# Photoreactions of N-Vinylcarbazole Induced by Metal Salts. IV. Kinetic Studies of the Thermal and Photosensitized Cationic Polymerization Induced by Silver(I) Perchlorate in Benzene

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ABSTRACT: Thermal and photosensitized cationic polymerizations of N-vinyl-carbazole (VCZ) induced by silver (I) perchlorate were investigated in benzene at 30°C. Cationic propagation was confirmed by means of the additive effect of inhibitors. The following kinetic expressions for the polymerization rate ($R_p$) were obtained:

For thermal polymerization: $R_p \oslash [AgClO_4]_0^{0.47}$

For photopolymerization: $R_p \oslash I_0^{0.65}[AgClO_4]_0^{1.0}$.

In the thermal polymerization, $R_p$ saturated with an increase in monomer concentration. The dependence of $R_p$ of photopolymerization on monomer concentration was examined in two systems: at constant optical length and at constant optical density.

$R_p \oslash [VCZ]_0^{0.53}$; thickness of the cell=1 cm.

$R_p \oslash [VCZ]_0^{1.62}$; (thickness of the cell) $\times [VCZ]_0 = 0.25\,M$ cm.

Various kinetic quantities determining the degree of polymerization were calculated from the viscosity-average molecular weights of the polymers. These values are almost identical for both thermal and photosensitized systems. This suggests that propagation in these systems proceeds *via* the carbonium ion ion-paired with the counter anion of $ClO_4^-$.

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

In the preceding article[1], kinetic and mechanistic features of the photosensitized cationic polymerization of N-vinylcarbazole (VCZ) initiated by $YAuX_4$(Y=Na, $(n\text{-}C_4H_9)_4N$; X=Cl, Br) in various aprotic solvents were investigated. As the most probable mechanism of initiation, it was proposed that $YAuX_4$ undergoes photoredox decomposition, and thus its transient species (possibly a halogen atom) reacts with VCZ to produce the initiation species (possibly hydrogen halide). However,

gold(III) complexes change valence in a complicated manner, *i.e.*, a stepwise reduction to zero valent state, so that it seems to be rather difficult to investigate its catalytic actions.

Besides gold(III) species, silver(I) perchlorate in the same $I_b$ group has been reported to catalyse the thermal polymerization of styrene and methyl methacrylate in solution by Smets,[2] and of VCZ in bulk by Solomon.[3] Under photochemical conditions silver(I) nitrate has been known as a sensitizer for photopolymerization of acrylonitrile and methyl methacrylate in solution[4] and also photopolymerization and/or photocyclodimerization of VCZ depending upon solvent and atmosphere under irradiation at 365 nm.[5]

In the present investigation, benzene was used as a solvent in which the polymer formed *via* cationic propagation and was indifferent to atmosphere. Kinetic studies of the rate of polymeri-

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zation were carried out in both thermal and photosensitized polymerizations. Kinetic results were analyzed on the basis of the kinetic theory of photoreaction by Mauser.[6] A Special procedure for keeping the amount of energy absorption constant regardless of monomer concentration was applied by changing the thickness of the reaction vessel. Furthermore, various kinetic quantities determining the degree of polymerization were calculated from the viscosity-average molecular weights of the polymers. Finally, the chain-transfer constants for methanol were compared with that obtained previously in the thermal polymerization initiated by perchloric acid in benzene.[7]

## EXPERIMENTAL

N-vinylcarbazole (Koch-light Laboratories) was recrystallized from hot n-hexane and dried in vacuo; mp 64.0°C. Anhydrous silver perchlorate free from perchloric acid was prepared by heating the commercial reagent under a pressure of less than $10^{-5}$ Torr at 120°C; the dried perchlorate was stored in ampoules. Benzene was dried over sodium sulfate after washing with concentrated sulfuric acid and dilute aqueous sodium hydroxide, then distilled twice before use. All other reagents were as described previously.[1]

The irradiation apparatus and polymerization procedures were the same as described previously[1]. Monochromatic light of 365 nm was selected by filtering the emission from a 300-W high-pressure Hg lamp with a combination of glass filters Toshiba UV-DIA and UV-35. The light intensity was measured by means of a ferric oxalate actinometer.[8] The incident intensity of light of 365 nm was of the order of $7 \times 10^{-8}$ einstein/cm² min. The intensity of light was controlled by inserting wire nets into the optical path.

