INITIATION OF PHOTOPOLYMERIZATION BY CHARGE TRANSFER INTERACTIONS

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ABSTRACT

Initiation processes of photopolymerization involving charge transfer interaction are divided into the following categories and discussed with relevant examples mainly on the polymerization of *N*-vinylcarbazole. (i) Excitation of organic charge transfer complexes. (ii) Charge transfer interaction between two organic molecules, one of which is excited. (iii) Excitation of metal complexes monomers. (iv) Excitation of a metal complex which then reacts with monomer. (v) Interaction of excited monomers with a metal complex. A peculiarity of photoinduced charge transfer polymerization is to initiate ionic and/or radical polymerization.

INTRODUCTION

In the long history of photosensitized polymerization, the name of 'photosensitized charge transfer polymerization'[1] came into use only recently. The area of research involved in this category is vast since the term of charge transfer concerns the principle of reactions regardless of the components employed. One may realize the difference between photosensitized charge transfer polymerization and other conventional classifications of photopolymerization such as dye-sensitized photopolymerization. The former has its basis in phenomena observed in the course of producing initiating species whereas the latter is named after components responsible for photosensitization. In other words, the former is more dynamic terminology than the latter. Consequently, photosensitized charge transfer polymerization provides a new mechanistic viewpoint to elucidate photoinitiation systems, in which some conventional photopolymerization via radical intermediates may also be included.

The major peculiarity of a photosensitized charge transfer process is the requirement for the coexistence of donor (D) and acceptor (A). In conventional photoinduced radical polymerization, photoenergy is absorbed by isolated molecules such as monomer, sensitizer and solvent eventually to yield radicals via π–π^* or n–π^* excitation. On the other hand, a typical initiation scheme of a charge transfer system is to excite the charge transfer band resulting from complex formation between donor and acceptor and to provide ion–radical pairs. Although, as will be discussed later, the possibilities of an exciplex mechanism introduce complexity, two components are always expected to participate in the primary process. From the viewpoint of polymerization, the important point is to induce ionic propagation. The

application of charge transfer interaction is certainly a potential but not an exclusive† technique to photoinitiate ionic polymerization.

In this lecture, the author intends to exclude the area of overlap with conventional photopolymerization such as photoirradiation effects upon a redox catalyst. Discussions are focused on the charge transfer interaction under photoirradiation in which the monomer participates at least as one component of the charge transfer interaction, since the author believes that the direct photoactivation of monomer is the representative feature of photosensitized charge transfer polymerization.

Various fields of chemistry relevant to the present study are shown in *Figure 1*.

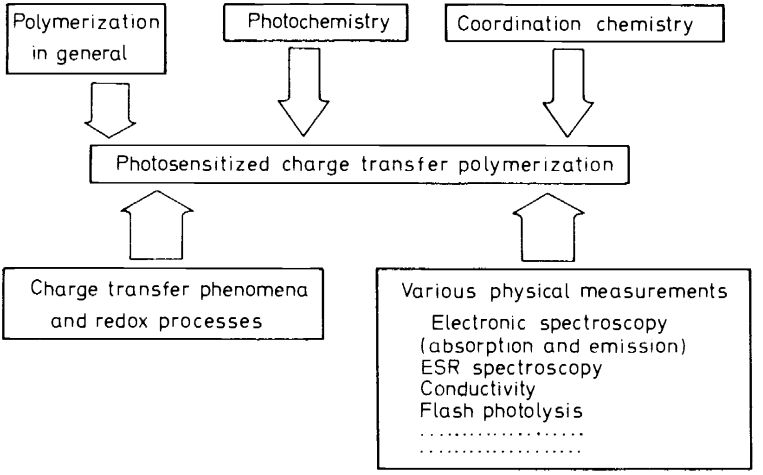
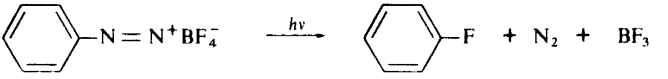


Figure 1. Photosensitized charge transfer polymerization and its relevant fields.

BACKGROUND OF PRESENT TOPICS

As the theory of charge transfer interaction indicates, the ground state of a charge transfer complex mostly consists of no-bond structures whereas the contribution of dative bond structure predominates in the excited state. Thus, as a result of charge transfer absorption, the EDA (electron donor acceptor) complex is extremely polarized so that it dissociates to ion radicals in appropriate polar media. As expressed by simple quantum chemical equations [(1) and (2)] and neglecting the overlap integral where N and E represent the

† For example, photoinduced cationic polymerization is possible by the following reaction. reaction.



ground and the excited states and $a^2 + b^2 = 1$, the difference in electron distri-

$$\psi_N = a\psi(D{\cdot}A) + b\psi(D^+A^-) \quad (1)$$

$$\psi_E = -b\psi(D{\cdot}A) + a\psi(D^+A^-) \quad (2)$$

bution between ground and excited states is larger for a weak complex ($a \gg b$) than for a strong complex. This is an important theoretical prediction that ionic active species would be produced more readily from photoexcitation of weak EDA complexes although the energy of charge transfer excitation may be higher.

Even if the charge transfer interaction could not be detected in the ground state, there is another possibility of participation of charge transfer phenomena in the excited state. When an isolated molecule is electronically excited, the ionization potential decreases whereas the electron affinity increases[2]. Consequently, the excited molecule is a stronger donor as well as a stronger acceptor. Complex formation is therefore facilitated if either donor or acceptor is photoexcited. The complex formed in the excited state is called an exciplex[3] which is defined to include both homopolar excimer and heteropolar excimer. The presence of an exciplex can be experimentally confirmed only if the exciplex provides emission spectra. Photochemical primary

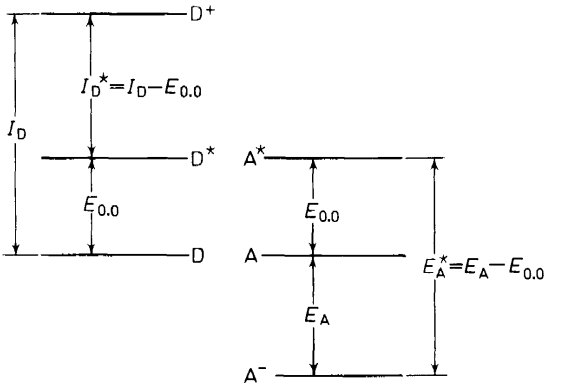


Figure 2. Enhancement of donor and acceptor strength by electronic excitation[2].

processes involving organic donor acceptor interaction are expressed as follows.

$$\text{case 1 } D + A \underset{}{\overset{K}{\rightleftharpoons}} DA \xrightarrow{h\nu} (DA)^* \text{ excited EDA complex} \quad (3)$$

$$\text{case 2 } D \xrightarrow{h\nu} D^* \xrightarrow{A} D^*A \quad \text{exciplex} \quad (4)$$

$$\text{case 3 } A \xrightarrow{h\nu} A^* \xrightarrow{D} DA^* \quad \text{exciplex} \quad (5)$$

So the molecular orbital is constructed between D and A in the excited state, and the electronic state of an exciplex or an excited EDA complex at their lowest excited state would be the same for both excited EDA complex

and exciplex. The fluorescence spectroscopy of the α-methyl styrene–tetracyanobenzene (TCNB) system, however, draws a distinction between $^1(DA)^*$ and $^1(DA^*)$[4].

Whole reaction processes relevant to charge transfer interactions are summarized in *Figure 3*. From the standpoint of synthetic polymer chemists, subsequent chemical reactions which have been little studied are more important than studying the detailed mechanisms of the primary processes.

