

STUDIES ON CHARGE TRANSFER POLYMERIZATION —POLYMERIZATION OF ACRYLONITRILE INITIATED WITH PHENYL HYDRAZINE AND ITS DERIVATIVES

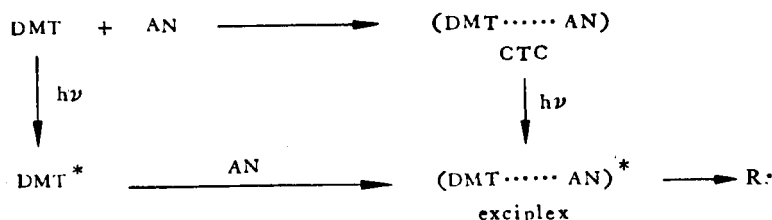
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ABSTRACT

The photopolymerization of acrylonitrile (AN) initiated with phenyl hydrazine (PHZ) and its derivatives has been studied. The initiator exponent and monomer exponent were determined from the kinetic investigation to be 0.66th and 2.1th respectively and the overall activation energy was 33.4 KJ/mol for the PHZ-AN system. Spectral analysis and other data indicate that a charge transfer complex between PHZ as a donor and AN as an acceptor is formed. The initiation mechanism was proposed.

The charge transfer polymerization has been attracted much attention since Scott and Ellinger suggested independently the mechanism of charge transfer complex (CTC) for the polymerization of N-vinylcarbazole^[1-3]. Recently Feng^[4] summarized the rules for the polymerization of polar vinyl monomers initiated with aromatic tertiary amines as follows: 1. The vinyl monomers with α -methyl group on double bond such as methacrylic esters would polymerize through the mechanism of amine- O_2 complex in the absence of light. 2. The monomers without methyl group such as acrylonitrile (AN) or methyl acrylate etc. only polymerize under irradiation through the formation of exciplex. The mechanism of photopolymerization of AN initiated by dimethyltoluidine (DMT) has been suggested as follows:



where CTC and exciplex represent the charge transfer complex in ground state and excited state respectively. This mechanism is also fit to the polymerization initiated by diphenyl ether.^[5] Phenyl hydrazine (PHZ) is a derivative of aromatic amine but that, whether it could initiate the photopolymerization of vinyl monomers or not, has not been reported yet.

In this article we wish to present some results concerning the photopolymerization and thermopolymerization of AN initiated with PHZ and its derivatives or with CTC consisting

of PHZ as an electron donor and benzoquinone as an electron acceptor.

EXPERIMENTAL

1. Material

PHZ was purified by distillation under reduced pressure protected with N_2 . The middle fraction was collected and stored in a sealed ampoule for use. Dimethylformamide (DMF) was dried with CaH_2 then distilled under reduced pressure. Dimethylsulfoxide (DMSO) was dried with molecular sieve before distillation and the middle fraction was collected. Other reagents are all of analytical grade and used without further treatment.

2. Polymerization

Photopolymerization was carried out in a rigid glass ampoule or in a quartz dilatometer as shown in Ref. [6]. The absorption spectra were determined with UV-VIS spectrometer using methanol as solvent at room temperature. The fluorescence spectra were obtained by the MPF-4 type fluorescence spectrophotometer.

RESULTS AND DISCUSSION

1. The photopolymerization of AN initiated by PHZ and its derivatives

Table 1 summarizes the results of polymerization of AN in sealed ampoule using PHZ or its derivatives as initiator. Fig. 1 shows the conversion-time curves of polymerization determined with quartz dilatometer.

Table 1 The rate of polymerization of AN and $\bar{M}_v$ of PAN

Initiator*	$R_p \times 10^{6**}$	$\bar{M}_v \times 10^{-5***}$
Methyl phenylhydrazine (MPHZ)	7.26	6.75
Phenylhydrazine (PHZ)	4.24	6.27
Acetyl phenylhydrazine (APHZ)	3.02	6.06
Benzoyl phenylhydrazine (BPZ)	1.50	7.95
<i>p</i> -Nitrophenylhydrazine (NPHZ)	0.51	8.80
Without initiator	0.68	9.67

* [Initiator] = $\sim 3 \times 10^{-5}$ M.

