Photoreactions of *N*-Vinylcarbazole Induced by Metal Salts.

V. Mechanistic Studies of the Cationic Polymerization Induced by Silver(I) Salts in Aromatic Solvents

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ABSTRACT: Photosensitized cationic polymerizations of *N*-vinylcarbazole (VCZ) induced by silver(I) perchlorate and tetrafluoroborate in various aromatic solvents were investigated under irradiation at 365 nm at 30°C. The polymerization rates decreased in the following order: nitrobenzene > benzene > toluene $\gg$ *p*-xylene $\sim$ 0. The specific interaction between VCZ and silver which was observed spectroscopically only in the perchlorate—benzene system does not participate in the initiation processes. It was concluded that the effective absorption species leading to initiation is VCZ itself. Arguing from the kinetic behavior and the similarity in molecular weights of the polymers, the polymerization in benzene and toluene proceeded *via* an identical mechanism. The poor photochemical reactivity in *p*-xylene was assumed to be attributable to the initial processes. Moreover, excitation of the charge-transfer band of the VCZ-nitrobenzene complex in the presence of silver perchlorate enhanced the polymerization rate in comparison to the photopolymerization without silver perchlorate. The following initiation mechanism was proposed: The electron transfer from excited VCZ* to solvent molecule produces a cation radical, VCZ⁺, which in turn reacts with AgClO₄ to produce the initiating species.

KEY WORDS *N*-Vinylcarbazole / Cationic Polymerization / Silver(I) Salts / Photopolymerization / Charge Transfer Polymerization /

In the preceding paper,¹ kinetic features of the photosensitized cationic polymerization of *N*-vinylcarbazole (VCZ) induced by silver(I) perchlorate in benzene (Bz) were investigated under irradiation at 365 nm at 30°C. The present article describes the mechanistic studies of the initiation processes; here two sorts of problems are examined: What is the effective light absorbing species leading to initiation? And what is the role of silver(I) salt—silver cation or counter anion? To elucidate these problems, photopolymerizations were carried out in various aromatic solvents such as toluene (Tol), *p*-xylene

(*p*-Xy), and nitrobenzene (NB) as well as Bz, using silver(I) tetrafluoroborate and tetra-*n*-butylammonium perchlorate, as well as silver perchlorate, as catalysts. The molecular interaction between VCZ and silver salt in the ground state was measured by absorption spectroscopy. From these results, a possible mechanism of initiation was proposed. Kinetic data obtained previously were interpreted in accordance with this mechanism.

EXPERIMENTAL

N-Vinylcarbazole, silver(I) perchlorate, and benzene were purified as described in the preceding article.¹ Toluene and *p*-xylene were purified by methods similar to that used for benzene. Nitrobenzene was purified as reported previously.² Silver(I) tetrafluoroborate was dried *in vacuo* for more than 10 hr at room temperature before use. Tetra-*n*-butylammonium perchlorate was prepared and purified using the

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procedures reported by Fujinaga, *et al.*³ All other experimental methods were the same as described in the preceding article.

RESULTS AND DISCUSSION

Photopolymerization in Benzene

As shown in the preceding paper,¹ the photo-sensitized cationic polymerization of *N*-vinylcarbazole (VCZ) in the presence of silver(I) perchlorate was induced under irradiation at 30°C in benzene, whereas thermal as well as noncatalytic photosensitized polymerization were negligibly slow. The problem of the photo-absorbing species is not straightforward, just as encountered in the photopolymerization system sensitized by tetrahaloaurate(III) in nitrobenzene.⁴ Under the polymerization condition ($[\text{VCZ}]_0 = 0.25M$) no change in absorption spectra (Figure 1) was observed by the addition of silver(I) perchlorate up to $2 \times 10^{-4}M$. However, in absorption spectroscopy in the short wavelength region under very dilute conditions, complex formation between VCZ and silver perchlorate was observed, as shown in Figure 2. Therefore, the photoabsorbing species effective for the initiation is either VCZ itself or some kind of VCZ—AgClO₄ complex.

Reference experiments using tetra-*n*-butylammonium perchlorate were performed as shown in Table I. Since the complete inertness of the

Figure 1. Absorption spectrum of the polymerization system: $[\text{VCZ}]_0, 0.25M$; $[\text{AgClO}_4]_0, 1 \times 10^{-4}M$; room temperature, solvent, benzene.