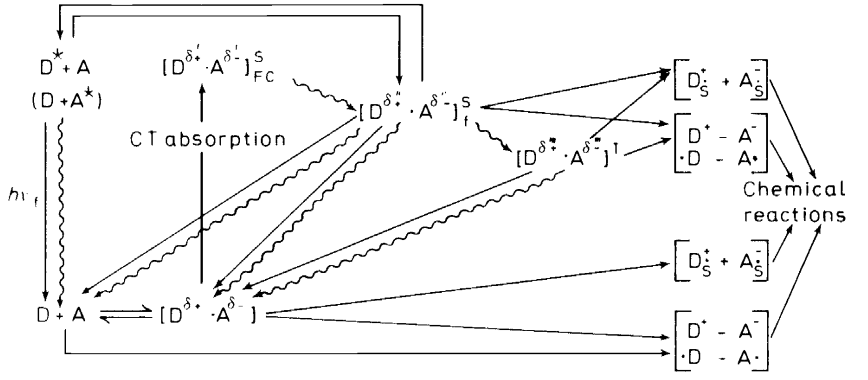


Figure 3. Various processes involved in charge transfer interactions. Inferior letters: FC; Franck Condon state. f: fluorescence state. s: solvated state. Superior letters: S: singlet state, T; triplet state.

Photochemistry of coordination compounds is another branch related to photosensitized charge transfer polymerization. As Pearson[5,6] discussed in his report on softness and hardness of acid–base interaction, ligand and metal ion can be interpreted from the viewpoint of donor–acceptor or base–acid interaction. The modes of photoabsorption by coordination compounds are roughly divided into a ligand field band (d–d transition) which is Laporte forbidden and weak ($\varepsilon \lesssim 100$) and a charge transfer band which is an allowed transition and strong. Besides these, photoabsorption by the ligand itself may also be observed. The types of reactions induced by photoexcitation could not so easily be correlated to the modes of photoabsorption[6]. Generally speaking, the ligand field absorption which corresponds to exciting an electron from non-bonding orbitals to antibonding orbitals weakens the ligand–metal bond and therefore is expected to promote the substitution and isomerization of coordination compounds. By contrast, the charge transfer absorption is assigned as either ligand to metal (CTTM), metal to ligand (CTTL) or complex to solvent (CTTS). Subsequent reactions caused by charge transfer excitation generally involve redox processes†. In conclusion, the charge transfer excitation does not necessarily lead to redox decomposition of metal complexes whereas redox reactions are induced almost exclusively by

† Detailed discussions on the nature of excited state and the subsequent reactions, see ref. 7.

charge transfer excitation. A typical example of the photochemical reaction of a metal complex is shown below.

$$[Co(NH_3)_5X]^{2+} \xrightarrow{h\nu(\text{d d band})} \text{aquation} \qquad \phi < 10^{-2} \quad (6)$$

(X: halogen or pseudohalogen)

$$\xrightarrow{h\nu(\text{CT band})} Co^{2+} + 5NH_3 + X\cdot \qquad \phi > 0.1 \quad (7)$$

The photochemistry of coordination compounds is still in its infancy and confined to the photoexcitation and subsequent reactions of a metal complex alone as expressed by (8).

$$\text{case 4 } M + nL \rightleftharpoons ML_n \xrightarrow{h\nu} (ML_n)^{\star} \longrightarrow \text{reaction products} \quad (8)$$

For the purpose of initiating photosensitized charge transfer polymerization, the following reactions are equally important. In particular, the reaction of an excited molecule with a metal complex (case 6) is very unique and there seems to be no known example confirmed unequivocally in the manner of case 6.

$$\text{case 5; } ML_n \xrightarrow{h\nu} (ML_n)^{\star} \xrightarrow{L'} \text{reaction products or unstable valency states of the metal} \quad (9)$$

$$\text{case 6; } L' \xrightarrow{h\nu} (L')^{\star} \xrightarrow{ML_n} \text{reaction products} \quad (10)$$

Any photosensitized charge transfer processes either in organic or inorganic systems will be expressed by one of these six cases.

Until now, discussions have been concentrated on the primary act accompanied by charge transfer phenomena. Although there are many examples of ion radical formation from an excited EDA complex or exciplex in polar media, we must bear in mind that photosensitized charge transfer initiation of polymerization is not identical to ion radical initiation. Examples will be presented later.

INDIVIDUAL CASES

A common kinetic feature observed for the polymerization of *N*-vinylcarbazole —rate/intensity of light relation

Photoinduced cationic polymerization of *N*-vinylcarbazole (VCZ) in nitrobenzene[8] is the first definitive example of initiating ionic polymerization of a vinyl compound by charge transfer excitation. This monomer has strong electron donating properties and in addition, the ion-radical and the carbonium ion from this monomer are expected to be highly stabilized as a result of resonance stabilization. Consequently, VCZ is one of the most active monomers for cationic polymerization. In the early 1960s, the new principle of charge transfer initiation was brought into vinyl polymerization mostly using VCZ as the monomer[9,10]. As the theory of charge transfer complexes predicts, photoinitiation is a powerful approach to this polymerization system. Various photopolymerizations of VCZ using both organic and inorganic acceptors have been investigated and a general kinetic relation of the form $R_p \propto I_0^{\frac{1}{2}}$ was found[11] as shown in *Figure 4* whereas the propagation process is always cationic.

Examples are: (1) VCZ–nitrobenzene, (2) VCZ–sodium tetrachloroaurate–nitrobenzene, (3) VCZ–carbon tetrabromide–ethylene chloride with and without acridine orange as sensitizer and (4) VCZ–silver perchlorate–aromatic hydrocarbon. As indicated by radical polymerization, the square root dependence of R_p on the intensity of light should imply bimolecular dissipation of the active species.

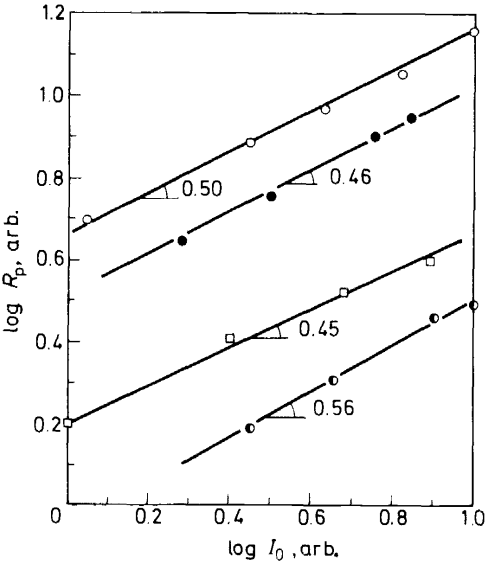


Figure 4. Dependence of R_p on the intensity of light. □: VCZ (0.25 M)—nitrobenzene at 30°C in air, multichromatic radiation. ●: VCZ (0.25 M)—$NaAuCl_4 \cdot 2H_2O$ (5×10^{-5} M)—nitrobenzene at 30°C in air, irradiation at 436 nm. ○; VCZ (0.5 M)—CBr_4 (5×10^{-2} M)—EDC at 30°C in air, irradiation at 436 nm. ◐: VCZ (0.25 M)—$AgClO_4$ (10^{-4} M)—benzene at 30°C in air, irradiation at 365 nm.

The excited charge transfer complex or the exciplex produced by reactions (3) to (5) will dissociate to give an ion-radical pair in a solvent cage or solvated ion radicals, as in reaction (11).

$$(DA)^{\star}, D^{\star}A \text{ or } DA^{\star} \rightarrow (D^{+}A^{\cdot-})_s \rightarrow D^{+}{}_s + A^{\cdot-}{}_s \qquad (11)$$

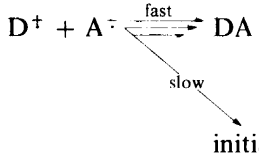
The importance of solvated ion-radicals relative to the ion-radical pair would be determined by the polarity of the solvent as well as by the stability of ion-radicals. To explain the rate data, $R_p \propto I_0^{\frac{1}{2}}$, it is required that the termination mechanism shall involve the recombination of solvated anion radicals with the growing carbonium ions as shown by reaction (12).

$$\sim\sim\sim P^{+} + A^{\cdot-} \rightarrow \text{termination} \qquad (12)$$

The term 'solvated' means the state in which ion radicals are randomly distributed so that each ion radical is no longer paired with its original partner. If recombination occurs within the solvent cage, the kinetic expression, $R_p \propto I_0^{\frac{1}{2}}$ does not hold. This interpretation is very similar to radiation induced

free cationic polymerization in which the propagating cationic species is supposed to be terminated by free electrons instead of anion radicals.

