

CHARGE-TRANSFER AND ENERGY-TRANSFER IN THE PHOTO-INDUCED COPOLYMERIZATION OF 2-VINYLNAPHTHALENE WITH MALEIC ANHYDRIDE*

LI Tong (李 潼), LUO Bin (罗 彬), LI Shanjun (李善君)

(Department of Material Science, Fudan University, Shanghai)

CHU Guobei (储国蓓)

(Department of Materials, Shanghai Institute of Building Materials)

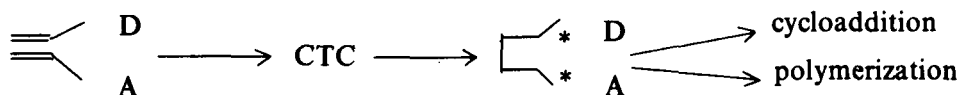
ABSTRACT

The initiation mechanism of the copolymerization of 2-vinylnaphthalene with maleic anhydride was studied under irradiation of 365 nm. The excited complex was formed from (1) the local excitation of 2-vinylnaphthalene followed by the charge-transfer interaction with maleic anhydride and (2) the excitation of the ground state charge-transfer complex, and then it collapsed to 1,4-tetramethylene biradical for initiation. A 1:1 alternating copolymer was formed in different monomer feeds. Addition of benzophenone could greatly enhance the rate of copolymerization through energy-transfer mechanism.

INTRODUCTION

Recently, there has been increasing interest in charge-transfer copolymerizations of electron donor/acceptor monomer pairs^[1, 2]. Some authors studied the copolymerization in the presence of initiators and concentrated their attention to the charge-transfer in the propagation, while the others paid more attention in the initiation mechanism.

Hall^[2, 3] studied the spontaneous reactions between electron-donor olefins and electron-acceptor olefins in the absence of initiators and proposed a "Bond-Formation Initiation" theory which successfully explained the copolymerization, cycloaddition and other reactions as follows:



** : + , - or . . .

where D and A represent electron-donating and electron-withdrawing substituents respectively and CTC the charge-transfer complex. The active center (**) may be 1,4- biradical which initiated the radical copolymerization or 1,4-zwitterion which initiates ionic homopolymerization.

Only few papers are dealing with photo-induced charge-transfer copolymerization

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appeared^[4-8] and the initiation mechanism has not been reported up to now. In this paper we have studied the photo-copolymerization of 2-vinylnaphthalene (VN) with maleic anhydride (MAN) and the effort has been devoted to describing the initiation mechanism.

EXPERIMENTAL

1. Materials

2-Vinylnaphthalene (VN) and benzophenone (BP) were purified by recrystallization in alcohol/water and maleic anhydride (MAN) was recrystallized in chloroform. The other monomers were all purified by distillation or recrystallization.

All the other reagents and solvents used in our experiment were A.R. reagents.

2. Methods

The rate of copolymerization was measured by combined dilatometric and gravimetric methods at 30 °C. A 300W high pressure mercury lamp served as the radiation source and a CuSO₄ solution filter was used to cut off the light above 365 nm wavelength^[9]. Before the polymerization the solution was bubbled with purified nitrogen to remove oxygen dissolved in the system. After polymerization the copolymer was precipitated with methanol.

If both the polymerization and small molecule formation reaction were studied, the photoreactions were run in a 15-ml pyrex tube equipped with a vacuum-line Teflon valve. The reaction vessel with the reaction mixture, was placed in a dry ice-acetone bath, degassed under full vacuum, and then closed off. After the reaction, the reactants were poured into methanol. The precipitated polymer was filtered off, dried and weighed. The remaining solution was rotaevaporated, and the products were analyzed.

Electron-absorption spectra and fluorescence spectra were recorded with Beckman DU-7 spectrophotometer and Hitachi MPF-4 fluorescence spectrophotometer respectively. GC/mass spectra were recorded with Hewlett Packard GC/MS system.