The reaction rate was measured by dilatometry as well as by weighing the polymer after it was precipitated in an excess of methanol. A cylindrical quartz cell with parallel windows (diameter 44 mm, optical length 5—30 mm) connected to a capillary tube was used as a dilatometer. All polymerizations were carried out at 30± 0.02°C. No special care was taken to eliminate dissolved air or traces of water from the reaction mixture.

The molecular weight of the polymer, which was prepared in the polymerization stopped at less than 10-% conversion, was determined by a viscosity measurement at 25°C in benzene.[9]

Absorption spectra were measured by a Shimadzu spectrophotometer MPS-50.

## RESULTS AND DISCUSSION

### Polymerization

Both polymerizations induced by silver perchlorate in benzene under the standard conditions: $[VCZ]_0 = 0.25\ M$, $[AgClO_4] = 10^{-4}\ M$, the thermal at 30°C and the photosensitized under irradiation at 365 nm, are shown in Figure 1. The thermal
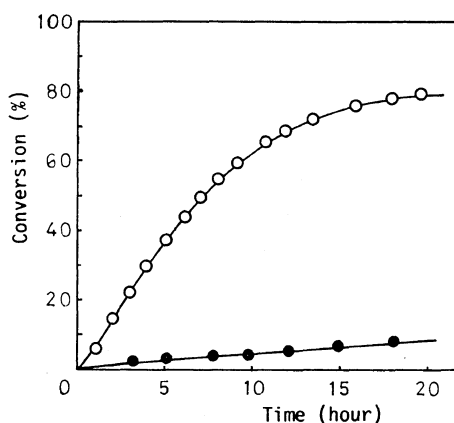


**Figure 1.** Thermal and photopolymerization of VCZ catalyzed by AgClO₄ in benzene: $[VCZ]_0$, $0.25\ M$; $[Ag^I]_0$, $1 \times 10^{-4}\ M$; 30°C: —●—, thermal polymerization; —○—, photopolymerization; $\lambda$, 365 nm.

polymerization can be neglected in kinetic studies of the photopolymerization, since the rate of the former was less than one eighth of the latter. Moreover, then noncatalytic photopolymerization was negligibly slow; that is the polymer yield was 0.3% after irradiation for 120 min under the standard conditions. The photopolymerization induced by silver perchlorate (Ag$^I$) proceeded up to complete conversion after a short acceleration period in the early stage of the reaction.

Additive effects for both thermal and photopolymerization were examined as tabulated in Table I. Polymerizations were retarded by addition of water, and completely inhibited in

**Table I.** Effects of various additives

| System | Additive | Time, min | Conversion, % |
|---|---|---|---|
| Photo | None | 100 | $15 \pm 5$ |
| $[VCZ]_0 = 0.25 M$ | water, $5 \times 10^{-3} M$ | 150 | 4.3 |
| $[Ag^I]_0 = 1 \times 10^{-4} M$ | ammonia, $6 \times 10^{-4} M$ | 90 | 0 |
| Thermal | None | 420 | $4 \pm 1$ |
| $[VCZ]_0 = 1 M$ | Water, $5 \times 10^{-3} M$ | 390 | 2.3 |
| $[Ag^I]_0 = 2 \times 10^{-4} M$ | Ammonia, $2 \times 10^{-4} M$ | 360 | 0 |
| | DPPH, $2.5 \times 10^{-4} M$ | 360 | 4 |

the presence of aqueous ammonia. Meanwhile, when oxygen was saturated in the reaction mixture, the rate of polymerization was reduced to a certain extent. Although DPPH as a radical scavenger could not be used in the photopolymerization because of its inner filtration effect on light absorption, there was no effect on the thermal polymerization. From these facts, there seems to be little doubt that the polymerization proceeds *via* a cationic mechanism in both systems.

