

Photo and Thermal Polymerization Sensitized by Donor-Acceptor Interaction. I. *N*-Vinylcarbazole-Acrylonitrile and Related Systems

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Synopsis

Spontaneous photo and thermal polymerization of *N*-vinylcarbazole (VCZ)-acrylonitrile (AN), VCZ-acetonitrile, AN-*N*-ethylcarbazole, and AN-ferrocene were studied. These combinations of electron donor with acceptor were thermally rather stable but showed prominent photopolymerizability when the systems were irradiated by near ultraviolet light. The VCZ-AN system showed multireactivity producing VCZ polymer and a copolymer of VCZ with AN. The composition of copolymer was approximately the same as that of polymer produced in radical copolymerization. The effects of additives (DPPH, NH₃, H₂O, air) indicated simultaneous occurrence of cationic and radical polymerization in the AN-VCZ and acetonitrile-VCZ systems. The results were interpreted on the assumption of initial formation of a cation radical-anion radical pair. The ratio of cationic to radical polymerization differed for photo and thermal polymerization. In no case was anionic polymerization detected.

INTRODUCTION

Polymerizations initiated by charge-transfer interaction between donor and acceptor have been extensively studied by various researchers with special reference to *N*-vinylcarbazole (VCZ), as reviewed by Hatano et al.¹ Factual knowledge has been accumulated on the polymerization of VCZ in combination with various organic as well as inorganic acceptors. Natures of initiating and propagating species are, however, still the subject of controversy. Ellinger has suggested that the polymerization of VCZ by a weak electron acceptor such as acrylonitrile (AN) or methyl methacrylate is initiated by mesomeric polarization without formation of an ion-radical resulting from complete electron transfer.² The state of incomplete charge transfer (mesomeric polarization) was claimed to control the propagation step as well, resulting in the formation of VCZ homopolymer alone in spite of the presence of another polymerizable monomer, such as acrylonitrile or methyl methacrylate. Later, Ellinger³ found thermal copolymerization of VCZ with methyl methacrylate, which seemed to contradict his previous concept. An alternative mechanism may be initiation by ion-radicals. For the strong donor-strong acceptor combination, dissociation of the charge transfer pair to ion-radicals is easily conceivable. For a weak acceptor-

VCZ system, it is, however, questionable as to whether complete electron transfer is energetically accessible. Formation of the ion-radical has been confirmed by ESR spectroscopy for polymerization of VCZ by inorganic acceptors⁴ and oxidizing metal salts.⁵ Although this seems to be a good support for ion-radical initiation, the same ESR spectra were observed for pairs of *N*-ethylcarbazole and oxidizing metal salts.⁵ The identity of the paramagnetic species with the initiating species is therefore an unsolved problem.

Even if the polymerization were initiated by an ion-radical, the propagating species could not be an ion-radical since the ion-radical conjugation system is separated into ion and radical after the first addition of monomer. Also, prior to addition of monomer, a cation-radical paired with an anion-radical might couple to diradical or cation-anion. Such coupling of ion-radicals was suggested as intermediate in the 1,2-cycloaddition between donor and acceptor ethylenic compounds.⁶

Confirmation of ion-radical initiation may be achieved if one proves simultaneous propagation of both ion and radical. The authors have already reported that a single oxidizing metal salt can initiate cationic or radical polymerization of VCZ or 4-vinylpyridine, respectively, and proposed electron transfer initiation via an ion-radical for both systems.⁷ In the present study simultaneous propagation of cation and radical is confirmed for photo and thermal polymerization of VCZ-AN system.

The photochemistry of charge transfer polymerization is an interesting subject which has been little examined. Since ion-radical formation or mesomeric polarization is caused by charge separation in a donor-acceptor pair, photoexcitation would be a powerful method for promoting initiation. Even a thermally stable charge-transfer pair such as VCZ-nitrobenzene could be easily brought into polymerization by photoirradiation.⁸ In addition, photochemically produced active species would be expected to have a different reactivity from a similar thermally produced one because of the Franck-Condon principle.

EXPERIMENTAL

Materials

VCZ (Koch-Light Lab.) was recrystallized once from *n*-hexane; mp 65.2°C.

Styrene and acrylonitrile were washed with alkali and acid then repeatedly with water, dried, and distilled twice over calcium hydride.

N-Ethylcarbazole as received (commercial reagent, chemical pure grade) was by no means pure and was purified by repeated recrystallization from methanol after decolorizing the methanol solution by activated charcoal.