RESULTS AND DISCUSSION

1. Electron-Absorption and Fluorescence Spectra

Although VN is a weak electron-donor, the charge-transfer interaction can still occur between it and the strong electron-acceptor MAN. As shown in Fig.1, the electron-absorption band of VN was broadened towards longer wavelength when MAN was added into its solution, indicating the formation of a weak charge-transfer complex (CTC) between the components^[10].

Fig. 2 shows the fluorescence spectra of VN and the fluorescence quenching by adding of MAN. Although no exciplex fluorescence emission was observed at longer wavelengths, the quenching would be attributed to the formation of the exciplex between the excited VN and the ground state MAN. The similar nonfluorescent exciplexes were also reported in many other systems^[11,12].

In our experiment the light of 365 nm entered the system which can be absorbed by either VN or the CT complex. So there are two routes to form an excited complex:

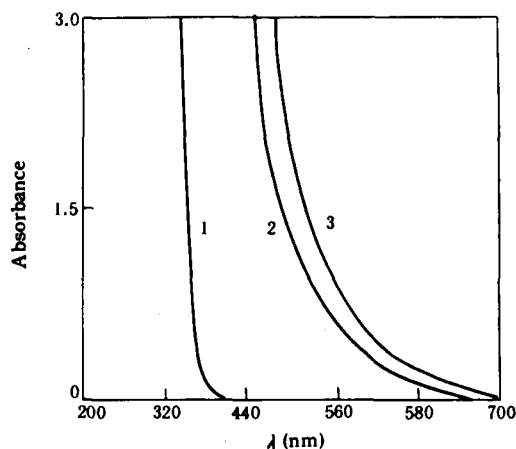
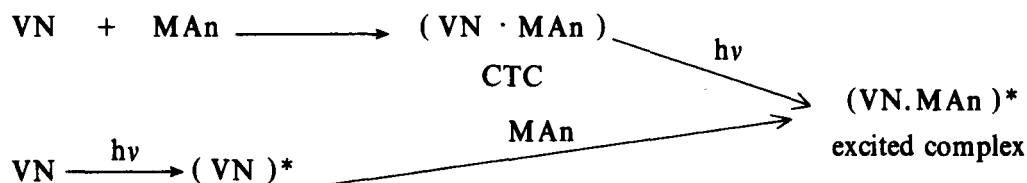


Fig. 1 Electron-absorption spectra (in CH_2Cl_2)

- 1) $[\text{MAn}] = 1.0 \text{ mol/L}$; 2) $[\text{VN}] = 0.2 \text{ mol/L}$;
 3) $[\text{MAn}] = 1.0 \text{ mol/L}$, $[\text{VN}] = 0.2 \text{ mol/L}$.

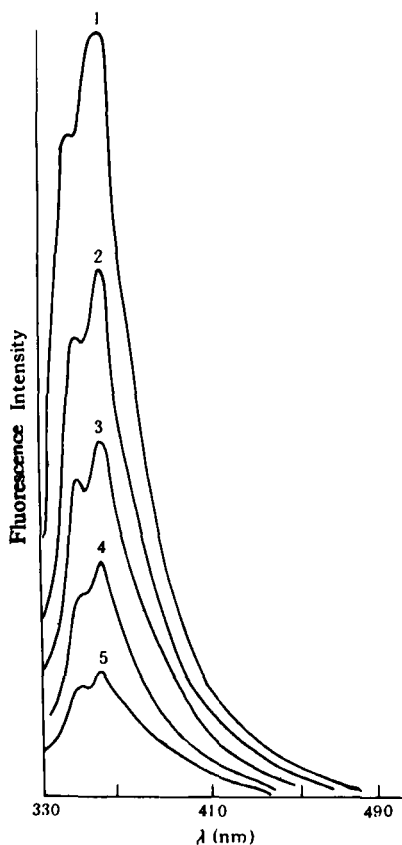
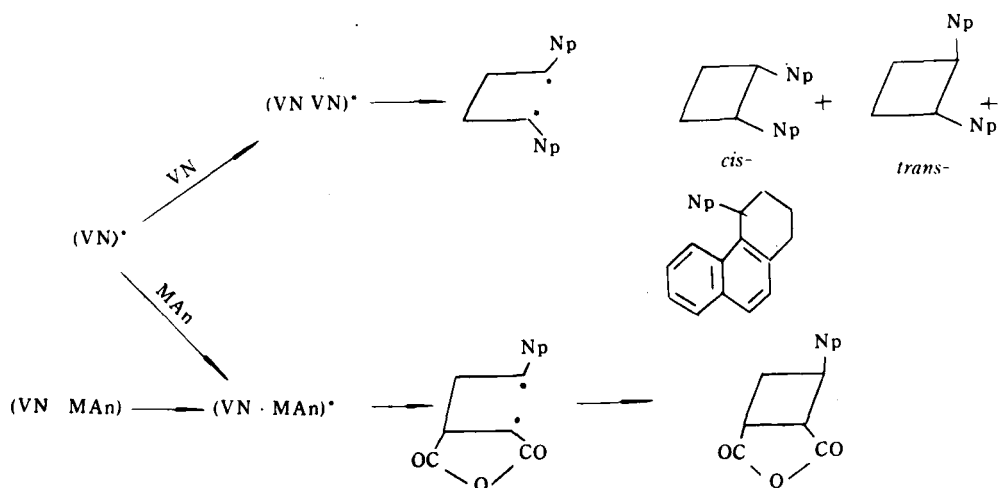