*The Rate of Polymerization ($R_p$)*
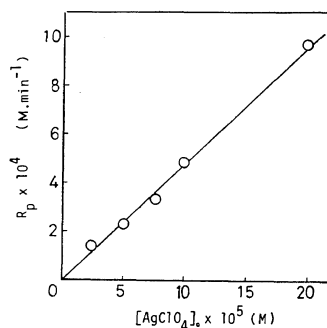
Figure 2 shows the dependence of $R_p$, as
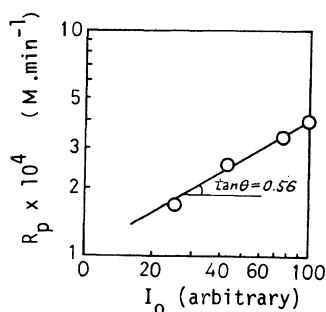


**Figure 2.** Dependence of $R_p$ on the incident intensity of light: $[VCZ]_0$, $0.25 M$; $[Ag^I]_0$, $1 \times 10^{-4} M$; 30°C; $\lambda$, 365 nm.

calculated from the pseudo-stationary slope of the time-conversion curve, on the incident intensity of light ($I_0$). $R_p$ is nearly proportional to the square root of $I_0$. The apparently unusual kinetic expression for a cationic polymerization has been found to be a rather general kinetic feature in the photocationic polymerization of VCZ in the presence of both organic[10-12] and inorganic acceptors.[10] As described previously, this may
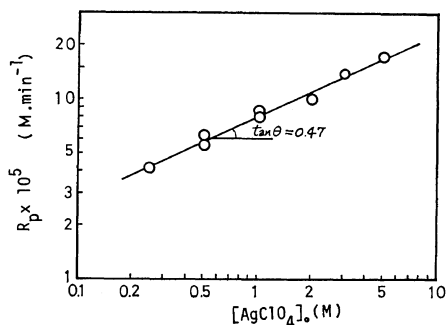


**Figure 3.** Dependence of $R_p$ on the initial concentration of AgClO$_4$: $[VCZ]_0$, $0.25 M$; thermal polymerization; 30°C.



**Figure 4.** Dependence of $R_p$ on the initial concentration of AgClO$_4$: $[VCZ]_0$, $0.25 M$; $\lambda$, 365 nm; 30°C.

be interpreted in terms of either bimolecular termination of propagating species or bimolecular dissipation of initiating species.[10]

The dependences of $R_p$ on the initial concentration of silver perchlorate in the thermal and photopolymerization are shown in Figure 3 and Figure 4, respectively. When the concentration of silver perchlorate went up to over $10^{-3} M$, the solution suddenly became turbid. This turbidity was attributed to the formation of strong complexes between VCZ and AgClO$_4$ (exclusively in benzene), which was confirmed by means of absorption and emission spectroscopies.[3] The extraordinary composition of about 1 : 50 of AgClO$_4$: VCZ was determined for this complex by the mole ratio method, as shown in Figure 5. The isolation of this complex, however, was unsuccessful because of its polymerizability in solid state. Values of $R_p$ of the thermal and photopolymerization are found to be pro-
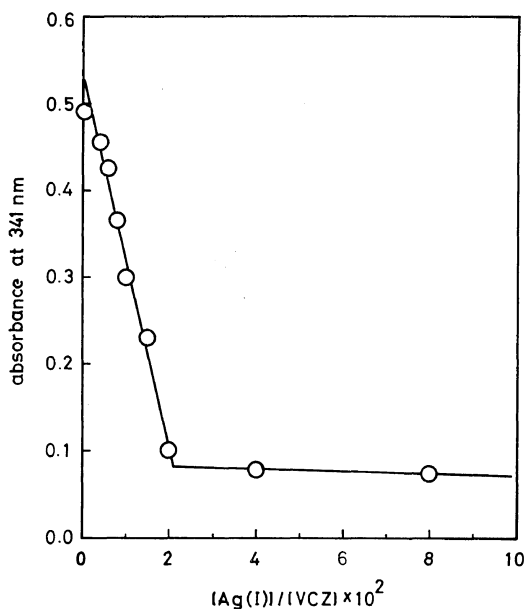
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**Figure 5.** Mole ratio method applied to the VCZ—AgClO$_4$—benzene system: [VCZ]$_0$, $1.0 \times 10^{-4} M$; [Ag$^I$]$_0$, variable.
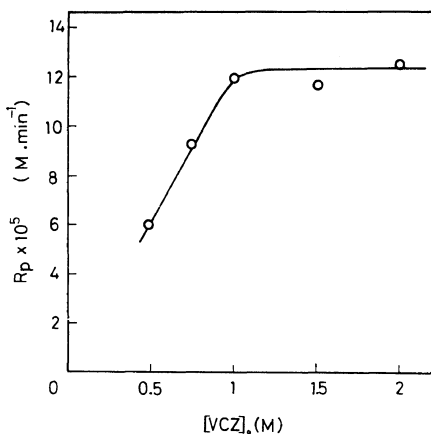


**Figure 6.** Dependence of $R_p$ on the initial concentration of monomer: [Ag$^I$]$_0$, $1 \times 10^{-4} M$; thermal polymerization, 30°C.

portional to the square root and the first power of the concentration of AgClO$_4$, respectively, suggesting different roles of this salt in these two systems.