An alternative explanation is to assume the coupling of primary active species. If the reverse reaction of (11) is efficient and only a small fraction of ion radicals functions as initiator for cationic polymerization, the rate of polymerization is again proportional to $I_0^{\frac{1}{2}}$ assuming the linear termination process for propagating species. The participating components of bimol-



(13)

ecular dissipation are not necessarily ion radicals. Any independent active species which are precursors of cationic initiating species could substitute for the ion radicals in (13). For example, a triplet–triplet annihilation process might be considered instead of (13).

The four examples shown in *Figure 4* were conducted in three different solvents. Nitrobenzene (D = 34.5 at 25°C) is polar enough to facilitate free cationic propagation of VCZ as studied by neutral salt effects[12]. It is therefore reasonable to consider bimolecular dissipation of oppositely charged ionic species. In support of this, the intensity dependence of R_p of the VCZ–nitrobenzene system is affected by additives as shown in *Table 1*. In the presence

Table 1. Dependence of R_p of VCZ–nitrobenzene system on the intensity of light in the presence of methanol and tetra-*n*-butylammonium perchlorate (TBP)

TBP	CH_3OH	Intensity exponent
0	0	0.45, 0.58
10^{-2}	0	0.62
0	5×10^{-3}	0.68
6×10^{-3}	5×10^{-3}	0.70
10^{-2}	10^{-2}	0.86

Polymerization conditions: [VCZ] = 0.25 M, 30 C in air.

of methanol and/or tetra-*n*-butylammonium perchlorate (TBP), the intensity exponent of photopolymerization approaches unity indicating that any second order dissipation of active species is suppressed. Methanol would promote linear termination of the propagating species whereas TBP would provide perchlorate anion as a stable counter anion so that the bimolecular termination process would become relatively unimportant. Although confirmatory evidence in support of the bimolecular dissipation of ionic species has been obtained, it is not possible to distinguish between the two mechanisms (12) and (13). As with radical polymerization, the determination of absolute rate constants by means of non-stationary kinetics under intermittent irradiation is possible. Professor Nishijima and his co-workers are

estimating the values of k_p and k_t for the photosensitized charge transfer polymerization of the VCZ–2,4,7-trinitrofluorenone–nitrobenzene system induced by irradiation at the charge transfer band of the VCZ–TNF complex[13]. The VCZ–sodium tetrachloroaurate system will be discussed later.

Table 2. Absolute rate constants for the polymerization of *N*-vinylcarbazole

k at 30 C l. mole^{-1}. sec^{-1}.	cationic polymerization*	radical polymerization†
k_p	2×10^4	2.0×10^3
k_t	2×10^{10}	5.1×10^8
k_{trm}	1.6×10	5.3

* Photopolymerization of VCZ 2,4,7-trinitrofluorenone–nitrobenzene system.

† Photopolymerization of VCZ diacetyl benzene system.

The photopolymerization of VCZ sensitized by carbon tetrabromide in ethylene chloride ($D = 10.23$ at 25° C) is controversial. From the study of neutral salt effects, the propagating polyVCZ cation seems to be ion paired. Moreover, the formation of anion radical from carbon tetrabromide is said to conduct dissociative reduction by photochemical reaction with amine.

In non-polar benzene ($D = 2.28$ at 20° C), dissociation of active species to free ion radicals is hardly conceivable. Also from the separate experiments of neutral salt effects on cationic polymerization it was suggested that the growing species are predominantly ion-paired. Consequently, the simple pattern of ion radical recombination successfully applied to the nitrobenzene system must be treated deliberately for polymerizations in less polar solvents.

Organic donor acceptor system

(1) Cationic and radical propagation

The factors determining the modes of polymerization are reactivity of monomer, nature of solvent, effects of impurities including atmospheric oxygen, temperature and kind of initiator. The first four factors are common with conventional radical and ionic polymerizations. In the case of radical polymerization, since the growing species is 'free', the activity of the initiating species is only a matter of concern in the initiation process. However, ionic propagation is controlled by counter ions unless free ionic propagation proceeds. In the organic donor–acceptor system, the counter ion of cationic propagation is expected to be originated from the acceptor and would be bulky and loose in comparison with the conventional cationic polymerization with Lewis acids. The carbonium ion would therefore be less stabilized by the counter ion and more susceptible to effect of surroundings such as solvents and impurities unless monomers from which highly resonance stabilized carbonium ions are obtained are employed.

Photopolymerization of the VCZ–acrylonitrile (AN) system[14] irradiated by a high pressure mercury lamp in a glass ampoule ($\lambda > 300$ nm) produces a mixture of copolymer and homopolymer of VCZ. The relative contents of copolymer and homopolymer depend on the reaction conditions. In the

presence of ammonia, the formation of polyVCZ is entirely suppressed whereas the addition of DPPH enhances the relative amount of polyVCZ to copolymer. The composition curves of copolymerization are shown in *Figures 5* and *6*. Although the bulk products from photopolymerization in

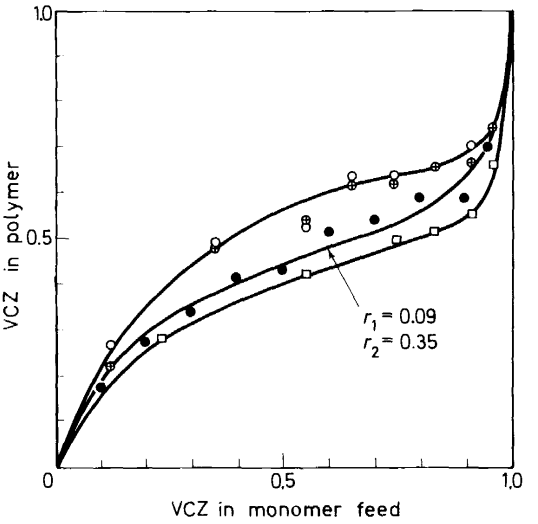


Figure 5. Photopolymerization of VCZ–AN without sensitizer; [VCZ] + [AN] = 5 m mol, benzene 2 ml. ⊕⊙: photopolymerization in air, ⊕ from i.r. spectrum, ⊙ from N content. ⊡ photopolymerization *in vacuo*, from i.r. spectrum. ● polymerization in the dark at 60°C, from i.r. spectrum; [VCZ] + [AN] = 2.5 mol/l. [AIBN] = 10^{-2} M.

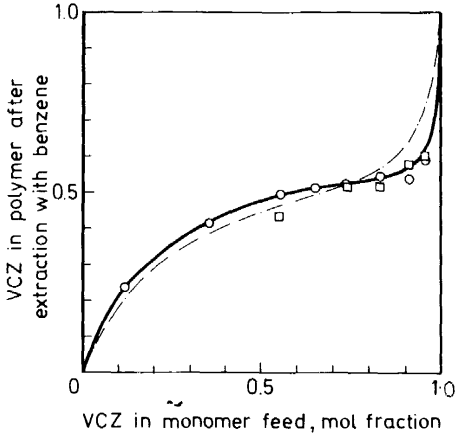


Figure 6. Composition curve for benzene-insoluble fraction produced by photopolymerization of VCZ—AN system. [VCZ] + [AN] = 5 m mol, benzene 2 ml. ⊙ photopolymerization in air at 30°C. □ photopolymerization *in vacuo* at 30°C. ··· ·–: for radical polymerization at 60°C.

air contain higher VCZ content than radical copolymers, the composition curve nearly overlaps that of radical copolymerization after removing poly-VCZ by benzene extraction. These results indicate simultaneous occurrence of radical and cationic polymerization under the influence of photoirradiation. Anionic polymerization expected to produce polyAN could not be detected. There is some evidence that cation and radical are not generated independently. If cation and radical are formed separately, inhibition of one active species will not influence the reactivity of the other. As shown in *Table 3*, the addition

