig. 5, the induction period is a linear

FIG. 4. Inhibition effect of TPT in the polymerization of VAc initiated with AIBN in bulk at 60°C. [VAc] = 10.85 mole/L; [AIBN] = 5×10^{-3} mole/L; [TPT] = 0, 0.75×10^{-3}, 1.0×10^{-3}, and 1.25×10^{-3} mole/L for a, b, c, and d, respectively.

function of the concentration of TPT. The rate of initiation of polymerization (R_i) was obtained from the slope of the line in Fig. 5. The ratio of the rate constants of propagation and termination reactions, $k_p^2/2k_t$, was calculated according to

$$k_p^2/2k_t = R_p^2/R_i[M]^2 \tag{3}$$

The results are tabulated in Table 2.

The average value of $k_p^2/2k_t$ was calculated as 0.386, which is in fair agreement with the value obtained by Schulz [19].

Chain-Transfer Reaction of TPT

In the thermal decomposition of 1,1,4,4-tetramethyl-2-tetrazene in benzene, Michejda found that the induced decomposition becomes important at a concentration greater than 0.2 $\underline{M}$ [20]. On the other
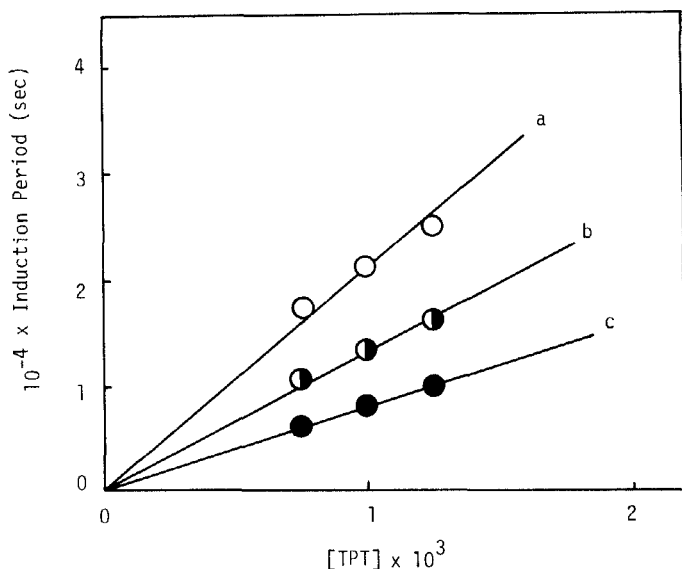
FIG. 5. Plots of induction period vs [TPT] in the polymerization of VAc [VAc] = 10.85 mole/L; [TPT] = 0.75×10^{-3}, 1.0×10^{-3}, and 1.25×10^{-3} mole/L; and [AIBN] = 2.5×10^{-3}, 5×10^{-3}, and 10×10^{-3} mole/L for a, b, and c, respectively.

hand, it was found that a series of 1,4-dimethyl-1,4-diaryl-2-tetra-zenes decomposes by attacking the initiating species and growing radical in the polymerization of acrylonitrile by AIBN [3]. The 2-tetrazenes thus act as chain transfer agents in polymerization. At the same time, it was also found that the chain transfer reaction involves an electrophilic attack of a polyacrylonitrile radical on the N^1 or N^4 of 2-tetrazene in the transition state [3].

In addition, the induced decomposition of TPT was also studied in the polymerization of methyl methacrylate initiated by AIBN in the presence of TPT [14]. In this connection our interest was directed to the chain transfer reaction of TPT in the polymerization of VAc in order to compare it with that of the chain transfer reaction in the polymerization of methyl methacrylate.