An abnormal dependence of $R_p$ on the initial monomer concentration was obtained in the thermal polymerization as shown in Figure 6, $R_p$ being constant above 1-$M$ VCZ. Similar

results have been reported by Plesch in the thermal polymerization of VCZ initiated by mercury(II) chloride in chlorobenzene.[14] He explained this saturation effect of $R_p$ with increase in impurities contained in the monomer. An alternate explanation would be possible assuming a saturation of complex formation between VCZ and AgClO$_4$ at above 1 $M$ of VCZ. If the VCZ—AgClO$_4$ complex is the initiating species, this kinetic sequence is understandable, since monomer termination is a likely chain-breaking process. Although the shape of the curve drawn in Figure 5 strongly indicated the high stability of the complex, the stability constant could not be determined and consequently further discussion on the kinetics of thermal polymerization is not possible. The complex will not, however, participate in photopolymerization, since the irradiation at 365 nm is not at all absorbed by the complex.

Examination on the dependence of $R_p$ on the monomer concentration in the photopolymerization should be carried out carefully, since the absorbed photoenergy at 365 nm is a complicated function of monomer concentration which will be described later. Excluding the short acceleration period, the time-conversion curve can be fitted to a linear plot up to 70-% conversion, as demonstrated in Figure 7.
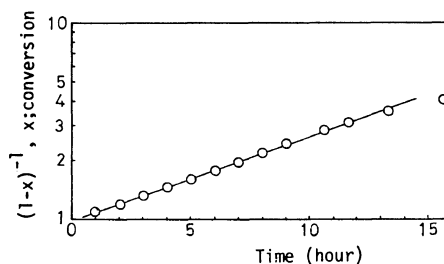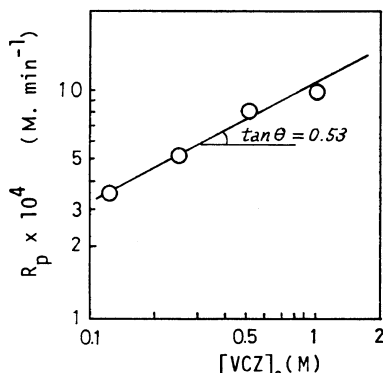


**Figure 7.** Linear plot of time-conversion relation in photopolymerization; from Figure 1.
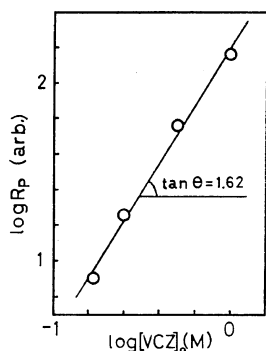
Dependence of $R_p$ on the initial monomer concentration was examined using cells of 1-cm optical length, as shown in Figure 8; the following result was obtained:

$$R_p \infty [VCZ]_0^{0.53} \qquad (1)$$

In this case, however, the absorbance of the reaction mixture varies with monomer concentration

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**Figure 8.** Dependence of $R_p$ on the initial concentration of monomer: $[Ag^I]_0$, $1 \times 10^{-4} M$; thickness of the cell, 1 cm; $\lambda$, 365 nm; 30°C.



**Figure 9.** Dependence of $R_p$ on the initial concentration of monomer: $[Ag^I]_0$, $1 \times 10^{-4} M$; [thickness of the cell)×[VCZ]_0, $0.25 M$ cm; $\lambda$, 365 nm; 30°C.

and consequently the energy uptake by the reaction system depends on the monomer concentration. To avoid this complexity, another experiment was carried out using cells of various thicknesses (0.5—3 cm) under constant absorbance, or keeping $[VCZ]_0 \times$(thickness of the cell)=0.25 $M$ cm. The energy uptake is therefore independent of monomer concentration. As shown in Figure 9, the following relation was obtained in this case:

$$R_p \infty [VCZ]_0^{1.62} \qquad (2)$$

This procedure seems to be the best method for the studies on the kinetic effects of photoabsorption in moderately high absorption systems.