Table 3. Photopolymerization of *N*-vinylcarbazole–acrylonitrile system

Atmosphere	Additive	Time, min	Yield, mg	VCZ in total polymer, mole-%	Benzene-soluble fraction, wt-%
Vacuum	None	10	490	20.8	8.3
Air	None	10	477	28.1	16.3
Vacuum	H_2O, 0.1 M	10	630	36.8	35.6
Vacuum	DPPH, 10^{-3} M	30	68	66.2	41.0
Vacuum	NH_3, 0.047 ml	5	400	19.4	0

[VCZ] = 1.0 M in AN (VCZ 582 mg + AN 2.07 g), 30 C, irradiation at 300 nm.

of ammonia inhibits the cationic process whereas the yield of radical polymerization even increases. Also, the content of polyVCZ in the total polymer produced in air is higher than that produced *in vacuo* whereas the total yield is unaffected by the change of atmosphere. The most likely explanation is that

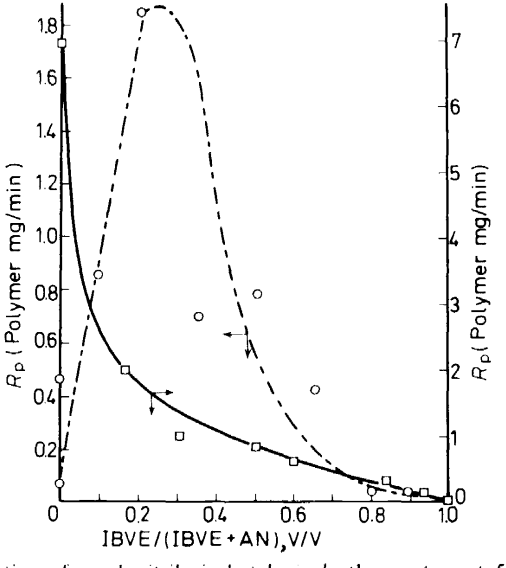


Figure 7. Polymerization of acrylonitrile–isobutyl vinyl ether system at 50 C *in vacuo*. ○: photopolymerization (absolutely dry system) AN + IBVE = 2 ml. □ catalysed polymerization in the dark, [AIBN] = 10^{-2} M, IBVE + AN = 1.5 ml.

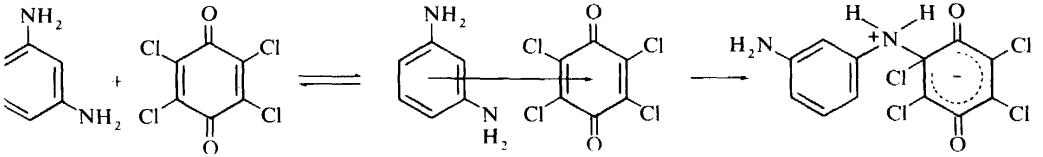
based on the assumption of ion radical initiation, in which the efficiency of ionic and radical initiations should be interrelated.

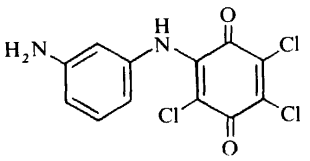
Absorption spectroscopy of the VCZ–AN system does not provide any evidence of charge transfer interaction in the ground state whereas fluorescence of VCZ is quenched by AN[15]. In addition, the absorption band of AN longer than 300 nm is negligible and the photoenergy is mostly absorbed by VCZ. This photopolymerization is therefore likely to belong to case 2.

Photopolymerization of the isobutyl vinyl ether (IBVE)–AN system[16] proceeds exclusively by a radical mechanism. The slow photopolymerization of AN when irradiated at $\lambda > 300$ nm is very much accelerated by a factor of ten if a small amount of IBVE is added as shown in *Figure 7*. On the other hand, radical polymerization of AN initiated by azobisisobutyronitrile is retarded with increasing amounts of IBVE. As a consequence, the different dependence of R_p on the monomer feed ratios as observed for thermal catalysis and photopolymerization must be interpreted in terms of the initiation process. Absorption spectroscopy of IBVE–AN in *n*-hexane provides evidence of 1:1 complex formation. Since the charge transfer band is very weak and overlaps the absorption bands of the monomers, it is not possible to irradiate the charge transfer band alone. Attempts to induce ionic polymerization (either cationic or anionic) using a rigorously dry system were unsuccessful. Probably carbonium ion from IBVE, if any, would not be stable enough to survive in the environment of a nitrile group.

(2) *Initiation by stable products of photoinduced charge transfer reactions*

From the preceding discussions, photoinduced charge transfer reactions could initiate radical and/or ionic polymerization. It is, however, difficult to accept ion radicals as initiating species. Excited states of the EDA complex might yield stable reaction products before dissociation to ion radicals. Also, ion radicals might proceed to further reaction before initiating polymerization. There are good possibilities that the reaction products are responsible for initiating polymerization. Thermal and photochemical reactions via charge transfer interaction have been reviewed by several authors[17]. A well investigated example is the amine–chloranil system[18].





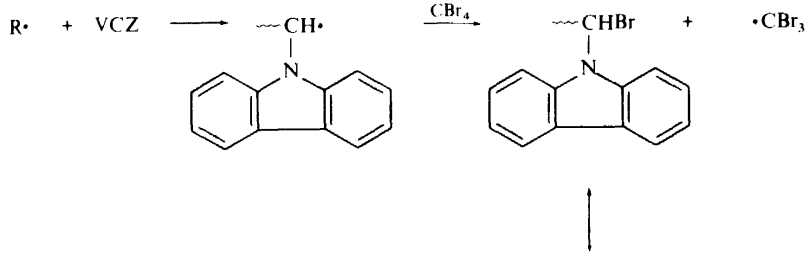
+ HCl → further reactions with amine (14)

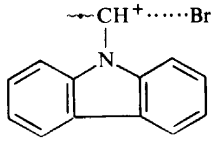
The weak carbon–halogen bond is loosened by electron transfer from the amine resulting in the elimination of hydrogen chloride. Photooxidation of amine in the presence of haloalkane is also well-studied and has been applied as an imaging system[19]. Dissociative reduction of the carbon–halogen bond seems to be a common trend of charge transfer reactions involving halogenated acceptors and the production of hydrogen halide generally in the form of an ammonium salt has been described[20].

Turning to photopolymerization systems, the reaction products such as hydrogen chloride are certainly capable of initiating polymerization if the monomer is susceptible to cationic polymerization. As will be discussed in detail in the following short communication, photopolymerization of VCZ–haloalkane systems falls in the category of 'initiation by stable reaction products via charge transfer interaction'. The VCZ forms an EDA complex with carbon tetrabromide in EDC. Irradiation at 436 nm which excites the EDA complex exclusively induces cationic polymerization of the monomer. Although it is tempting to consider ion-radical initiation, it definitely does not apply. The following findings strongly support the view that the initiating species is hydrogen bromide. (i) The initial accelerating period is observed indicating slow, stepwise processes of producing the initiating species. (ii) Polymerization continues even after cessation of irradiation. The active species are therefore long living. (iii) The role of VCZ as the donor component can be substituted by *N*-ethylcarbazole or by polyVCZ. The pre-irradiated solutions of VCZ, *N*-ethylcarbazole or polyVCZ in the presence of carbon tetrabromide are efficient initiators for the thermal polymerization of VCZ. In fact, the presence of a vinyl group is not a necessary condition for the yielding of cationic initiators. (iv) The active species thus obtained are volatile and contain bromide ion. All these findings are against direct initiation by cation radical. In particular, the last finding clearly indicates hydrogen bromide to be the actual initiating species.