Figure 2. Absorption spectra of relevant compounds in benzene: 1, benzene; 2, $[\text{AgClO}_4], 10^{-4}M$; 3, $[\text{VCZ}]_0, 10^{-4}M$; 4, $[\text{VCZ}]_0, 10^{-4}M$, $[\text{AgClO}_4]_0, 10^{-5}M$; room temperature,

Table I. Effect of $(n\text{-C}_4\text{H}_9)_4\text{NClO}_4$ (TBP) on the photopolymerization^a

TBP, <i>M</i>	$[\text{VCZ}]_0, M$	Time, min	Conv., %
1×10^{-2}	0.25	120	5
0	0.25	120	7

^a Under irradiation of unfiltered light, 30°C.

perchlorate anion as photosensitizer was proved, the active part of silver perchlorate must be Ag(I) itself and not the perchlorate anion. Also, silver(I) tetrafluoroborate as sensitizer was effective for the photopolymerization, although its activity was a little less than that of AgClO₄, as shown in Figure 3, indicating that the role of the anion is minor. However, the blue shift in absorption spectra attributed to the complex formation observed in the VCZ—AgClO₄ system was not detected in the VCZ—AgBF₄ system. The total amount of VCZ—AgClO₄ complex is negligibly small in comparison with the free VCZ under the present experimental conditions for polymerization ($[\text{Ag(I)}] = 10^{-4}M$, $[\text{VCZ}] = 0.1M$) even if the complex formation is nearly

Figure 3. Photopolymerizations catalyzed by AgClO_4 and AgBF_4 in benzene: $[\text{VCZ}]_0$, $0.5M$; λ , 365 nm ; 30°C : —●—, $[\text{AgClO}_4]_0$, $1 \times 10^{-4}M$; —○—, $[\text{AgBF}_4]$, $2 \times 10^{-4}M$.

completed. Furthermore, the blue shift of the absorption band of VCZ is brought about as a result of the complexation.⁶ Consequently, the photoenergy at 365 nm is absorbed exclusively by VCZ itself. The relation $R_p \propto I_0^{0.5} [\text{AgBF}_4]_0$, similar to the $\text{AgClO}_4\text{—Bz}$ system,¹ was obtained.

Polymerization Induced by Silver(I) Perchlorate in Several Aromatic Solvents (Figure 4)

In toluene, which is chemically close to benzene, photopolymerization proceeded with a somewhat slower rate than in benzene; the formation of VCZ—AgClO_4 complex was not observed, indicating light absorption by VCZ alone. Both thermal and noncatalyzed photopolymerizations were also negligibly slow. The kinetic investigation leads to the rate expression: $R_p \propto I_0^{0.5} [\text{AgClO}_4]_0$, which is again similar to that for the $\text{AgClO}_4\text{—Bz}$ system.¹ In contrast to benzene and toluene, however, photoirradiation of the reaction mixture in *p*-xylene was almost ineffective, whereas thermal and noncatalyzed photopolymerizations proceed with a rate comparable to other solvent systems. The absorbance of the polymerization solution was nearly identical for $\text{AgClO}_4\text{—Bz}$, $\text{AgClO}_4\text{—Tol}$, $\text{AgBF}_4\text{—Bz}$, and $\text{AgClO}_4\text{—}p\text{-Xy}$ systems. Consequently, the marked differences in R_p in these systems must be attributed either to the efficiency of initiation or to the propagation and/or termination processes. The latter possibility is precluded since the cationic polymerization of

Figure 4. Photopolymerizations catalyzed by AgClO_4 in various aromatic solvents: $[\text{VCZ}]_0$, $0.25M$; $[\text{AgClO}_4]_0$, $1 \times 10^{-4}M$; λ , 365 nm ; 30°C : —○—, benzene; —●—, toluene; —□—, *p*-xylene; —■—, nitrobenzene.

Table II. Thermal polymerization initiated by AgClO_4 in various solvents

Solvent	$[\text{VCZ}]_0$, M	$[\text{AgClO}_4]_0$, M	Temp, $^\circ\text{C}$	R_p , M/min
Benzene	0.25	1×10^{-4}	30	3.7×10^{-5}
Toluene	0.25	1×10^{-4}	30	3.1×10^{-5}
<i>p</i> -Xylene	0.25	1×10^{-4}	30	2.9×10^{-5}
Nitrobenzene	0.225	1×10^{-4}	30	6.5×10^{-5}

Figure 5. Dependence of R_p on I_0 in nitrobenzene: $[\text{VCZ}]_0$, $0.25M$; $[\text{AgClO}_4]_0$, $1 \times 10^{-4}M$: —●—, λ , 365 nm , 12°C ; —○—, λ , 436 nm , 23°C .

styrene derivatives in benzene, toluene, or *p*-xylene proceeds with almost identical rates,⁵ and in addition, the slow dark cationic polymerization of VCZ by silver perchlorate was hardly affected by the kind of solvent (Table II).