** 500 high pressure mercury lamp at distance of 30 cm AN was deaerated by bubbling N_2 and the ampoule was sealed under vacuum- N_2 alternatively three times.

*** $\bar{M}_v$ was from viscosity determination with DMF as solvent at $25^\circ C$ from the equation of $[\eta] = 3.92 \times 10^{-4} \bar{M}_v^{0.75}$.

From Table 1 and Fig. 1 we observed that the initiation ability of different derivatives of PHZ descends in the following order:

MPHZ > *p*-Bromophenyl hydrazine (BPHZ) > PHZ > APHZ > BHZ > NPHZ.

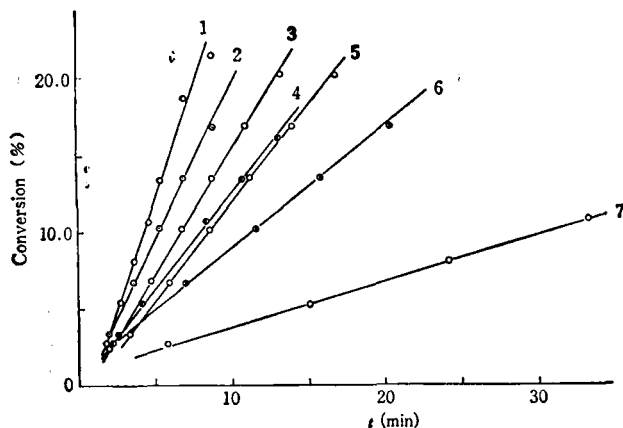


Fig. 1 Conversion-time plot of polymerization of AN. in dilatometer 300 W high pressure mercury lamp at distance of 7cm, 30°C in bulk; [hydrazine] = $1.8 \times 10^{-4}M$ 1—MPHZ; 2—BPHZ; 3—PHZ; 4—BHZ; 5—APHZ; 6—O; 7—NPHZ.

This order is in agreement with the electron density on the nitrogen atom of these compounds, i.e. the increase of electron density on the nitrogen atom will increase the rate of initiation.

2. The photopolymerization using PHZ-electron-acceptor system as initiator

As an electron-donor PHZ forms CTC with electron-acceptor easily and then the CTC decomposes to free radical species for initiation. Table 2 summarizes the results of photopolymerization using PHZ-acceptor system as initiators.

Table 2 The photopolymerization of AN initiated with PHZ-acceptor systems

Electron-acceptor	in 50% DMF solution*		in bulk **	
	$R_p \times 10^5$	R_p / R_p^0	$R_p \times 10^4$	R_p / R_p^0
—	1.2 (R_p^0)	1.0	1.1 (R_p^0)	1.0
Benzoquinone (Q)	14.0	11.7	1.2	1.09
Chloranil (CA)	7.0	5.8	1.3	1.18
Dichlorodicyanobenzoquinone (DDQ)	9.7	8.1	0.48	0.44
Tetracyanoethylene (TCNE)	2.9	2.4	0	0

* [PHZ] = $5.1 \times 10^{-4}M$, [acceptor] = $8 \times 10^{-4}M$.

** [PHZ] = $1.4 \times 10^{-4}M$, [acceptor] = $1 \times 10^{-3}M$.

The unit of R_p is mol/l.s., R_p^0 represents the rate of polymerization without electron-acceptor.

The results in Table 2 show that the rate of polymerization would increase obviously by adding electron-acceptors in DMF solvent. Among these, benzoquinone increases for 10.7 times while TCNE only 1.4 times. As a polar solvent DMF will enhance the decomposition of CTC. The ratio of polymerization rate R_p / R_p^0 in DMF is usually higher than that in the bulk. In the latter case the CTC formed by TCNE and PHZ is rather difficult to be decomposed and thus no polymerization will occur.

2. The kinetics of photopolymerization

It has been found that the photopolymerization rate R_p is proportional to the 0.66th power of PHZ concentration and 2.1th power of AN concentration, i.e. $R_p \propto [\text{PHZ}]^{0.66} [\text{AN}]^{2.1}$. Since the monomer power is greater than 1.5th and the initiation power is greater than 0.5th, this could be ascribed to the nature of precipitation polymerization.