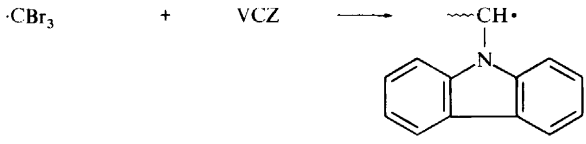
A recent study by Professor Breitenbach[21] produced an interesting suggestion on the mechanism of the photoreaction between VCZ and carbon tetrabromide. By analogy to thermal reaction of VCZ with carbon tetrabromide in the presence of azobisisobutyronitrile which leads to cationic polymerization, the following telomerization with a radical chain carrier has been proposed. The α-haloalkylcarbazole produced was claimed to be responsible for cationic initiation.

$$VCZ{\cdot}CBr_4 \xrightarrow{h\nu} R\cdot \qquad (15)$$



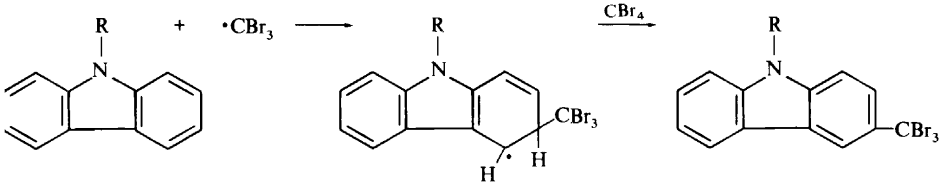


cationic initiation (16)



(17)

Although this mechanism explains the kinetic relation of $R_p \propto I_0^{\frac{1}{2}}$ well, the production of active species from alkylcarbazole and carbon tetrabromide could not be elucidated. In addition to the mechanism mentioned above, the attack of electrophilic radicals on the carbazole ring and subsequent elimination of hydrogen bromide would probably participate.



+ HBr + ·CBr_3

(18)

Metal complex systems

(1) Direct photoreactions of metal complexed monomers leading to initiation

N-Vinylimidazole[22] is a strongly coordinating monomer and metal salts dissolved in this monomer are expected to be present in the form of complexes as indicated by the absorption spectra shown in *Figure 8*. Photoirradiation of *N*-vinylimidazole–metal salts systems at $\lambda > 300$ nm brings about photopolymerization when the metal salts are oxidizing as shown in *Figure 9*. The major fraction of photoenergy is absorbed by the newly appearing absorption band. The finding that oxidizing metal salts alone are effective initiators would indicate the participation of photoredox processes in the initiation process. Possible mechanisms of initiation are (i) oxidation of anions and (ii) direct oxidation of the monomer. The former mechanism is, however, unlikely since this photoinitiation process is very selective and polymerization of styrene is not photosensitized when a styrene–acetonitrile mixture (1/1 by volume) containing 10^{-2} M of ceric ammonium nitrate or uranyl nitrate is irradiated *in vacuo* at 30°C. The pure *N*-vinylimidazole is photopolymerized under the present conditions of irradiation although the rate is much slower than in the presence of metal salts. Consequently, the possibility of a reaction of photoexcited monomer with the metal salts could not be precluded. The sequence of the intensity of absorption is $Ag^{I} < Hg^{II} < Au^{III}, Ce^{IV}, UO_2^{2+} < Cu^{II}$ which agrees well with the sequence of photosensitizing activity with the exceptions

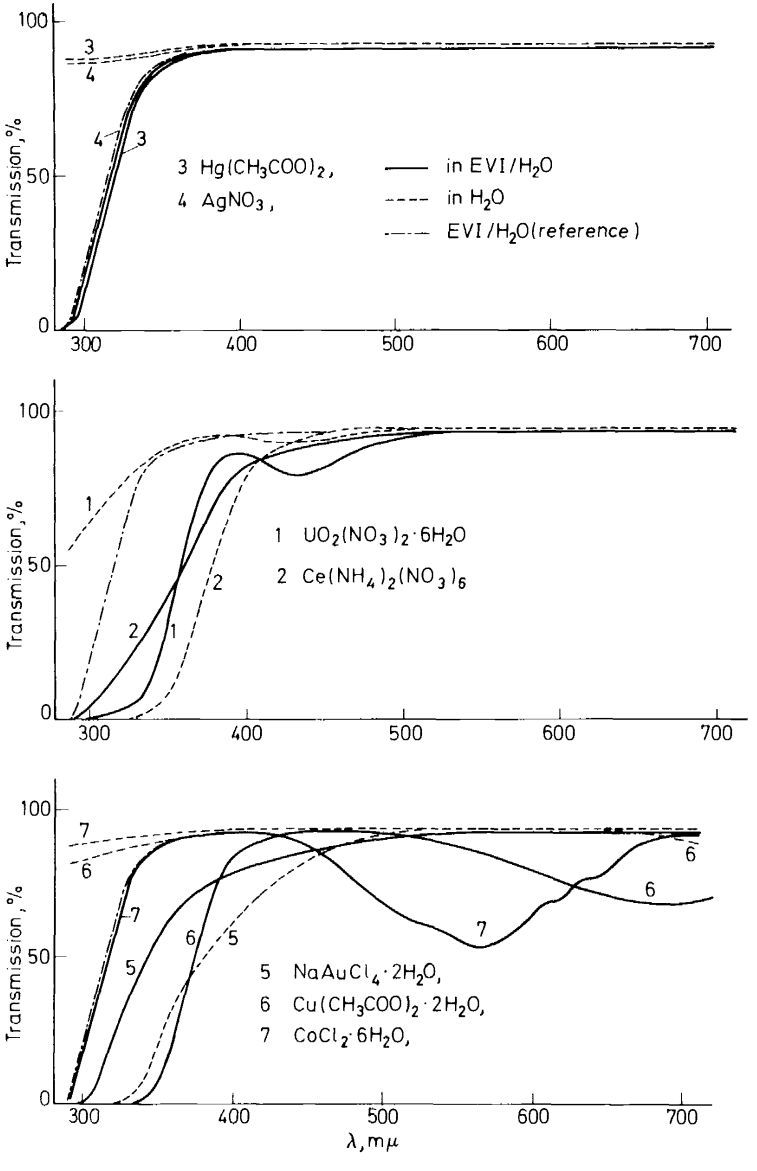


Figure 8. Absorption spectra of various metal salts (10^{-3} M) in water and EVI/water (1/1) mixture.

of Au^{III} and Cu^{II}. These two exceptions are due to efficient linear termination of propagating radicals by these metal salts. From the discussion above, the intra-complex photoredox process would be of major importance.

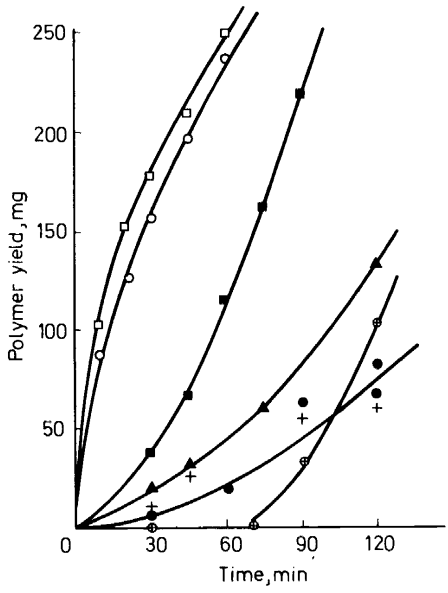


Figure 9. Photopolymerization of EVI at 30°C (EVI 1.5 ml; [metal salt] = 10^{-3} M); ● no metal salt; ▲ $AgNO_3$; ■ $Hg(CH_3COO)_2 \cdot 2H_2O$; ○ $Ce(NH_4)_2(NO_3)_6$; □ $UO_2(NO_3)_2 \cdot 6H_2O$; + $Zn(CH_3COO)_2 \cdot 2H_2O$; ⊕ $NaAuCl_4 \cdot 2H_2O$.

Photoreaction of VCZ in the presence of uranyl nitrate falls in this category as well[23]. As shown in *Figure 10*, there is weak but definite interaction between VCZ and the metal salt. Irradiation in THF or MEK in the presence of air initiates a chain reaction producing 1,2-*trans*-dicarbazyl cyclobutane probably via an ion radical intermediate[24]. The wavelength dependence of the rate of dimerization confirms the role of the complex as a photoabsorbing species since the irradiation at 405 nm is most effective. Photoinduced cationic polymerization of β-propiolactone sensitized by uranyl nitrate has also been interpreted assuming the complex between the monomer and the metal salt as a photoabsorbing species[25].

