PHOTOPOLYMERIZATION MECHANISM
OF N-VINYLCARBAZOLE

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1. Introduction
Photopolymerization is an important reaction for photorecording, photofabrication, painting, etc. The photopolymerization of N-vinylcarbazole (VCZ) has been extensively studied [1]. VCZ has several unique properties as an enamine monomer. However, there are few studies on the detailed initiation mechanism [2,3]. We have studied the photopolymerization mechanism of VCZ including photodimerization. The rate constant of the propagation reaction was estimated by the combination of the lifetime of propagation species and the kinetic quantities obtained in the photostationary polymerization. To elucidate the reactivity of the VCZ radical cation, the codimerization reaction between VCZ and styrene was studied in the presence of an electron acceptor.

2. Experimental
Materials. -- VCZ (Nacalai tesque) was purified by recrystallization three times from methanol and hexane, then it was dried in vacuo for two days at room temperature. Other reagents and solvents were purified by the usual way.
Apparatus and Procedures. -- The light source was a 300-watt high-pressure mercury lamp (Toshiba HF-300). The excitation light was selected using various optical cut-off filters (Toshiba UVD1A, VY-43, VO-52, VO-55). The dilatometry was carried out in a thermostatted bath. The absolute rate constant of propagation was determined by the rotating sector method (sector ratio \( r = 1 \)) at 30°C.
3. Results and Discussion

The photoreaction process of VCZ in the presence of an electron acceptor is shown in the Scheme. The VCZ radical cation which is photochemically produced by the charge-transfer interaction forms its dimer radical cation by the addition of the VCZ monomer. The dimer radical cation yields a cyclodimer under the ordinary condition. The dimer radical cation, however, induces cationic polymerization when the radical is trapped. If the cation of the dimer radical cation is solvated by a basic solvent, radical polymerization occurs. Thus, the photoreaction takes place in the following three ways: (i) cationic polymerization of VCZ, (ii) radical polymerization of VCZ, and (iii) cyclodimerization of VCZ through its radical cation. Now, each process will be discussed.

(i) A CT complex of VCZ with 2,4,7-trinitrofluorenone (TNF) was formed in the ground state [4]. When the VCZ-TNF complex was photo-excited in nitrobenzene, the cationic polymerization proceeded. The rate constant of the propagation $k_p$ was determined by the rotating sector method at 30°C and $k_p = 8.2 \times 10^3$ l mole$^{-1}$ sec$^{-1}$ was obtained. Bowyer et al. [5] reported $k_p = 3 \times 10^5$ l mole$^{-1}$ sec$^{-1}$ using tropylium ion in dichloromethane at 0°C. This difference may be accounted for by the differences in temperature and the kind of solvents.

(ii) North et al. [6] determined the rate constant of radical polymerization in THF at 10°C and obtained $k_p = 6.0$ l mole$^{-1}$ sec$^{-1}$. 

Scheme
We have determined the rate constant of radical polymerization for the VCZ-diacetyl system in benzene at 30°C. Fig. 1 shows the determination of the lifetime $\tau$ of propagating radical species, where $\tau = 0.87$ sec was obtained. The rate constant of radical polymerization $k_p = 9.3 \times 10^2$ 1 mole$^{-1}$ sec$^{-1}$ was obtained. These results show that the rate constant of radical polymerization is smaller than that of cationic polymerization.

![Graph showing variation of $R_p/(R_p)_s$ with duration of light flash at 30°C.](image)

Fig. 1 Variation of the ratio $R_p/(R_p)_s$ with the duration of light flash at 30°C.

(iii) In the mechanism of photopolymerization of VCZ in the presence of an electron acceptor, VCZ radical cation and its dimer radical cation play an important role. The product of the dimer radical cation was mostly a ring-closed one: 1,2-trans-dicarbazolylcyclobutane. To elucidate the reactivity of cyclodimerization reaction, the effect of additives was examined. The cyclodimerization reaction was inhibited by the addition of a small amount of a cation scavenger, triethylamine or a radical scavenger, 1,1-diphenyl-2-picrylhydrazyl. Next the codimerization between VCZ and styrene was investigated. In VCZ-styrene-dimethylterephthalate system, VCZ radical cation was produced through the exciplex of VCZ-dimethylterephthalate, then the codimerization gave a hetero- and homo-dimer of VCZ. Here it was found that the hetero-dimer is trans-1-carbazolyl-2-phenyl-cyclobutane (Fig. 2) and the homo-dimer is 1,2-trans-dicarbazolyl-
The MO calculation for VCZ radical cation shows that the radical is localized on the β-carbon of the vinyl group and the cation is on the α-carbon. Styrene is liable to be attacked on β-carbon of the vinyl group. Hence, the result suggests that the comonomer styrene is attacked by the radical site of VCZ radical cation. In addition, the reaction of VCZ with a radical initiator initiated the radical polymerization, but the cyclodimerization did not occur. These results indicate that the cyclodimerization takes place neither in a cationic nature, nor in a radical nature, but in a radical-cationic nature to give its characteristic cyclodimer.

The conformation and reactivity of the VCZ dimer radical cation are crucial to understand the initiation mechanism of the photopolymerization of VCZ. This point is being investigated by nanosecond laser photolysis and will be reported shortly.

References
1. For example, A. Ledwith, Accounts Chem. Res., 5 (1972) 133.