Acetonitrile was distilled twice over calcium hydride.

Ammonia was prepared by warming concentrated aqueous ammonia. The evolved ammonia was dried by being passed through a barium oxide

column, purified by trap-to-trap distillations, and finally transferred to the reaction vessel under high vacuum.

All other reagents were commercial materials and used without further purification.

Light Source and Polymerization

The apparatus for photoirradiation was the same as described in the previous report.⁸ Polymerization was carried out in a glass reaction tube of 12 mm diameter. The glass tubes absorbed 98.0–99.9% of light at 290 m μ . Small differences in absorption by reaction vessel were not serious problems for polymerization systems which have strong absorption at wavelengths over 300 m μ , such as those systems containing VCZ or ECZ. Depending upon the transparency of the reaction vessels in the near-ultraviolet region, however, considerable fluctuation of polymer yield was observed for the photopolymerization of pure AN, which showed absorption only up to 280 m μ . Since the reaction vessel does not have a flat surface, it was not possible to determine absolute amount of photoenergy absorbed by the reaction system. As a relative measure, the photoreduction of potassium ferrioxalate solution⁹ was examined in the same reaction vessel. The rate of reaction was 7.15×10^{-6} – 7.60×10^{-5} mol/l-sec when the initial concentration of Fe^{III} was $6 \times 10^{-3}M$.

The reaction tube was sealed either in the presence of air or after degassing at a pressure of 10^{-4} mm Hg by several freeze-thaw cycles.

When polymerization was to be carried out in dark, the reaction tube was wrapped with aluminum foil to ensure complete darkness.

Polymerizations of AN-VCZ, AN-ECZ, VCZ-CH₃CN systems in bulk and some copolymerizations, depending upon monomer feed ratio, proceeded as precipitation polymerization. In particular, the VCZ-AN polymer formed on the glass wall of the reaction tube was partly insoluble even in dimethyl-formamide and dimethyl sulfoxide. Viscosity measurements were therefore not attempted.

The polymerization mixtures were poured into methanol, filtered, and washed with the precipitant.

Fractionation of Polymers Obtained in VCZ-AN System

The polymerization products of VCZ-AN system were fractionated by benzene extraction at 60°C for 3 days. The benzene extract was precipitated in methanol, and the precipitate was confirmed as polyvinyl-carbazole by infrared spectroscopy.

Extraction of polymer by saturated zinc chloride aqueous solution at boiling point was used to determine the presence of polyacrylonitrile. Polyacrylonitrile prepared by ordinary radical polymerization was completely soluble in such a zinc chloride solution.

Determination of Polymer Composition

Copolymer compositions of AN-VCZ and AN-St were determined by both elemental analysis and infrared spectroscopy. The key bands for infrared spectroscopy were 2240 cm^{-1} for AN and $920\text{--}930\text{ cm}^{-1}$ for VCZ and St. Results by both methods agreed well, and in later studies, determination by infrared spectroscopy was mainly used.

RESULTS AND DISCUSSION

AN-VCZ System

Thermal polymerization of this system was first studied by Ellinger² and was reported to produce polyvinylcarbazole alone. His results are, however, reproducible only for thermal polymerization in the presence of air. Results of polymerization are shown in Figures 1 and 2 and Table I. Acceleration by photoirradiation is striking. Benzene extraction yields two fractions. The benzene-soluble part was confirmed to be polyvinylcarbazole (PVCZ). The weight fraction of PVCZ depends very much on reaction conditions and additives. In photopolymerization, addition of ammonia completely suppresses the formation of PVCZ (Table I) whereas the total polymer yield increases, as shown in Figure 3. On the other hand,