According to Bartlett and Kwart [21], the reaction of terminator with free radicals is

$$p \xrightarrow{\quad k_1 \quad} 2R \qquad\qquad (4)$$

$$R + M \xrightarrow{\quad k_2 \quad} R \qquad\qquad (5)$$

TABLE 2. The Rate of Initiation, R_i, and the Ratio of the Rate Constants of Propagation and Termination Reaction, $k_p^2/2k_t$, for the Polymerization of VAc ([VAc] = 10.85 mole/L)

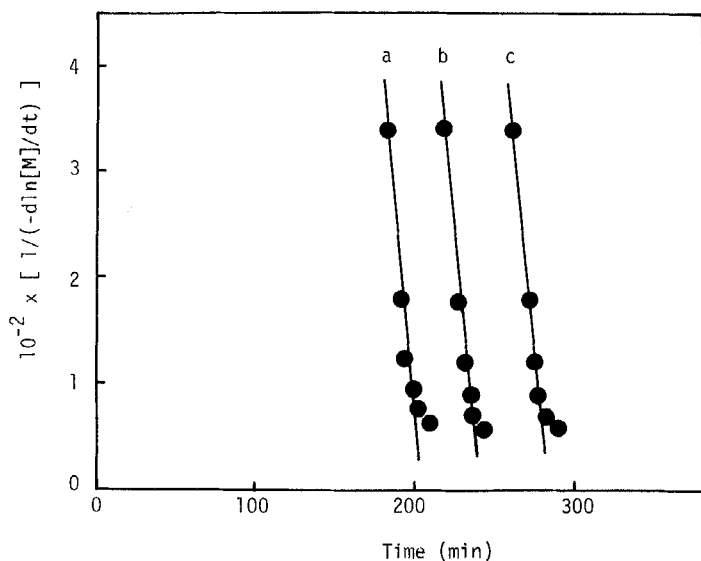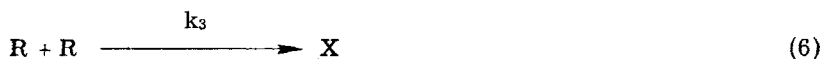| 10^2[AIBN]	$10^7 R_i$	$10^3 R_p$	$k_p^2/2k_t$
mole · L^{-1}	mole · L^{-1} · sec^{-1}	mole · L^{-1} · sec^{-1}	L · mole^{-1} · sec^{-1}
0.25	0.480	0.663	0.0778
0.50	0.780	1.81	0.357
1.0	1.25	3.26	0.722
		Average	0.386

FIG. 6. Plots according to Eq. (9) for the polymerization of VAc
initiated with AIBN in the presence of TPT in bulk. $[VAc] = 10.85$
mole/L; $[AIBN] = 5 \times 10^{-3}$ mole/L; and $[TPT] = 0.75 \times 10^{-3}$, $1.0 \times$
10^{-3}, and 1.25×10^{-3} mole/L for a, b, and c, respectively.

$$R + R \xrightarrow{\quad k_3 \quad} X \qquad\qquad (6)$$

$$R + Z \xrightarrow{\quad k_4 \quad} X \qquad\qquad (7)$$

where P, M, R, Z, and X represent initiator, monomer, any free radi-
cal chain carrier, terminator, and stable product, respectively.
k_4/k_2 may be written as

$$1/(-d \ln [M]/dt) = (k_4/2k_1k_2)([Z_0]/[P]) - (k_4/k_2)t \qquad (8)$$

It can be seen that in a plot of $1/(-d \ln [M]/dt)$ vs time t, the slope
measures k_4/k_2. The value of $-d \ln [M]/dt$ at each time was calcu-
lated from plots of $\ln [M_0]/[M]$ against time, the ordinates being
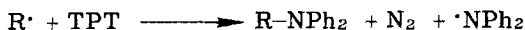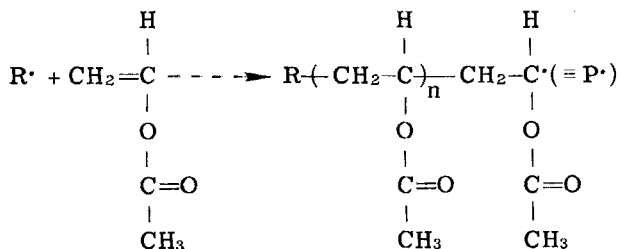evaluated from the data in Fig. 4.