Fig. 2 Fluorescence of VN and fluorescence quenching by adding MAn in benzene

- ($[\text{VN}] = 5 \times 10^{-3} \text{ mol/L}$, $\lambda_{\text{ex}} = 320 \text{ nm}$)
 $[\text{MAn}]$ (mol/L): 1) 0; 2) 5.5×10^{-4} ;
 3) 2×10^{-3} ; 4) 3.2×10^{-3} ; 5) 6.5×10^{-3} .

2. Copolymerization and Small Molecule Formation

Shirota^[8] reported several VN/NV dimers and VN/MAn dimers in this system under irradiation. We also found that the copolymerization of VN/MAn was accompanied by small molecule formation, and the small molecule products were analyzed by GC/MS to be VN/VN dimers (with molecular weight 308) and VN/MAn dimers (with molecular weight 252). We proposed a reaction scheme as follows:



Np : 2-naphthyl

Although the polymerization of VN is easily initiated by radical initiators (e . g . AIBN), we obtained mainly dimer products with only very little polymer by irradiating VN alone . So we think VN/VN biradical is inefficient for the initiation and responsible mainly for the cyclization . Kopecky^[13] also reported that a similar aromatic biradical 1,4-diphenyl-1,4-butadiyl biradical was inefficient in the initiation of styrene polymerization . On the other hand , the polymerization of VN/MAn was fast , so VN/MAn biradical must play a more important role in the initiation .

If 1,4-biradical is involved in both the initiation of polymerization and the cyclization , we would expect a dependence of the ratio of the two competitive reactions on the total monomer concentration . At low concentration , the chance of a monomer reacting with the biradical is small , so the radicals stay in the " cage " and react with each other to form cycloadducts or other small molecule products . At high concentration , biradicals are trapped by monomers , therefore , copolymerization is the main route . This is clearly shown in Table 1 .

Table 1 Dependence of Copolymer and Oligomer Yield on the Initial Monomer Concentration *

Initial conc . of each monomer (mol / L)	yield of copolymer %	yield of oligomer %
0.75	77.3	15.7
0.25	60.5	34.2
0.10	40.3	50.2
0.05	30.1	63.1

* In 1,2-dichloroethane , irradiation for 48 hours .

3 . Relationship between Molecular Weight of the Copolymer and the Conversion

It is known that in biradical polymerization the polymer molecular weight will increase with the conversion^[3] . This has been now observed in VN/MAn system , as shown in Fig . 3 .