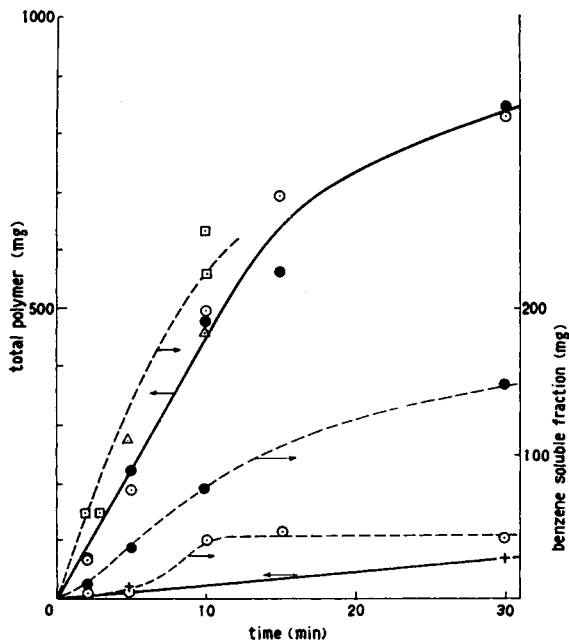


Fig. 1. Plots of (—) total yield and (---) benzene-soluble fraction for photopolymerization of VCZ-AN systems at 30°C : (○) *in vacuo*; (●) in air; (Δ) in CO_2 ; (◻) *in vacuo*, $[\text{H}_2\text{O}] = 0.1M$; (+) *in vacuo*, $[\text{DPPH}] = 10^{-3}M$. $[\text{VCZ}] = 1M$ in AN; volume of solution: 3 ml; VCZ 582 mg, AN 2070 mg.

TABLE I
Polymerization of VCZ-AN System^a

Polymeri- zation	Atmosphere	Additive	Time, min	Yield, mg	D_{2340}/D_{930}^b	VCZ in total polymer, mole-%	Benzene- soluble fraction wt.-% ^c
Photo	Vacuum	None	10	490	4.05	20.8	8.3
"	Air	"	10	477	2.72	28.1	16.3
"	Vacuum	H ₂ O, 0.1M	3	149	1.16	48.2	
"	"	"	10	630	1.96	36.8	35.6
"	"	DPPH, 10 ⁻³ M	5	18	0.453	73.0	
"	"	"	30	68	0.601	66.2	41.0
"	"	NH ₃ , 0.047 ml	5	400	4.39	19.4	0
Thermal	Vacuum	None	480	77	0.573	67.8	
"	Air	"	480	56	0.0	100	
"	Vacuum	H ₂ O, 0.1M	311	59	0.437	74.1	
"	"	DPPH, 10 ⁻³ M	311	—	—	—	
"	"	NH ₃ , 0.025 ml	2880	47	5.12	17.1	

^a [VCZ] = 1.0M in AN, volume of solution: 3 ml; VCZ 582 mg, AN 2.07 g; Reaction at 30°C for photopolymerization and at 60°C for thermal polymerization.

^b Intensity ratio of infrared spectra at 2240 cm⁻¹ and 930 cm⁻¹.

^c Extracted fraction after treating the total polymer with benzene at 60°C for 3 days.

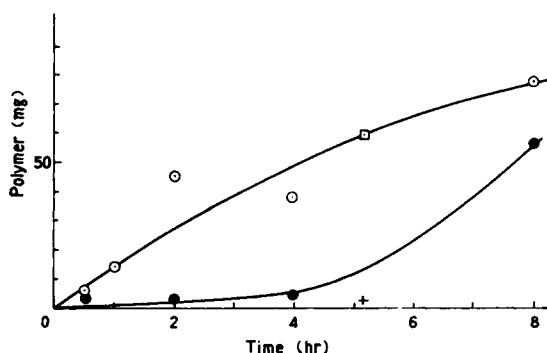


Fig. 2. Thermal polymerization of VCZ-AN systems in the dark at 60°C: (○) *in vacuo*, (●) in air, (◻) *in vacuo*, [H₂O] = 0.1M; (+) *in vacuo*, [DPPH] = 10⁻³M. VCZ 582 mg, AN 2070 mg.

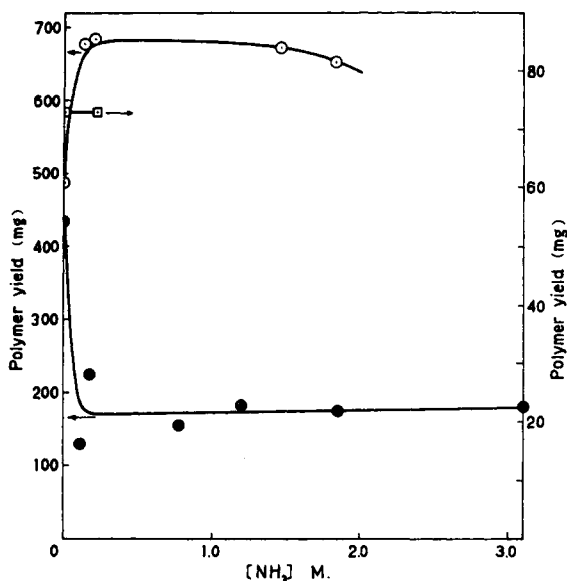


Fig. 3. Effect of ammonia on yield in photopolymerization at 30°C *in vacuo*: (○) VCZ-AN (VCZ 582 mg, AN 2070 mg), polymerization for 10 min; (●) VCZ-CH₃CN (VCZ 582 mg, CH₃CN 2.58 ml), polymerization for 60 min; (◻) VCZ-AN (VCZ 582 mg, AN 2070 mg, azobisisobutyronitrile 10⁻³M), dark polymerization at 60°C for 30 min.