There are scattered examples suggesting the participation of metal complexed monomer in the initiation process such as in the silver nitrate–acrylonitrile system[26]. A conclusion should be drawn after establishing the dependence of rate on the wavelength of irradiation.

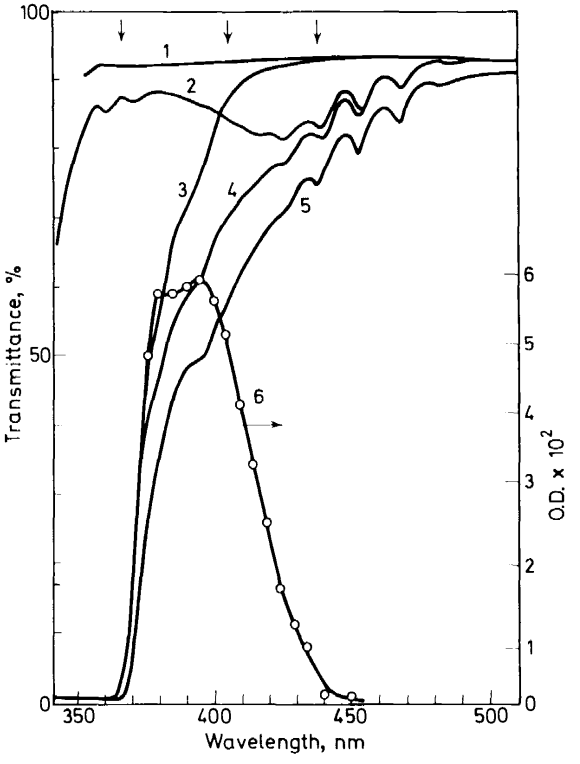


Figure 10. Electronic spectra of UO_2^{2+}–VCZ system in MEK. 1: solvent; 2: $[UO_2^{2+}] = 10^{-3}$ M; 3: [VCZ] = 0.5 M; 4: 2×10^{-3} M UO_2^{2+} + 0.5 M VCZ; 5: after irradiation of 4; 6: interaction between UO_2^{2+} and VCZ. ↓ indicates the wavelength of irradiated light.

(2) *Reactions of monomer with unstable photochemical intermediates of metal complexes*

The photoinduced polymerization of VCZ by sodium chloroaurate in nitrobenzene is one of the first examples of ionic photopolymerization of a vinyl compound[8]. Kinetic investigation of both thermal[27] and photo[28] polymerization led to the conclusion that the decomposition products of the auric salt would be responsible for initiation. Kinetic quantities obtained for thermal and photopolymerization are summarized in *Table 4*. Although the problem of photoabsorption is complicated due to various photoabsorbing species besides the auric salt for the irradiation at 436 nm, the kinetic sequence could be interpreted if the photoenergy absorbed by the auric salt induces polymerization. The unusual dependence of R_p on monomer concentration was interpreted as the result of an internal filter effect of the VCZ–nitrobenzene complex which reduces efficient photoabsorption by the auric salt. The excitation of the VCZ–nitrobenzene complex at 436 nm also induces cationic polymerization, but the rate is negligible in comparison with that of

Table 4. Comparison of kinetic aspects of dark- and photo-polymerization

	Dark	Photo (437 mμ)
Rate of polymerization		
relative rate	small	very large
dependence on [VCZ]	$R_p \propto [VCZ]$	$R_p \propto [VCZ]\exp(-k[VCZ]_0)$
dependence on $[Au^{III}]_0$	$R_p \propto [Au^{III}]_0$	$R_p \propto [Au^{III}]_0^{\frac{1}{2}}$
dependence on I_0	—	$R_p \propto I_0^{\frac{1}{2}}$
activation energy	~15 kcal/mole	~4 kcal/mole
Degree of polymerization	11×10^4*	7×10^4*
$(k_t + k_{tr}^M)/k_p$	1.0×10^{-3} (1.16×10^{-3})†	0.8×10^{-3}
$k_{tr}^Y[Y]/k_p$	1.5×10^{-4} (10^{-4})†	5.0×10^{-4}
$k_{tr}^{H_2O}/k_p$	3×10^{-3}	43×10^{-3}
dependence on $[Au^{III}]_0$	none	none
dependence on I_0	—	none

* [VCZ] = 0.25 M, $[Au^{III}]_0 = 5 \times 10^{-5}$ M, conversion: 60%. Polymerization at 30°C.
† Catalyst is $(NO_2)_4C$, solvent: nitrobenzene, 30°C. (Pác and Plesch).

polymerization sensitized by the auric salt. With the aid of information from the thermal polymerization, the following reaction path has been proposed.

$$\begin{array}{ccccccc} & & & & Au^{III}/M\ \text{complex} & \xrightarrow{h\nu} & \text{polymerization?} \\ & & & & \uparrow\downarrow & & \\ M^{\dagger} & \xleftarrow{M} & Au^{II} & \xleftarrow{\text{reduction}} & Au^{III} & \xrightarrow{h\nu} [\text{intermediate}] & \xrightarrow{M} \text{polymerization} \\ & & \text{thermal} & \longleftarrow & \multicolumn{2}{c}{\longrightarrow \text{photochemical}} & \end{array} \qquad (19)$$

It is suggestive that the thermal polymerization is accelerated by the addition of reducing agents such as ferrocene, metallic mercury or ascorbic acid. The sequence of oxidation potentials shown in *Table 5* does not contradict the concept that the auric salt is reduced by these reducing agents to unstable Au^{II} species which are stronger oxidants than the auric salt and capable of oxidizing VCZ to ion radical.

To study the initiation process, the difficulty of elucidating photoabsorption by multiple species should be avoided. While studying sodium chloroaurate

Table 5. Additive effects on R_p of the VCZ–$NaAuCl_4 \cdot 2H_2O$–nitrobenzene system and standard redox potentials of relevant compounds

Redox pair	E^0, volt	Polymerization* [Additive]	time, min	Conv. %
$AuCl_4^-/Au^{II}Cl$	−0.5 to −0.96			
$Au^{II}Cl/AuCl_2^-$	−1.4			
VCZ$^+$/VCZ	−1.3			
Ferrocene$^+$/ferrocene	+0.56	5×10^{-3} M	30	100
Hg_2^{2+}/Hg^I	−0.792	insoluble	120	100
Ascorbic acid	+0.1 to +0.3	insoluble	120	100
	Reference	without additive	120	67.5 ± 5

* [VCZ] = 0.25 M, $[NaAuCl_4 \cdot 2H_2O] = 1.0 \times 10^{-4}$ M in nitrobenzene at 30°C.

which is soluble only in nitrobenzene among the solvents usable for cationic polymerization, synthesis of tetra-*n*-butylammonium tetrachloroaurate and tetrabromoaurate and interpretation of their electronic spectra were reported[29]. These tetraalkylammonium salts are soluble in common organic

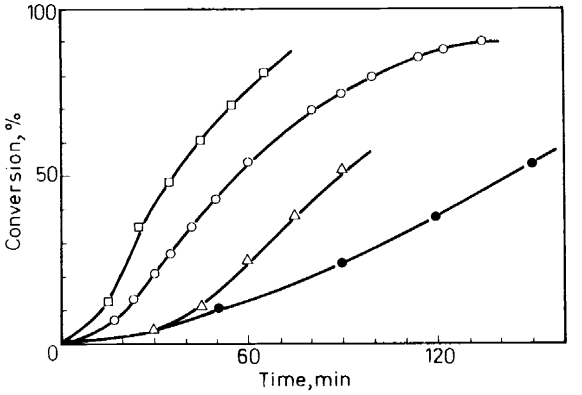


Figure 11. Photopolymerizations of VCZ by Au(III). [VCZ] = 0.25 M; irradiation at 436 nm, at 30 C: □ in EDC; ○ in acetophenone, $[AuBr_4^-] = 5 \times 10^{-5}$ M; △ in THF, $[AuBr_4^-] = 2.5 \times 10^{-4}$ M; ● in nitrobenzene. $[AuCl_4^-] = 1.6 \times 10^{-4}$ M.