Barton et al .^[5] has already reported an increase of polymer molecular weight with the comonomer conversion in St/MAn system . These are strong evidences for

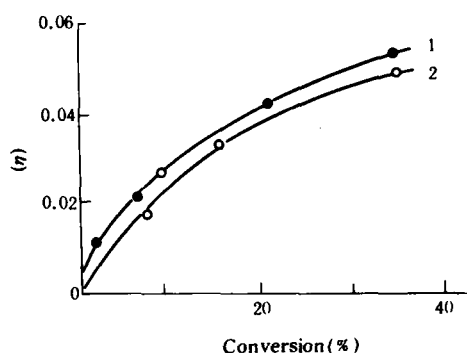


Fig. 3 Relationship between $[\eta]$ on the copolymer and conversion %

1) $[VN] = [MAn] = 1.0 \text{ mol/L}$;

2) $[VN] = [MAn] = 0.5 \text{ mol/L}$.

($[\eta]$ was measured in DMF at 30°C)

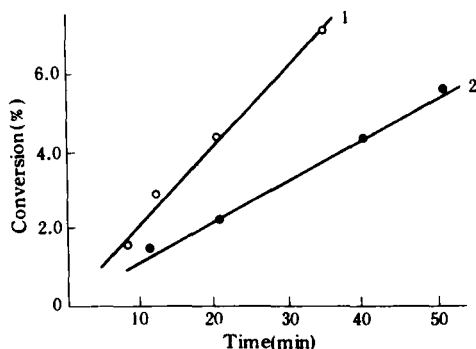


Fig. 4 Relationship between conversion and time

($[VN] = [MAn] = 1.0 \text{ mol/L}$)

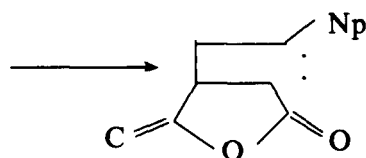
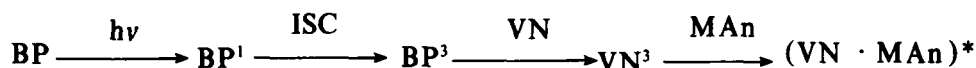
1) $[BP] = 4 \times 10^{-2} \text{ mol/L}$;

2) $[BP] = 0$.

biradical propagation. So the "Bond-Formation Initiation" theory is applicable to photo-induced charge-transfer copolymerization as well as to thermal charge-transfer copolymerization.

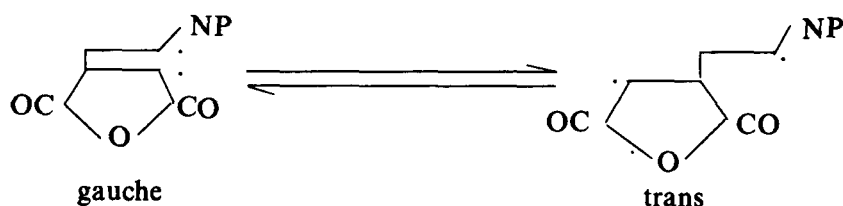
4. Enhancement effect of BP on the copolymerization

The excited triplet of BP can transfer its energy to naphthalene group^[14]. When BP was added into VN/MAn copolymerization system, the rate of polymerization (R_p) was found to increase remarkably (Fig. 4). This result can be explained by the energy transfer from excited triplet BP to VN, followed by the formation of triplet exciplex of the latter with BP, which then collapsed to 1,4-triplet biradical:



triplet 1,4-biradical

Triplet biradical has longer life-time than singlet biradical^[15], so it favors the transformation from gauche conformation to trans conformation:



Cycloaddition more easily occurs in the former conformation while the latter conformation is favorable for the addition of monomers^[2], so the triplet biradical will

favor the initiation of polymerization .

5 . Dependence of copolymer composition on monomer feed composition

Fig . 5 shows the dependence of the instantaneous copolymer composition on the comonomer feed composition for VN/MAn system . The copolymer compositions were determined with elemental analysis and IR spectra (the ratio between carbonyl absorption of MAn at 1776 cm^{-1} and naphthyl absorption at 1553 cm^{-1}). The copolymer possesses an alternating 1:1 structure and this is even the case in 3:1 or 1:3 feed ratios .