addition of 2,2-diphenyl-1-picrylhydrazyl (DPPH) reduces the total polymer yield and increases the VCZ fraction in the polymer.

These findings would indicate that there are at least two simultaneous polymerization mechanisms, which lead to formation of PVCZ and VCZ-AN copolymer. PVCZ is very likely to be formed by a cationic mechanism and the copolymer is by radical mechanism. The presence of air does not hinder polymerization, the yield of PVCZ being higher than in the vacuum system. This result and the similar finding that the rate of polymerization

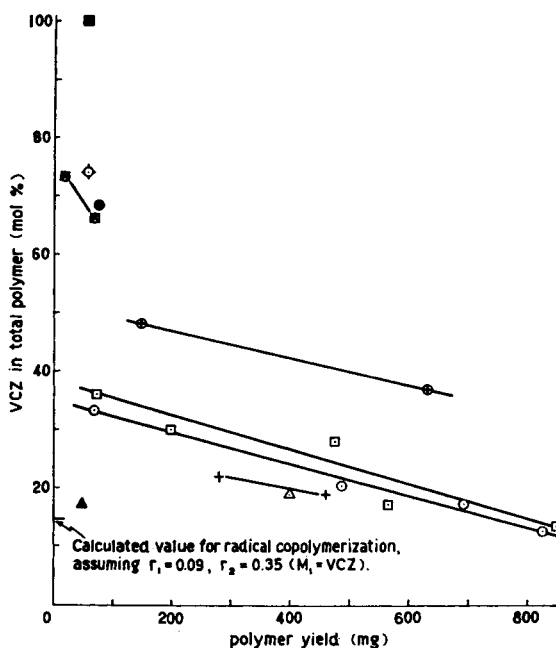
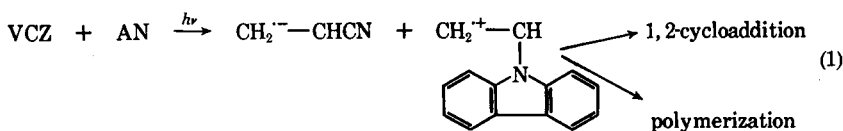


Fig. 4. Plots of content of VCZ in product vs. polymer yield: (\square) $h\nu$, in air; (\odot) $h\nu$, in vacuo; (\oplus) $h\nu$, in vacuo, $[\text{H}_2\text{O}] = 0.1M$; (\boxtimes) $h\nu$, in vacuo, $[\text{DPPH}] = 10^{-3}M$; (Δ) $h\nu$, in vacuo, $[\text{NH}_3] = 0.4\text{--}0.75M$; ($+$) $h\nu$, in CO_2 ; (ϕ) thermal, in vacuo, $[\text{H}_2\text{O}] = 0.1M$; (\blacktriangle) thermal, in vacuo, $[\text{NH}_3] = 0.176M$; (\blacksquare) thermal, in air; (\bullet) thermal, in vacuo. VCZ 582 mg, AN 2.07 g; 30°C for photopolymerization, 60°C for thermal polymerization.

increases whereas formation of PVCZ is inhibited in the presence of ammonia, are difficult to explain if one assumes cationic and radical initiating species to be independent of each other. Air and ammonia would not influence the conventional cation and radical, respectively. The most likely explanation is given by the assumption of ion-radical initiation. Ion-radical pairs [eq. (1)] would either initiate polymerization or couple to cyclobutane derivatives. Although products of 1,2-cycloaddition have not been isolated in the present system, the occurrence is very probable by analogy to the reaction between donor vinyl compounds such as vinyl ethers and acceptor ethylenic compounds such as tetracyanoethylene.⁶ The present results of additive effect seem to indicate multireactivity of initiating species. These ion-radicals could act as both radical and ionic initiators. It is well conceivable that additives would enhance the initiating efficiency of the ion-radical by converting it to an ordinary radical or ion which might be otherwise totally lost by 1,2-cycloaddition:



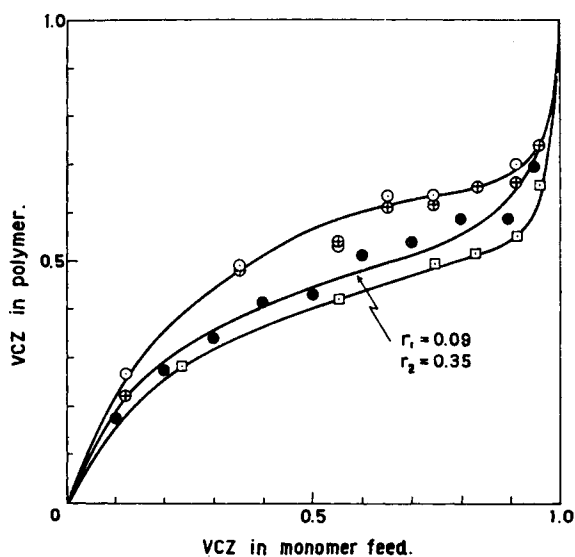


Fig. 5. Composition of polymers from VCZ-AN system: (\oplus) photopolymerization in air, 30°C, $[\text{VCZ}] + [\text{AN}] = 5 \times 10^{-3}$ mol, 2 ml benzene, from N content; (\circ) photopolymerization in air, 30°C, $[\text{VCZ}] + [\text{AN}] = 5 \times 10^{-3}$ mol, 2 ml benzene, from infrared spectrum; (\square) photopolymerization in dark, 60°C, $[\text{VCZ}] + [\text{AN}] = 2.5M$, AIBN = $10^{-2}M$, from infrared spectrum.

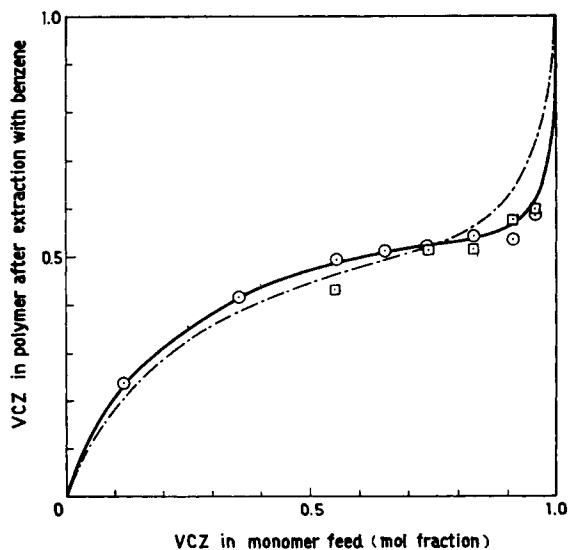


Fig. 6. Composition of photopolymer after benzene extraction: (\circ, \square) same as in Fig. 5; (---) radical polymerization at 60°C.

In support of the view mentioned above, ammonia acts as retarder for polymerization of the VCZ-acetonitrile system, in which 1,2-cycloaddition is not expected.

The content of VCZ in polymer under various polymerization conditions is shown in Figure 4 as a function of conversion. These results are understandable if radical and cationic polymerizations occur simultaneously. The effect of water needs to be explained. For an extremely basic monomer such as VCZ, water does not inhibit cationic polymerization but acts as chain-transfer agent. VCZ can be even polymerized by acid in aqueous suspension. Consequently, water might change the cationic activity of the initial ion-radical pair by promoting conversion to proton through chain transfer.

Although formation of anionic polymer is expected, a fraction extractable by saturated zinc chloride solution is not detected; homopolymer of AN does not therefore seem to be formed.

To confirm the polymerization mechanism, the copolymerization of VCZ-AN in benzene was studied. Polymerization was stopped at less than 10% (in most cases, less than 5%) conversion. As shown in Figure 5, there are considerable discrepancies between radical copolymerization and photopolymerization without initiator, in particular in air. The difference is far too large to be attributed to the difference in polymerization temperature (30°C for photopolymerization and 60°C for thermal polymerization). Copolymers by photopolymerization apparently consist of two fractions. After benzene extraction, photopolymers produced in air show decreased content of VCZ and the compositions are nearly identical to photopolymer produced *in vacuo*. The composition curves are close to that of polymer obtained in radical polymerization, as shown in Figure 6.