Table III. Photopolymerizations of VCZ catalyzed by silver(I) salts under irradiation at 365 nm

Ag(I) salt	[Ag(I)] ₀ , <i>M</i>	[VCZ] ₀ , <i>M</i>	Temp, °C	Solvent	$R_p \propto I_0^x [\text{Ag(I)}]_0^y$		UV spectra
					<i>x</i>	<i>y</i>	
AgClO ₄	0.3—2 × 10 ⁴	0.25	30	Benzene	1/2	1	Blue shift
AgClO ₄	0.5—5 × 10 ⁴	0.5	30	Toluene	1/2	1	No shift
AgClO ₄	1 × 10 ⁴	0.5	30	<i>p</i> -Xylene	No polymerization		No shift
AgClO ₄	0.5—2 × 10 ⁴	0.25	23	Nitrobenzene	1/2	0	—
AgBF ₄	1 —5 × 10 ⁴	0.5	30	Benzene	1/2	1	No shift

In nitrobenzene, another type of aromatic solvent, a rapid photopolymerization resulted under irradiations at 365 nm and 436 nm, although the problem of absorption species was considerably different from the above systems; this will be discussed later. R_p was again proportional to the square root of I_0 , as shown in Figure 5, whereas R_p was independent of $[\text{AgClO}_4]_0$.

Initiation Mechanism

The kinetic sequence and the degree of polymerization in various photopolymerization systems induced by silver(I) salts are summarized in Tables III and IV, respectively.

The complex formation, which is observed as a blue shift of the absorption spectra of VCZ, between VCZ and silver salt is a specific phenomenon for the combination of VCZ—AgClO₄—Bz. The fact that photopolymerization of VCZ proceeds equally in the systems AgClO₄—Bz, AgClO₄—Tol, and AgBF₄—Bz, regardless of complex formation, provides further support that the efficient photoabsorbing species is VCZ itself. The silver salt themselves are transparent to the irradiation at 365 nm and could not be energy-absorbing species.

A mechanism of photopolymerization which does not contradict the observed mechanistic and kinetic findings may be expressed as follows:

Table IV. Degree of polymerization for photopolymerization in various solvent

Solvent	[VCZ] ₀ , <i>M</i>	[AgClO ₄] ₀ , <i>M</i>	$\bar{P}$
Toluene	0.5	1 × 10 ⁻⁴	4.4 × 10 ²
Benzene	0.5	1 × 10 ⁻⁴	5.4 × 10 ²
Nitrobenzene	0.225	1 × 10 ⁻⁴	8.8 × 10 ²
Benzene	0.25	1 × 10 ⁻⁴	3.4 × 10 ²

where M, S, and AgX denote VCZ, benzene-like solvent, and silver salt, respectively.

Another possible elementary process may be the reaction of excited VCZ with silver salt leading to the initiation of polymerization, as expressed by (9):

This mechanism is tempting since fluorescence of VCZ is quenched by AgClO₄ with the quenching constant of 10² M⁻¹ in benzene.⁶ It is, however, difficult to explain either the peculiar solvent effects upon the initiation process or the kinetic expressions presented in Table III with this initiation mechanism. As discussed in the preceding section, the sequence of R_p with respect to solvent, benzene > toluene >> *p*-xylene ~ 0 is presumably from the initiation processes. Moreover, the polymerization mechanisms in AgClO₄—Bz, AgBF₄—Bz, and AgClO₄—Tol systems will be the same as judged from the identity of their kinetic behaviors (Table III) as well as their degrees of polymerization (Table IV).

The electron-accepting property of AgClO_4 should be a determining factor for (9). Reaction (9) should therefore be suppressed by charge-transfer complex formation of AgClO_4 with solvent as a consequence of the decreased electron-accepting capacity of complexed Ag(I) . The sequence of the equilibrium constants of complexes between alkylbenzenes and Ag(I) has been reported as toluene > *p*-xylene > benzene,⁷ which could not explain the solvent effect upon R_p if we assume (9) as the initiating process.

The mechanism expressed by (1)–(8) could explain the kinetic expression. The evidence in support of this mechanism is circumstantial and given as follows.

Since the strong donor character of VCZ in the ground state would be enhanced by photoexcitation, an electron-transfer process (2) from excited VCZ to ground state solvent molecule would be possible. Electron transfer from excited amine to aromatic hydrocarbon has been demonstrated in the *N,N*-dimethylaniline–biphenyl system⁸ and the *N,N,N',N'*-tetramethyl-*p*-phenylenediamine–pyrene or naphthalene derivatives system.⁹ The sequence of R_p in these solvents agrees with the decreasing order of the acceptor strength of solvents. The expected order of acceptor strength is: $\text{NB} > \text{Bz} > \text{Tol} > p\text{-Xy}$. This order is supported by the following facts: i) the ease of producing anion radicals when alkyl substituted benzenes react with metallic potassium is $\text{Bz}, \text{Tol} \gg p\text{-Xy}$;¹⁰ ii) The electron affinity decreases with increasing number of methyl groups introduced into the benzene ring.¹¹ Although this process proceeding via the excited singlet state of VCZ would result in a reduction in the fluorescence yield or the appearance of excimer emission, no such physical evidence was observed within the experimental errors. These results might well be due to their extremely low efficiency via the triplet state of VCZ.