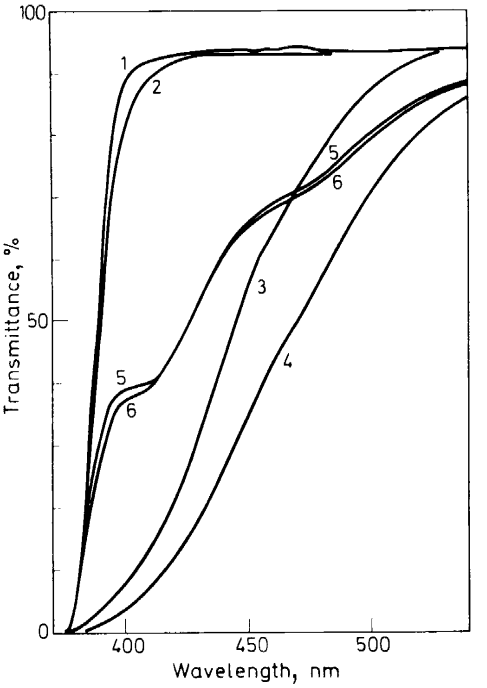


Figure 12. Electronic spectra of polymerization systems, solvent: acetophenone. 1: solvent; 2: VCZ; 3: $[AuCl_4^-] = 2 \times 10^{-3}$ M; 4: $[AuCl_4^-] = 2 \times 10^{-3}$ M, [VCZ] = 0.25 M; 5: $[AuBr_4^-] = 5 \times 10^{-5}$ M; 6: $[AuBr_4^-] = 5 \times 10^{-5}$ M, [VCZ] = 0.25 M.

solvents and have the advantage of simplifying the problem of photoabsorption. Examples of time/conversion curves are shown in *Figure 11*[30]. The mechanism of propagation is always cationic. The absorption spectra of relevant species are shown in *Figure 12*. There is no interaction between $AuBr_4^-$ and VCZ whereas considerable changes in the spectra of $AuCl_4^-$ are observed in the presence of VCZ. Consequently, the irradiation at 436 nm excites $AuBr_4^-$ exclusively whereas the primary act in the case of $AuCl_4^-$ is to excite either $AuCl_4^-$ or the complex of $AuCl_4^-$–VCZ. The absorption of auric species at 436 nm was assigned by Gray[29] on the basis of molecular orbital calculations as the CT transition corresponding to CTTM type (i.e. $X^- - Au^{3+}$). Now, the next step is to know the role of the monomer in the course of producing initiating species. The quantum yield of decomposition of $AuBr_4^-$ in acetophenone at 30°C is constant at 0.2 independent of the presence of VCZ or *N*-ethylcarbazole as determined by equation (20), indicating that the monomer reacts with the decomposition products of $AuBr_4^-$ or with the unstable

$$-d[Au^{III}]/dt = \Phi I_0(1 - e^{-\varepsilon[Au^{III}]}) \qquad (20)$$

intermediates but not with $AuBr_4^-$ itself or its excited states which are in equilibrium with the ground state. The results of polymerization by intermittent irradiation indicate the presence of long lived active species. Such observations resemble very much those of the VCZ–carbon tetrabromide system. The pre-irradiation experiments as shown in *Table 6* confirm the view that the photodecomposition of $AuBr_4^-$ alone does not produce active initiators.

Table 6. Pre-irradiation effects of AuX_4^- systems

Exp. run	System	Pre-irradiation $[Au^{III}]$(M)	[CZ](M)	[VCZ](M)	Post-polymerization $[Au^{III}]_{pre.}$(M)	polymer yield (mg)
I	$AuCl_4^-$	4×10^{-3}	0	0.25	2×10^{-3}	17
				0.25	2×10^{-3}	13*
	$AuBr_4^-$	10^{-4}	0	0.25	5×10^{-5}	11
				0.25	5×10^{-5}	8*
II	$AuBr_4^-$	5×10^{-5}	0	0.29	2.15×10^{-5}	8
	$AuBr_4^-$/ECZ	5×10^{-5}	0.25	0.29	2.15×10^{-5}	11
	$AuBr_4^-$/VCZ	5×10^{-5}	0.25	0.29	2.15×10^{-5}	45
III	$AuBr_4^-$/ECZ	2.5×10^{-4}	0.25	0.25	5×10^{-5}	52
	$AuBr_4^-$/VCZ	2.5×10^{-4}	0.25	0.25	5×10^{-5}	64
				0.25	5×10^{-5}	12*

Pre-irradiation for 30 min, at 436 nm, at 30°C.
Post-polymerization in the dark, for 90 min, at 30°C.
* Dark polymerization by Au^{III} not pre-irradiated.

The total initiation process will be expressed as follows.

$$AuBr_4^- \xrightleftharpoons{h\nu} [AuBr_4^-]^{\star} \rightarrow \underbrace{Au^{II}Br_3^- + Br\cdot \rightarrow \text{further decomposition}}_{\text{VCZ}} \qquad (21)$$

$\Phi = 0.2$

cationic polymerization

The reaction mechanism of $AuCl_4^-$ would be very much the same by analogy.

(3) Role of metal complexes reacting with excited monomers (Case 6)

Reactions between photoexcited organic molecules and metal complexes are totally unsurveyed and therefore the most exciting field for future research. Cationic photopolymerization of VCZ in aromatic hydrocarbons in the

Table 7. Photopolymerization of VCZ sensitized by Ag^I salts. Irradiation at 365 nm at 30°C

Ag^I	$10^4[Ag^I]$ (M)	[VCZ] (M)	Solvent	$R_p \propto I_0^x[Ag^I]_0^y$ x	y	UV spectra of VCZ
$AgClO_4$	0.3–2	0.25	benzene	$\frac{1}{2}$	1	blue shift
$AgClO_4$	0.5–5	0.5	toluene	$\frac{1}{2}$	1	no shift
$AgClO_4$	1	0.5	*p*-xylene	—	—	no shift
$AgClO_4$	0.5–2	0.25	nitrobenzene	$\frac{1}{2}$*	0*	—
$AgBF_4$	1–5	0.5	benzene	$\frac{1}{2}$	1	no shift

* irradiation both at 365 nm and 436 nm.

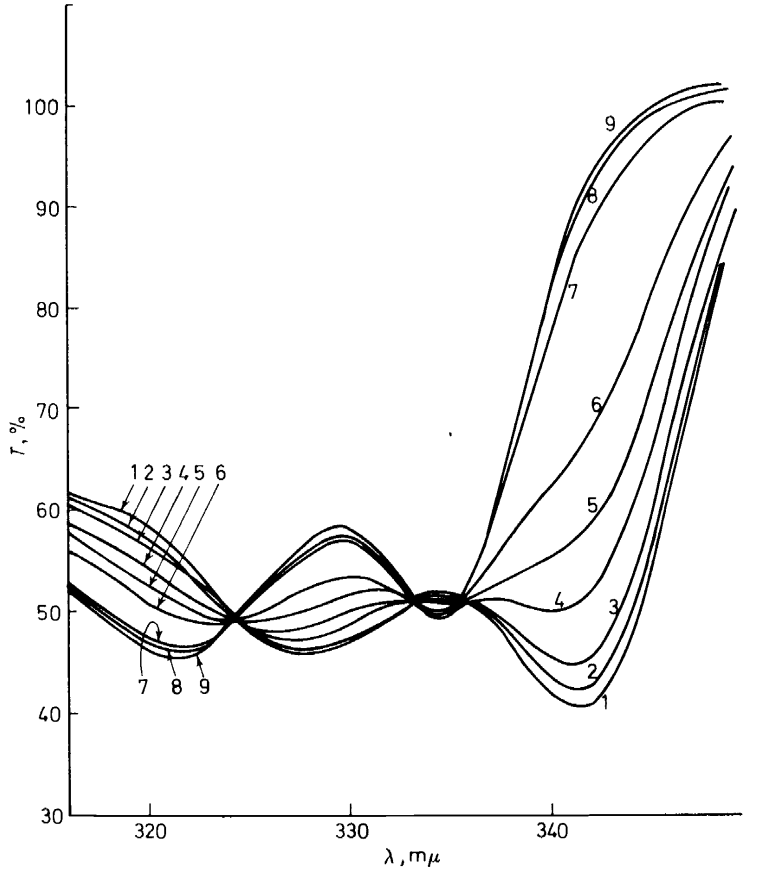


Figure 13. Absorption spectra of VCZ (10^{-4} M) in the presence of silver perchlorate. 1: VCZ alone; $[Ag^I]$M; 2: 4×10^{-7}; 3: 6×10^{-7}; 4: 8×10^{-7}; 5: 10^{-6}; 6: 1.5×10^{-6}; 7: 2×10^{-5}; 8: 4×10^{-6}; 9: 6×10^{-5}.