Figure 6 is a plot of Eq. (8) for the bulk polymerization of VAc in
the presence of TPT. From the slopes of the lines, the chain transfer
constant of TPT (C_{TPT}) is estimated as 12.5. This value is larger

than the value found from the polymerization of methyl methacrylate in the presence of TPT (C_{TPT} = 11.6) [14]. It is consistent with the fact that the polyvinyl acetate radical is more reactive than the polymethyl methacrylate growing radical [15]. The mechanism of the chain transfer reaction may be proposed to be similar to that in the case of the polymerization of acrylonitrile in the presence of 1,4-dimethyl-1,4-diaryl-2-tetrazenes [3].
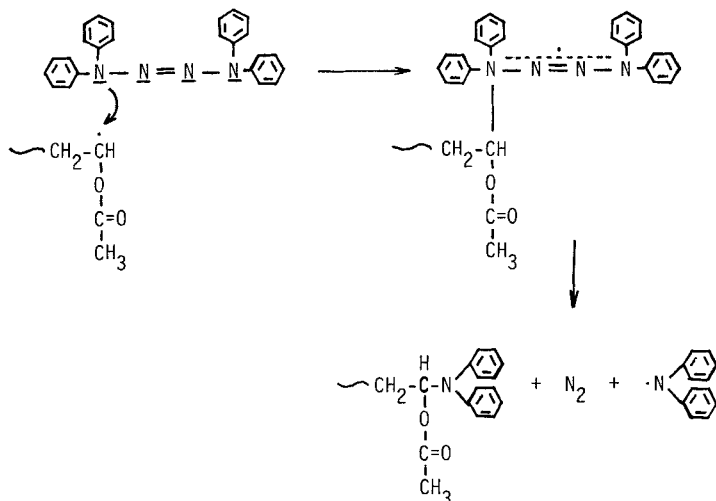
Accordingly, the polymerization of VAc was inhibited by the diphenyl aminyl radicals derived from the radical decomposition of TPT itself and from any free radical induced decomposition of TPT. The overall inhibition mechanism is proposed to be as follows:

$$TPT \xrightarrow{k_d} 2Ph_2N\cdot + N_2$$

$$AIBN \xrightarrow{k_d'} 2Me_2C\cdot(\equiv R\cdot) + N_2$$
$$\underset{\displaystyle CN}{|}$$

$$R\cdot + \cdot NPh_2 \longrightarrow R-NPh_2$$

$$R\cdot + CH_2 = \underset{\underset{\underset{CH_3}{|}}{\underset{C=O}{|}}{\overset{H}{\underset{|}{\underset{|}{O}}}}}{C} \quad - - - - \rightarrow \quad R \left(CH_2 - \underset{\underset{\underset{CH_3}{|}}{\underset{C=O}{|}}{\overset{H}{\underset{|}{\underset{|}{O}}}}}{C} \right)_n - CH_2 - \underset{\underset{\underset{CH_3}{|}}{\underset{C=O}{|}}{\overset{H}{\underset{|}{\underset{|}{O}}}}}{C}\cdot (= P\cdot)$$

$$P\cdot + \cdot NPh_2 \longrightarrow P-NPh_2$$

$$R\cdot + TPT \longrightarrow R-NPh_2 + N_2 + \cdot NPh_2$$

$$P\cdot + TPT \longrightarrow P-NPh_2 + N_2 + \cdot NPh_2$$
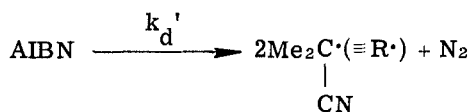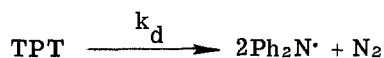
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