These kinetic dependences of the initial monomer concentration may be interpreted on the basis of the kinetic theory of photoreaction by Mauser[6]

in the following manner. Assuming the bimolecular deactivation of chain-carriers and effective light absorption by monomer, the rate of polymerization at a distance $x$ from a front face of the cell, symbolized $(R_p)_x$, is expressed by the following expression:

$$(R_p)_x \infty (I_{abs}^M)_x^{1/2}[VCZ] \qquad (3)$$

where $(I_{abs}^M)_x$ is the local absorption by monomer in a unit volume at $x$, which can be expressed with the extinction coefficient of monomer $(\varepsilon_M)$ and the light intensity at $x$ $(I_x)$ in accordance with the Lambert—Beer's law as follows:

$$(I_{abs}^M)_x = \varepsilon_M[M]I_x = \varepsilon_M[M]I_0 \exp\left(-\int_0^x \varepsilon_M[M]dx\right) \qquad (4)$$

The average rate $(\bar{R}_p)$ observed experimentally

$$\bar{R}_p = \frac{1}{L}\int_0^L (R_p)_x dx \qquad (5)$$

where $L$ denotes the thickness of the cell. Substituting into eq 5 the results of eq 3 and 4 then yields the following kinetic expression:

$$\bar{R}_p \infty \frac{(\varepsilon_M[VCZ])^{1/2}}{\varepsilon_M[VCZ]L}\left\{1-\exp\left(-\frac{\varepsilon_M[VCZ]L}{2}\right)\right\}[VCZ] \qquad (6)$$

From this equation the following relations can be derived:

at constant absorbance: $\bar{R}_p \infty [VCZ]^{3/2}$ (7)

at large absorbance and constant $L$:
$$\bar{R}_p \infty [VCZ]^{1/2} \qquad (8)$$

These expressions agree with the experimental results very well.

An interpretation of these kinetics based on the mechanistic studies of the photopolymerization will be made in a subsequent article.

*The Degree of Polymerization*

The viscosity-average molecular weights of the polymers were in the range of 50000—150000 in both the thermal and photosensitized polymerizations. The dependences of molecular weight on the initial initiator concentration as well as on the incident intensity of light were very slight, as shown in Figure 10. However, the degree of polymerization $(\bar{P})$ increased with the initial
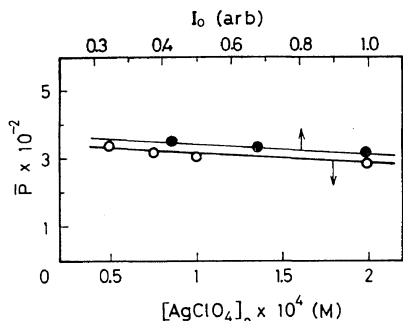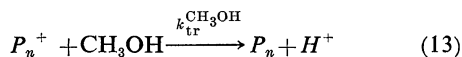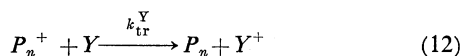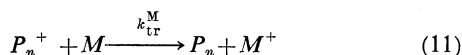
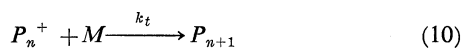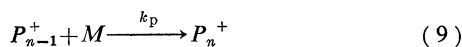**Figure 10.** Dependences of $\bar{P}$ on $[AgClO_4]_0$ and $I_0$: $[VCZ]_0$, $0.25\,M$; $[Ag^I]_0$, $1 \times 10^{-4}\,M$; $\lambda$, 365 nm; 30°C.
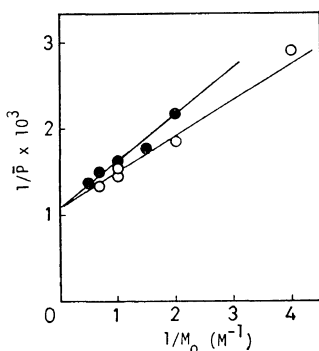


**Figure 11.** Dependence of $\bar{P}$ on the initial concentration of monomer: —○—, photopolymerization; $\lambda$, 365 nm; $[Ag^I]_0$, $1 \times 10^{-4}\,M$; 30°C; —●—, thermal polymerization, $[Ag^I]_0$, $2 \times 10^{-4}\,M$; 30°C.

monomer concentration, as shown in Figure 11. Moreover, additive effects of methanol as a chain transfer agent were also examined in Figure 11.