AN-ECZ System

In the preceding section, both donor and acceptor are vinyl compounds. It is obvious that polymerization of VCZ is initiated by AN. However, VCZ might as well initiate polymerization of AN. To confirm the action of donor on the polymerization of AN, ECZ was chosen as a nonpolymerizable donor.

Results in Table II indicate that ECZ is an effective photosensitizer for radical polymerization of AN although the system is thermally very stable. The retarding effect of hydrochloric acid might, however, indicate contribution of an anionic species. Copolymerization of AN with styrene initiated by donor confirms the radical mechanism as shown in Figure 7. Donors other than ECZ can be also used. Ferrocene is known to be a strong donor, forming a charge-transfer complex with tetracyanoethylene and other compounds.¹⁰ Photopolymerization of AN is sensitized by ferrocene, as shown in Figure 8. However, charge-transfer interaction between AN and ferrocene is uncertain, since ferrocene is also active for polymerization of styrene. The relative ratio of ferrocene-initiated polymerization of AN to that of styrene is about 6, which is about equal to the

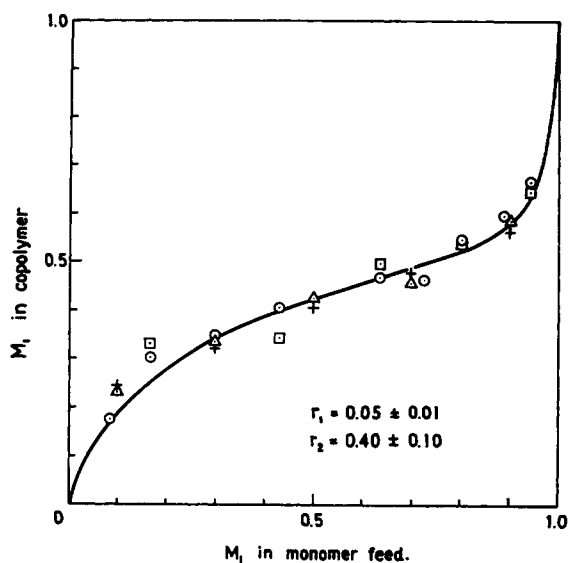


Fig. 7. Composition of photopolymers from AN-styrene at 30°C in bulk: (○) AN-St-AIBN ($10^{-2}M$); (●) AN-St-ferrocene ($10^{-2}M$); (+) AN-St-ECZ, in air, $[AN] + [St] = 2 \times 10^{-2}M$, ECZ 0.35 g; (Δ) AN-St-ECZ *in vacuo*, $[AN] + [St] = 2 \times 10^{-2}$ mol, ECZ 0.35 g.

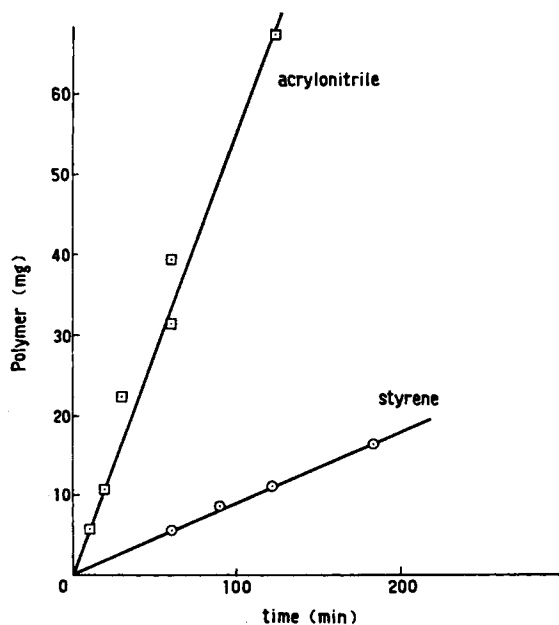


Fig. 8. Photopolymerization of AN and styrene sensitized by ferrocene at 30°C *in vacuo*. [Ferrocene] = $1.0 \times 10^{-2}M$, monomer 1.5 ml.