Irradiation of VCZ–NB system at 436 nm excites the VCZ–NB contact charge-transfer complex exclusively and cationic polymerization is brought about even in the absence of the silver salt.¹² The addition of silver perchlorate to this system enhanced the rate of polymerization, as shown in Figure 6. Since the primary act of photoirradiation both in the presence and

Figure 6. Photopolymerization of VCZ catalyzed by AgClO_4 in nitrobenzene: $[\text{VCZ}]_0$, 0.25 M; 23°C: —●—, λ , 365 nm, $[\text{Ag(I)}]_0$, $1 \times 10^{-4} \text{ M}$; —○—, λ , 436 nm, $[\text{Ag(I)}]_0$, $1 \times 10^{-4} \text{ M}$; —△—, λ , 436 nm, $[\text{Ag(I)}]_0$, 0 M.

absence of the silver salt is most likely to be expressed by (10);

the role of silver salt will presumably enhance the initiation efficiency after electron transfer from VCZ to the solvent occurs. Although the VCZ–NB system exhibiting charge-transfer interaction in the ground state is not strictly comparable to the VCZ–alkylbenzene systems, these findings seem to be in favor of the proposed mechanism for the VCZ–alkylbenzene– AgClO_4 systems.

The cyclodimer cation radical (D^+) in process (4) has been proposed by Ledwith¹³ as a intermediate in the cyclodimerization of VCZ, in which the following equilibrium has been confirmed in the ring-opening reaction of the cyclodimer. This intermediate assumed from the chemical viewpoint was recently ascertained from its direct observation in the pulse

radiolysis studies of VCZ in benzonitrile by Imamura, *et al.*¹⁴ They have suggested that D^+ is a precursor for both cyclodimerization and cationic polymerization of VCZ; moreover, the equilibrium of process (4) has been confirmed experimentally.

Initiation species I is assumed to be produced from some type of interaction of D^+ with silver salt in process (5). A possible role of the silver ion is to stabilize D^+ by formation of a charge-transfer complex with a radical part, envisaged as follows, and to prevent the backward reaction of (4):

I initiates the cationic propagating species bearing perchlorate ion as counter anion, as discussed in the preceding paper. Interactions of radicals with closed shell ions including silver (I) ion (d^{10}) have been reported in the ESR studies of various compounds.¹⁵ Another possibility for the role of $AgClO_4$ is the oxidation of geminate S^- to prevent recombination of the cation radical (M^+ or D^+) with the anion radical as follows:

A similar role for a metal salt has been reported in the pulse radiolysis of THF/pyrene in the presence of $LiAlH_4$, which removes the geminate cation and stabilize the pyrene radical anion with the inert lithium cation.¹⁶

By applying the assumptions, $k_d[M^+] \gg k_2[M]$, $k_{-2} \gg k_3[Ag^I]$ and $[M^+] = [S^-]$, the following rate expression is derived:

$$(R_p)_x = \frac{k_p k_3 k_2}{k_t k_{-2}} \{ (I_{abs}^{VCZ})_x \}^{1/2} [Ag^I]_0 [VCZ] \quad (14)$$

where $(R_p)_x$ and $(I_{abs}^{VCZ})_x$ denote the rate at a distance x from the front face of the reaction cell, as described in the preceding article,¹ and the amounts of light absorbed by monomer in a unit volume at x , respectively. This equation explains the experimental results obtained in $AgClO_4$ -Bz, $AgClO_4$ -Tol, and $AgBF_4$ -Bz systems very well. The detailed kinetic treatment in $AgClO_4$ -Bz system was described in the preceding article.¹ Moreover, the rate expression; $R_p \propto I_0^{1/2} [AgClO_4]_0^0$ as observed in nitrobenzene may be interpreted on the assumption $k_{-2} \ll k_3 [Ag^I]$, which means rapid stabilization reaction (12) in this highly polar solvent. In this case the rate expression corresponding

to eq 14 is as follows:

$$(R_p)_x = \frac{k_p k_2}{k_t k_3} \{ (I_{abs}^{VCZ})_x \}^{1/2} [Ag^I]_0^0 \quad (15)$$

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