These chain breaking reactions were analyzed on the assumption of five elementary reactions:

$$P_{n-1}^+ + M \xrightarrow{k_p} P_n^+ \tag{9}$$

$$P_n^+ + M \xrightarrow{k_t} P_{n+1} \tag{10}$$

$$P_n^+ + M \xrightarrow{k_{tr}^M} P_n + M^+ \tag{11}$$

$$P_n^+ + Y \xrightarrow{k_{tr}^Y} P_n + Y^+ \tag{12}$$

$$P_n^+ + CH_3OH \xrightarrow{k_{tr}^{CH_3OH}} P_n + H^+ \tag{13}$$

where eq 11—13 are the chain-transfer reactions to monomer, chain-transfer agent Y, and metha-



(a)



(b)
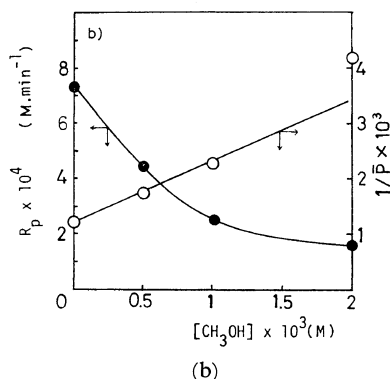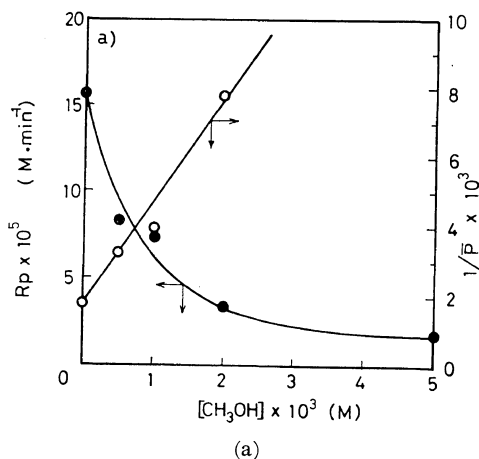
**Figure 12.** Dependence of $1/\bar{P}$ and $R_p$ on the concentration of metanol: $[VCZ]_0$, $1\,M$; $[Ag^I]$, $2 \times 10^{-4}\,M$; 30°C; (a), thermal polymerization; (b), photopolymerization; $\lambda$, 365 nm.

nol, respectively. The termination reaction was assumed to be a monomer termination, as proposed previously.[1] From eq 9—13, the following conventional expression can be derived:

$$\frac{1}{\bar{P}} = \frac{k_{tr}^{CH_3OH}[CH_3OH] + k_{tr}^Y}{k_p} \frac{1}{[M]} + \frac{k_{tr}^M + k_t}{k_p} \tag{14}$$

This relation agrees with the experimental results obtained above. Consequently various kinetic quantities can be calculated and are tabulated in Table II. It is confirmed that both thermal and photosensitized polymerizations proceed *via* the same propagation mechanism. It is noteworthy to compare these chain-transfer constants, especially $k_{tr}^{CH_3OH}$, with those obtained in the

**Table II.** Kinetic quanties of the degree of polymerization

| Rate constant | Photopolymerization | Thermal polymerization |
|---|---|---|
| $\dfrac{k_{tr}^{M}+k_{t}}{k_{p}}$ | $1.1\times10^{-3}$ | $1.1\times10^{-3}$ |
| $\dfrac{k_{tr}^{Y}}{k_{p}}$ | $4\times10^{-4}$ | $5\times10^{-4}$ |
| $\dfrac{k_{tr}^{CH_3OH}}{k_{p}}$ | $1.2$ | $3$ |

studies[7] of the salt effect on the cationic polymerization of VCZ, in which free-ion and ion-pair mechanisms of propagation were characterized by means of the measurements of $k_{tr}^{CH_3OH}$ in the presence and absence of tetra-*n*-butylammonium perchlorate. In comparison with $k_{tr}^{CH_3OH}(0.5)$ obtained in the perchloric acid initiated thermal polymerization in benzene, which was thought to be ion-pair propagation, both thermal and photopolymerizations in the present investigation are very likely to be characterized as ion-pair with perchlorate counter-ions.

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