TABLE II
Polymerization of AN-*N*-Ethylcarbazole (ECZ) System^a

Polymerization	Atmosphere	Additive	Time, min	Yield, mg
Photo	Vacuum	None	60	245, 234
"	Air	"	60	112, 105
"	Vacuum	DPPH, $10^{-3}M$	60	20, 31
"	Air	"	60	15, 12
"	Vacuum	HCl, $0.1M$	60	71, 75
"	Air	"	60	11, 14
Thermal	Vacuum	None	360	0
"	Air	"	2900	0

^a AN 1.5 ml, ECZ 0.35 g; 30°C for photopolymerization, 60°C for thermal polymerization.

ratio $k_p/k_t^{1/2}$ for AN to that for styrene. There seems to be no special preference to AN when ferrocene is used as sensitizer. For polymerization sensitized by ECZ, the rate ratio of AN to styrene is over 20, to judge by data in Tables II and IV.

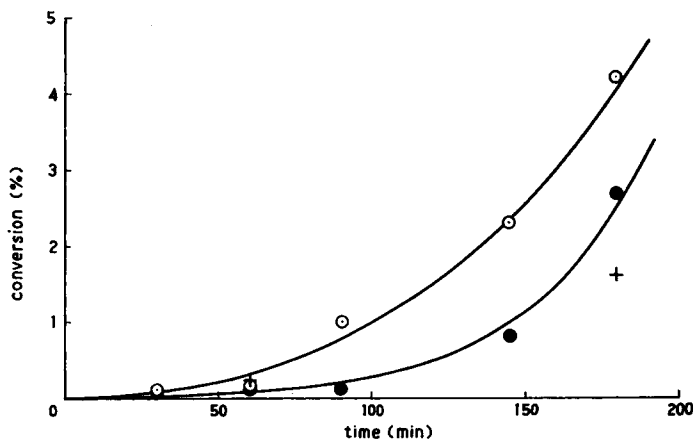


Fig. 9. Photopolymerization of styrene in the presence of ECZ and CH_3CN at 30°C: (○) in air, styrene 2 ml, CH_3CN 0.16 ml, ECZ 600 mg; (●) *in vacuo*; (+) styrene alone *in vacuo*.

VCZ-Acetonitrile System

When the nitrile compound has no vinyl group, polymerization of VCZ is also easily induced by photo irradiation, as shown in Table III. Thermal polymerization is extremely slow, and it is difficult to compare the rates. Thermal polymerization seems to be cationic as judged by effects of additives. The retarding effect of DPPH and ammonia (Fig. 3) supports a radical cationic mechanism of photopolymerization. The effect of DPPH in the photopolymerization system, however, might in part be due to a

TABLE III
 Polymerization of VCZ-Acetonitrile System^a

Polymerization	Atmosphere	Additive	Time, min	Yield, mg
Photo	Vacuum	None	60	432
"	Air	"	60	445
"	Vacuum	H ₂ O, 0.1 <i>M</i>	60	441
"	"	DPPH, 10 ⁻³ <i>M</i>	60	4.7
Thermal	Vacuum	None	200	4.5
"	"	"	1440	15.5
"	Air	"	200	6.0
"	"	"	1440	16.4
"	Vacuum	H ₂ O, 0.1 <i>M</i>	1440	1.6
"	"	DPPH, 10 ⁻³ <i>M</i>	180	3.7
"	"	"	1440	13.1
"	"	NH ₃ , 0.045 ml	1440	5.7
"	"	NH ₃ , 0.015 ml	1440	4.8

^a [VCZ] = 1.0*M* in acetonitrile, volume of solution 3 ml; VCZ = 582 mg, acetonitrile = 2.58 ml; 30°C for photopolymerization, 60°C for thermal polymerization.

filter effect which would reduce the intensity of light absorbed by the charge-transfer pair, since DPPH has strong absorption bands in the region above 320 m μ which is employed in the present experiment.

Polymerization Systems Not Containing Donor or Acceptor

Since photo and thermal polymerizations of vinyl compounds may be brought about by prolonged irradiation or heating without donor-acceptor combination, several sets of reaction systems were examined for their polymerizability as described in Table IV.