From the rates of polymerization carried out in bulk at different temperature (20, 30, 40°C) the overall activation energy was calculated as 33.4 KJ/mol according to the Arrhenius equation. This higher value of activation energy is also ascribed to the precipitation polymerization.

3. The polymerization of AN using PHZ-quinone system as initiator

The PHZ-quinone can initiate the polymerization of AN in the dark as indicated in Table 3 but no polymerization would take place in absence of quinone.

Table 3 The polymerization of AN initiated by PHZ-quinone system*

Benzoquinone (mol/l)	Temp. of polymn. (°C)	Weight of polymer (mg)
1.2×10^{-3}	0	6.6
1.2×10^{-3}	23	43.3
1.2×10^{-3}	60	134.6
0	60	0

[PHZ] = 3×10^{-4} M; AN: 3 ml, 125 h.

* The ampoules were enclosed with black paper.

Table 4 summarizes the effect of different quinones on the polymerization of AN. It reveals that all the systems composed of PHZ and quinones will initiate the polymerization of AN in the absence of light. The higher rate for the system of PHZ-naphthalene quinone (NQ) may be due to that the NQ is a rather weak acceptor and the CTC formed from PHZ would decompose easily. The dichlorodicyanobenzenequinone (DDQ) is a rather strong acceptor and the corresponding CTC would be rather stable so that the rate of polymerization is quite low.

Table 4 The polymerization of AN initiated with systems composed of PHZ and different quinones

Quinone	Weight of polymer (mg)
Benzenequinone	71.5
1, 4-naphthalene quinone	110.0
Chloranil	104.8
Indol quinone	61.5
Dichlorodicyanobenzene quinone	25.0

[PHZ] = 4.2×10^{-2} M; [Quinone] = 1.1×10^{-2} M; AN: 3 ml in sealed ampoule at 0°C/13 h, 22°C/24 h, 60°C/31h, 110°C/24 h.

Similarly other derivatives of PHZ as α -methyl phenylhydrazine, *p*-bromophenylhydrazine, *p*-nitro-phenylhydrazine with quinone can also initiate the polymerization of AN in the dark.

Owing to its stability the CTC from TCNE and PHZ will not initiate the polymerization of AN in bulk but will do in DMF or ethanol solution.

4. The initiation mechanism

Similar to aromatic tertiary amine the lone pair electrons on nitrogen atom of PHZ will be responsible for polymerization. So the mechanism of polymerization of AN using PHZ as initiator may be suggested similar to that of other aromatic amine as follows:

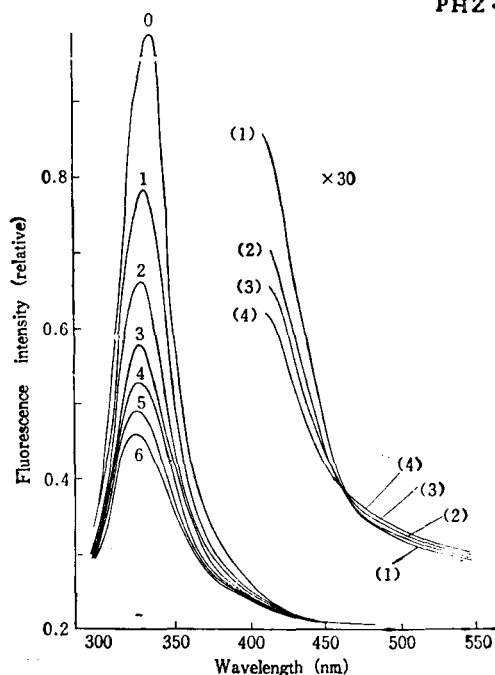
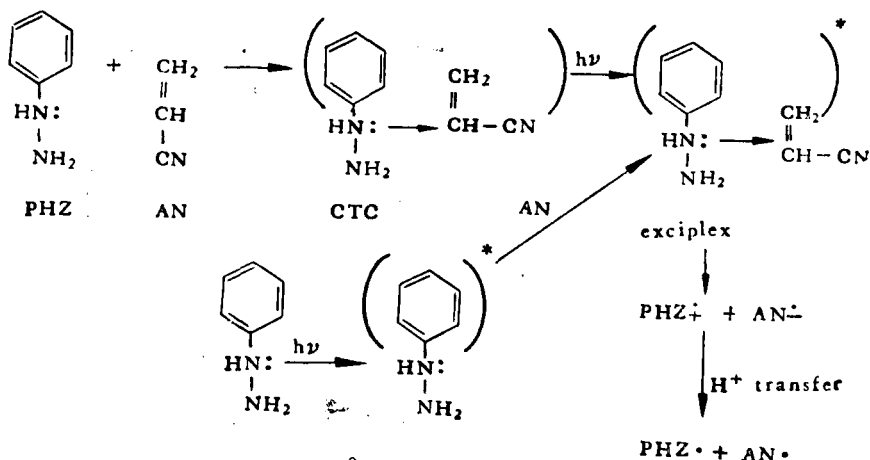