presence of silver salts belongs to this class of reaction. The kinetic sequence of photopolymerization of the VCZ–$AgClO_4$–benzene system[30] is summarized in *Table 7*. The rate of thermal polymerization is less than one eighth of photopolymerization under the present conditions of photoirradiation. Since reference experiments using tetra-*n*-butylammonium perchlorate proved the complete inertness of the perchlorate anion as photosensitizer, the active part of silver perchlorate must be Ag^I but not the perchlorate anion. Also, the activity of silver tetrafluoroborate as sensitizer is very much the same as silver perchlorate as shown in *Table 7*, indicating that the role of the anion is minor.

The problem of the photoabsorbing species and the initiation mechanism are again not straightforward. Under the polymerization condition ([VCZ] = 0.25 M), the change in absorption spectra is not observed by the addition of silver perchlorate up to 2×10^{-4} M. However, in absorption spectroscopy in the short wavelength region under very dilute conditions, complex formation between VCZ and silver perchlorate is observed as shown in *Figure 13*. This is a specific phenomenon for the combination of VCZ–silver perchlorate –benzene. When other silver salts and/or other solvents are used, complex formation is not detected. Fluorescence spectra of VCZ are quenched by silver perchlorate with the quenching constant of $\sim 10^2\,M^{-1}$ in benzene. The fact that photopolymerization of VCZ proceeds equally in the systems $AgClO_4$–benzene, $AgClO_4$–toluene and $AgBF_4$–benzene regardless of complex formation strongly suggests the efficient photoabsorbing species to be VCZ itself. The silver salts are transparent to the irradiation at 365 nm and could not be energy absorbing species.

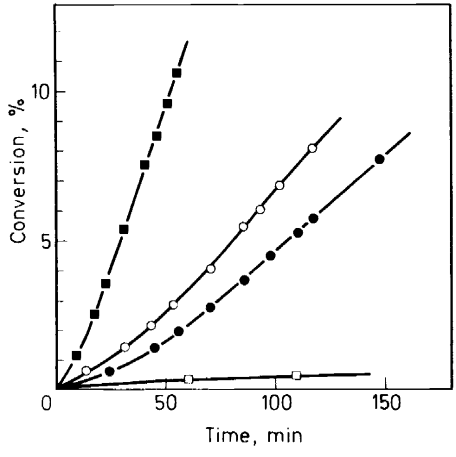


Figure 14. Time/conversion curves for photopolymerization of VCZ in various solvents at 30°C sensitized by $AgClO_4$. $[AgClO_4] = 1 \times 10^{-4}$ M. ■ [VCZ] = 0.225 M in nitrobenzene; ○: [VCZ] = 0.25 M in benzene; ●: [VCZ] = 0.25 M in toluene; □: [VCZ] = 0.25 M in *p*-xylene.

It is very tempting to consider that the interactions of excited VCZ with silver salts as evidenced by fluorescence spectroscopy lead to the initiation of polymerization. Peculiar solvent effects upon R_p shown in *Figure 14*, however, introduce a more sophisticated view of the photochemical primary

act. The sequence of R_p with respect to solvents is nitrobenzene > benzene > toluene > *p*-xylene ≈ 0. With the exception of nitrobenzene, the optical density of the polymerization solution is identical for all solvent systems. Consequently, the marked differences in R_p must be attributed either to the efficiency of initiation by the excited VCZ or to the propagation and/or termination processes. The latter possibility is precluded since the cationic polymerization of styrene derivatives in benzene, toluene or *p*-xylene proceeds with almost identical rate[31] and in addition, the slow dark cationic polymerization of VCZ by silver perchlorate is not affected by the kind of solvent. The mechanism of photopolymerization which does not contradict all known mechanistic kinetic findings may be expressed as follows.

$$\mathrm{VCZ} \xrightleftharpoons{h\nu} \mathrm{VCZ}^{\star} \tag{22}$$

$$\mathrm{VCZ}^{\star} + \mathrm{Bz} \rightleftharpoons \mathrm{VCZ}^{+\cdot} + \mathrm{Bz}^{-\cdot} \xrightarrow{\mathrm{AgClO_4}} \mathrm{P}^{+} \tag{23}$$

$$\mathrm{P}_n^{+} + \mathrm{VCZ} \rightarrow \mathrm{P}_{n+1}^{+} \tag{24}$$

$$\mathrm{P}_n^{+} \rightarrow \mathrm{P}_n \tag{25}$$

Since the donor character of VCZ would be enhanced by photoexcitation, an electron transfer process such as (23) would be possible. Electron transfer from excited amine to aromatic hydrocarbon has been demonstrated in the *N*,*N*-diethylaniline and biphenyl system[34]. The sequence of R_p in these four solvents agrees with the decreasing order of the acceptor strength of solvents. The expected order of acceptor strength is: nitrobenzene > benzene > toluene > *p*-xylene. This order is supported by the following facts. (i) The ease of producing anion radical when alkyl substituted benzenes react with metallic potassium is benzene, toluene ≫ *p*-xylene[32]. (ii) The electron affinity of quinone decreases with increasing number of methyl groups introduced into the benzene ring[33]. More direct support for this mechanism of initiation is obtained from the VCZ–silver perchlorate–nitrobenzene system irradiated at 436 nm. Under this condition of irradiation, the CT band of the VCZ–nitrobenzene complex is excited and cationic polymerization is brought about even in the absence of the silver salt. The addition of silver perchlorate to this system enhances the rate of polymerization considerably indicating that silver perchlorate participates in the production of initiating species via electron transfer between VCZ and the solvent.

Two possible roles of silver perchlorate are envisaged as follows.

$$\mathrm{Bz}^{-\cdot} + \mathrm{Ag}^{+} + \mathrm{VCZ}^{+\cdot} + \mathrm{ClO_4^{-}} \rightarrow \mathrm{Bz} + \mathrm{Ag}^{0} + \mathrm{VCZ}^{+\cdot} \ldots \mathrm{ClO_4^{-}}$$

$$\downarrow$$

cationic initiation (26)

$$\mathrm{VCZ}^{+\cdot} + \mathrm{AgClO_4} \longrightarrow \mathrm{H_2C{-}CH^{+}} \longrightarrow \text{cationic initiation} \tag{27}$$

(Ag$^{\mathrm{I}}$ coordinated to the nitrogen of the carbazole ring)

The former is the oxidation of the benzene anion radical to prevent recombination of the cation radical with the anion radical. The latter is the stabilization of the cation radical to facilitate cationic initiation.

CONCLUDING REMARKS

Six possible mechanisms of photoinitiation via charge transfer interactions have been discussed based mostly on recent work from my research group. Although these six cases will cover all types of photoinduced charge transfer processes, the allocation of a certain reaction system to one of these six cases is in general laborious.

This field of research is on the border between synthetic chemistry and very basic physical chemistry. New types of reactions explored by ambitious synthetic chemists should be carefully analysed by physical and theoretical chemists to construct the theoretical framework. Good collaboration between synthetic chemists interested in exploratory research and basic physical chemists will be most important to promote research in this new field of photochemistry.

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