6. Effect of solvent polarity on copolymerization

Table 2 shows the influence of the solvent polarity on the copolymerization rate of VN/MAn system . In many polar solvents (with greater dielectric constant ϵ value) the copolymerization rate decreases . We suppose that the initiating biradical is formed in the intimate radical-ion pair state of the excited complex rather than its solvated ion radical state . This is in agreement with our previous investigation^[16,17] . In polar solvents, such as acetonitrile, dissociation of the excited complex into the solvated ion radicals is more favorable because these solvent will stabilize the ion radicals . So the free radical formation as well as the copolymerization will be hindered .

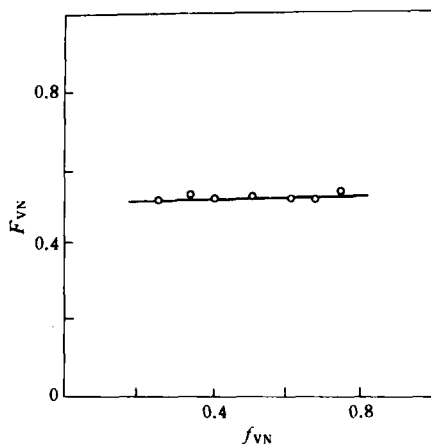


Fig . 5 Dependence of the instantaneous copolymer composition F_{VN} on the comonomer feed composition f_{VN}

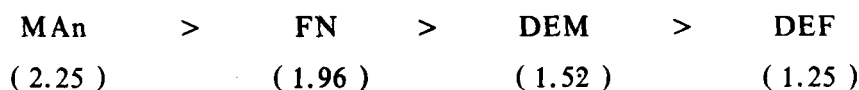
Table 2 Effect of Solvent Polarity on the Copolymerization Rate
([VN] = [MAn] = 0.5 mol / L)

Solvent	ϵ	$R_p \times 10^6$ (mol . L . s)
CH ₃ CN	37.5	0.1
CH ₂ ClCH ₂ Cl	10.6	0.8
CH ₂ Cl ₂	8.93	1.6
CH ₃ COOC ₂ H ₅	6.0	2.8
CHCl ₃	4.8	1.0 *

* Precipitation polymerization

7 . Effect of the strength of the donor and the acceptor on copolymerization

Four acceptor monomers were used in our experiments to investigate the effect of acceptor strength on the copolymerization : MAn , fumaronitrile (FN) , diethyl maleate (DEM) and diethyl fumarate (DEF) . Their electron-accepting abilities decrease in the following order :



The numbers in the brackets show the e values of Price-Alfrey equation. It is noteworthy that the copolymerization activity of DEM is lower than that of DEF due to steric effect.

The donor monomers we used are α -methyl styrene (MSt), styrene (St), VN and vinyl acetate (VAc). The electron-donating abilities decrease in the following order:

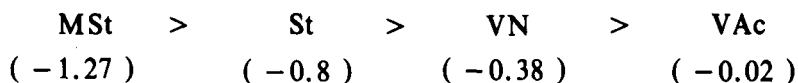


Table 3 R_p of photo-induced copolymerization of D/A pairs*
(mol/L · s)

D/A	MAN	FN	DEF	DEM
MSt	2.3	0.63	0.33	0.23
St	15.2	0.75	/**	/
VN	2.3	3.5	/	/
VAc	0.28	/	/	/

*[D]=[A]=1.0 mol/L, in chloroform at 35 °C.

** No photo-copolymerization was observed.

Table 3 shows the results of photo-copolymerization of different monomer pairs. The copolymerization takes place in strong donor (D)/strong acceptor (A), strong D/weak A and weak D/strong A pairs but not in weak D/weak A pairs. The rate of photo-copolymerization of the strongest pairs such as MSt/MAN is somewhat lower than that of moderate strong monomer pairs such as St/MAN and VN/FN. This is attributed to the easier occurring of complete electrontransfer under irradiation for too strong monomer pairs. The produced solvated ion-radicals are unfavorable for the initiation of radical polymerizations.

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