Fig. 2 The fluorescence spectra of PHZ-AN system in cyclohexane as solvent

$\lambda_{\text{ex}} = 280 \text{ nm}$, $[\text{PHZ}] = 4.16 \times 10^{-4} \text{ M}$.

$[\text{AN}] \text{ [M]}$: 0, 0; 1, 5.66×10^{-3} ; 2, 1.70×10^{-2} ; 3, 1.70×10^{-2} ; 4, 2.66×10^{-2} ; 5, 2.83×10^{-2} ; 6, 3.39×10^{-2} . (1) 0; (2) 2.83×10^{-2} ; (3) 5.66×10^{-2} ; (4) 8.49×10^{-2} .

The formation of radical species in the polymerization was confirmed by the inhibition effect with addition of 2,2,6,6-tetramethylpiperidine nitroxyl radical (PNPO•) as scavenger. For example the induction period of polymerization would increase from 4 minutes to twenty five hours in the presence of 500 ppm of PNPO•. The formation of exciplex was justified by fluorescence spectroscopy. The maximum wavelength of emission spectra ($\lambda_{\max}$) for PHZ appeared at 320 nm in cyclohexane by excitation in 280 nm wavelength. The emission spectra will be quenched by adding AN as quencher. The relation of [AN] and the intensity of fluorescence I is in agreement with the Stern-Volmer equation. From the plot the $K_q\tau$ value was determined to be 63.0 l/mol•s. with increasing of [AN] the exciplex emission, though very weak, was observed at the tail of fluorescence spectra after magnifying the sensitivity of fluorescence to about thirty times (Fig. 2).

The intensity of fluorescence increases with AN concentration in the range of 2.8×10^{-2} M to 0.09 M and after that it will drop down and disappear, so the exciplex is rather weak.

The polymerization mechanism of AN with PHZ-Q system in the absence of light has been tentatively proposed that the CTC formed between PHZ and quinone will decompose to zwitterion radical species for initiation as follows:

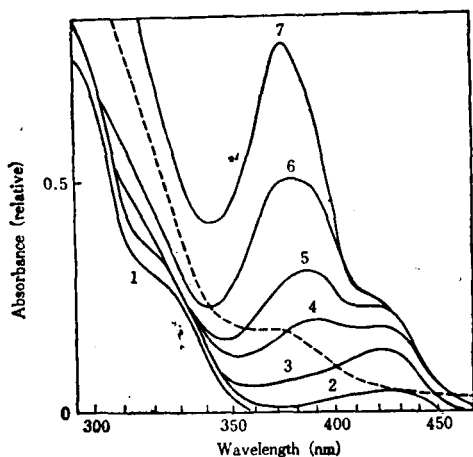
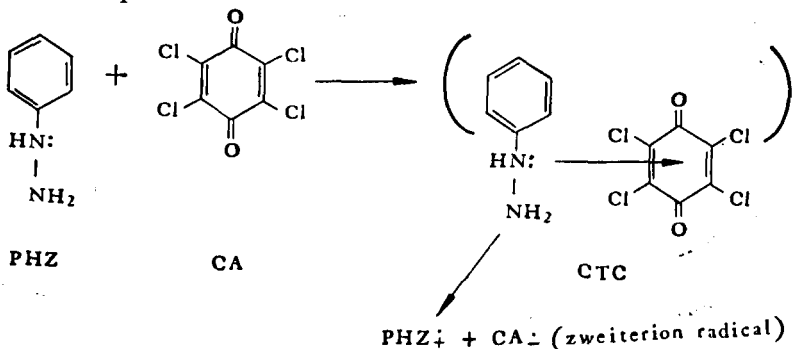