 TABLE IV
 Slow Polymerization Systems without Charge Transfer Interaction^a

Polymerization system	Polymerization	Atmosphere	Time, min	Yield, mg
VCZ (0.3 g)-benzene (1.0 ml)	Thermal	Air	1140	2.7
" " "	Photo	"	150	10.0
VCZ (0.3 g)-styrene (1.0 ml)	Thermal	"	270	0.4
" " "	Photo	"	300	69.3
ECZ (0.35 g)-styrene (1.5 ml)	Photo	Vacuum	61	10.7
" " "	Photo	"	61	3.6
Styrene (0.34 ml)-CH ₃ CN (2.58 ml)	Photo	"	460	0
" " "	Thermal	"	460	0
AN (1.5 ml)	Photo	"	60	15 \pm 15
Styrene (2.0 ml)-ECZ (600 mg)-CH ₃ CN (0.16 ml)	Thermal	"	1920	39.0
" " "	"	Air	1920	34.2
Styrene (2.0 ml)	"	Vacuum	1920	52.7

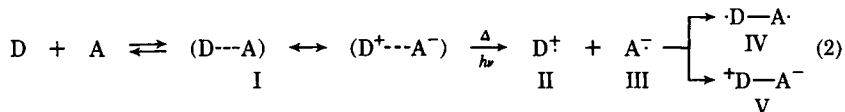
^a 30°C for photopolymerization, 60°C for thermal polymerization.

Both VCZ and AN are stable to heat and light when the counterpart of the charge transfer pair is absent. Combination of VCZ with styrene shows very low sensitivity towards thermal and photo reaction. When both of donor and acceptor lack a vinyl group, the donor-acceptor pair does not show photosensitivity. The ECZ-acetonitrile pair is an inefficient initiator for polymerization of styrene, as shown in Figure 9.

It is concluded that the presence of a donor-acceptor pair, at least one of which is a polymerizable monomer, is a necessary condition for rapid photopolymerization.

Polymerization Mechanism

Coexistence of cationic and radical polymerization is clearly shown by the results mentioned above. Formation of initiating species would be as shown in eq. (2):



State I indicates mesomeric polarization which has been claimed as initiator by Ellinger.² Although there is no evidence in support of or against the possibility of initiation by I, consideration of I alone as the initiating species is apparently insufficient to explain the whole of polymerization. Assumption of ion-radicals in pairs would be more reasonable to interpret the fact that cationic and radical active species are interrelated. However, the fate of anionic species is still unknown and should be studied under rigorously dry conditions in future.

Further reaction of II and III would yield diradical or cation-anion. Contribution of the diradical in the initiation process, as mentioned by Zutty et al.,¹¹ is probable in the autocatalytic copolymerization of norbornene with sulfur dioxide, but uncertain for the present system. More than 10 years ago, Gilbert et al.¹² claimed the coexistence of cation and anion in the autocatalytic ionic polymerization of vinylidene cyanide and vinyl ethers. This description is too brief for further comments on the mechanism.

The nature of the initiating species in thermal and photopolymerization is qualitatively the same, since cationic and radical polymerizations are observed for both systems. However, the radical nature of polymerization seems to predominate over the cationic one in photopolymerization compared to the thermal system, although the absolute yield of PVCZ in photopolymerization is much higher than that in thermal polymerization. This might indicate a difference in reactivity of the photoexcited ion-radical pair from the thermally produced one.

References

1. M. Hatano, H. Nomuri, and N. Tamura, *High Polymers*, **18**, 823, 905 (1967).
2. L. P. Ellinger, *Polymer*, **5**, 559 (1964).
3. L. P. Ellinger, *Polymer*, **6**, 549 (1965).
4. M. Nishii, K. Tsuji, K. Takakura, K. Hayashi, and S. Okamura, *Kabunshi Kagaku*, **23**, 254 (1966).
5. S. Tazuke, T. B. Tjoa, and S. Okamura, *J. Polym. Sci. A-1*, **5**, 1911 (1967).
6. E. M. Kosower, *Progr. Phys. Org. Chem.*, **3**, 112 (1965).
7. S. Tazuke, K. Nakagawa, and S. Okamura, *J. Polym. Sci. B*, **3**, 923 (1965).
8. S. Tazuke, M. Asai, S. Ikeda, and S. Okamura, *J. Polym. Sci. B*, **5**, 453 (1967).
9. C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc. (London)*, **A235**, 518 (1956).
10. M. Rosenblum, R. W. Fish, and C. Bennet, *J. Amer. Chem. Soc.*, **86**, 5166 (1964).
11. N. L. Zutty, C. W. Wilson III, G. H. Porter, and D. C. Priest, *J. Polym. Sci.*, **49**, 143 (1963).
12. H. Gilbert, F. F. Miller, S. J. Averill, E. J. Carlson, V. L. Folt, H. J. Heller, F. D. Stewart, R. F. Schmidt, and H. L. Trumbull, *J. Amer. Chem. Soc.*, **78**, 1669 (1956).

Received November 6, 1967

Revised March 4, 1968