Fig. 3 The UV-VIS spectra for system of PHZ-DDQ in methanol

The point line: [PHZ]=0, [DDQ]= 1.2×10^{-4} M.
The solid line: [PHZ]= 4.2×10^{-4} M; [DDQ](M):
1, 0; 2, 1.2×10^{-5} ; 3, 3.6×10^{-5} ; 4, 8.0×10^{-5} ;
5, 8.4×10^{-5} ; 6, 1.2×10^{-4} ; 7, 2.4×10^{-4} .

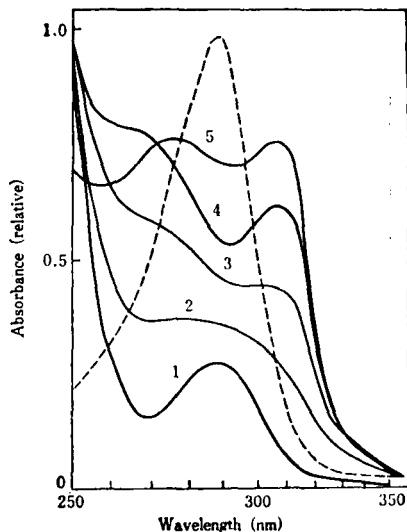


Fig. 4 The UV-VIS spectra for system of PHZ-CA in methanol

The point line: [PHZ]=0, [CA]= 2.0×10^{-4} M.
The solid line: [PHZ]= 4.2×10^{-4} M; [CA](M):
1, 0; 2, 1.0×10^{-4} ; 3, 2.0×10^{-4} ; 4, 3.1×10^{-4} ;
5, 4.1×10^{-4} .

The evidences of CTC formation for PHZ-quinone system are obtained from the appearance of new peaks on the UV-VIS spectra for the systems of PHZ-CA and PHZ-DDQ (Figs. 3, 4).

Because DDQ is a more strong donor than CA so the CTC absorption for DDQ-PHZ system is more obvious than that of CA-PHZ system. Benzoquinone is a rather weak acceptor with weak ability of formation CTC with PHZ, hence no new absorption peak appears on the UV-VIS spectra.

TCNE is a very strong acceptor, the solution of PHZ in methanol becomes yellow with addition of TCNE and a new absorption peak appears at 365 nm on UV-VIS spectra (Fig. 5). The CTC between PHZ and TCNE is so stable that no polymerization of AN will take place in bulk with PHZ-TCNE system as initiator.

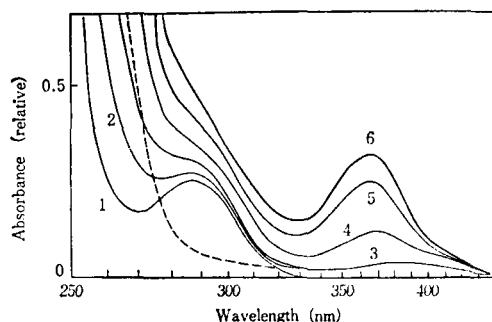


Fig. 5 The UV-VIS spectra for system of PHZ-TCNE in methanol

The point line: $[\text{PHZ}] = 0$, $[\text{TCNE}] = 1.3 \times 10^{-4} M$,

The solid line: $[\text{PHZ}] = 4.2 \times 10^{-4} M$;

$[\text{TCNE}] (M)$: 1, 0; 2, 2.6×10^{-5} ; 3, 6.4×10^{-5} ; 4, 1.3×10^{-4} ; 5, 1.9×10^{-4} ; 6, 2.6×10^{-4} .

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