Photo and Thermal Polymerizations Sensitized by Donor–Acceptor Interaction. II. Photopolymerization and Electronic Spectroscopy of the Isobutyl Vinyl Ether–Acrylonitrile System

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Synopsis

Photopolymerization of acrylonitrile (AN), an acceptor monomer, was found to be accelerated in the presence of isobutyl vinyl ether (IBVE), a donor monomer. The propagation is completed by a radical mechanism as judged by copolymer compositions; in contrast to the *N*-vinylcarbazole–AN system studied previously. This photopolymerization system is entirely stable if kept in the dark. The comparison of the relation between R_p and [IBVE]/[AN] ratio in the monomer feed found for the spontaneous photopolymerization with that for radical polymerization initiated by azobisisobutylonitrile in the dark leads to the conclusion that the rate of photoinitiation is enhanced by the interaction between AN and IBVE, whereas the propagation step by a radical mechanism is retarded by increasing concentration of IBVE. The contact charge-transfer complex between IBVE and AN was confirmed by electronic spectroscopy of the polymerization system, which showed photosensitization by charge-transfer interaction. The spectroscopic study of other weak donor–weak acceptor systems is also discussed.

INTRODUCTION

In the previous reports,[1,2] the multimode polymerization of *N*-vinylcarbazole–acrylonitrile (AN) was discussed. The initiation of the polymerization is very likely to be a charge-transfer interaction between electron donor and electron acceptor. Of those so far examined, all electron donor–electron acceptor combinations in which at least one component of the pair is a vinyl compound, exhibit considerable photosensitization of polymerization. The photosensitivity seems to be consequently a general property of charge-transfer pairs. The irradiation of charge-transfer complexes does not, however, necessarily lead to the initiation of polymerization. The formation of small molecules such as dimers or cyclic condensates might be detected besides polymerization. A solid monomer such as vinylcarbazole (VCZ) is not suitable to study these side reactions, because of the experimental difficulties of purification and analysis.

We have found that the photopolymerization of AN is greatly enhanced in the presence of a small amount of isobutyl vinyl ether (IBVE). In the

present system both electron-donating monomer (IBVE) and electron-accepting monomer (AN) are liquid at room temperature and distillable. This permits us to work under absolutely anhydrous conditions and to examine the formation of by-products other than polymer. Electron spectroscopy of the donor–acceptor system in the quartz ultraviolet region, which was not possible for the system containing VCZ, provided additional information to elucidate the phenomena of photosensitization.

EXPERIMENTAL

Materials

Acrylonitrile was washed with sodium hydroxide solution, phosphoric acid, and repeatedly with water, dried by partial freezing and then over calcium hydride, and distilled twice under nitrogen. Isobutyl vinyl ether was washed with alkaline solution until no color was observed in the aqueous layer, then with water; it was distilled under nitrogen over calcium hydride. Azobisisobutyronitrile(AIBN) was recrystallized twice from methanol. Other reagents used for spectroscopic measurement were all purified by accepted procedures.

When photopolymerization was to be carried out under absolutely dry conditions, the two monomers, purified as mentioned above, were put in separate vessels connected to a vacuum line. After degassing by several freeze–thaw cycles, the monomer was transfered into a vessel containing barium oxide which had been previously baked for 24 hr at 360°C under high vacuum and was left in contact with the drying agent for at least 24 hr. This drying procedure was repeated again and finally the required amounts of the two monomers were distilled into reaction vessels. All operations were conducted under reduced pressure (10^{-5} mm Hg).

Polymerization

Photopolymerization was carried out at 50°C in a glass tube of 12mm outside diameter at a distance of 5 cm from a 300-W high-pressure mercury lamp. Thermal polymerization systems in the dark were wrapped with aluminum foil to protect them from diffused light. The polymerization mixture was poured into methanol and the precipitated polymer was collected.

The copolymer compositions were determined by elemental analysis.

Spectroscopy

Electronic spectra of donor–acceptor systems were measured at room temperature as n-hexane solutions with the use of a quartz cell of 1 mm thickness. The continuous variation method was conveniently carried out by means of a spectrocell so devised that the solution of donor or acceptor could be diluted continuously with additional acceptor or donor solution respectively.

RESULTS AND DISCUSSION

Polymerization of AN–IBVE System

Radical polymerization of AN is considerably retarded in the presence of IBVE, whereas the spontaneous photopolymerization is strongly accelerated by the addition of IBVE, as shown in Figures 1 and 2 and Table I.   As will

TABLE I

Spontaneous Photopolymerization and Thermally Catalyzed Polymerization of the Acrylonitrile–Isobutyl Vinyl Ether System at 50°C *in Vacuo*

VE, ml	AN, ml	Time, min	Yield, mg	Polymer, mg/min
0	2.0	153	71.0	0.465
0.2	1.8	209	178.0	0.861
0.4	1.6	212	391.5	1.85
0.7	1.3	175	122.0	0.697
1.0	1.0	212	166.6	0.786
1.3	0.7	356	150.0	0.422
1.6	0.4	681	21.1	0.031
1.85	0.2	635	30.5	0.047
2.0	0	635	0	0.000
Thermal Polymerization in the Dark ($[AIBN] = 10^{-2} M$)				
0	1.50	23	159.9	6.95
0.25	1.25	54	104.3	1.93
0.45	1.05	110	111.3	1.00
0.75	0.75	208	174.2	0.838
0.90	0.60	259	156.1	0.603
1.25	0.25	646	203.0	0.315
1.40	0.10	646	90.9	0.141
1.50	0	646	0	0

be discussed later, since the photopolymerization proceeds by a radical mechanism alone, the different dependence of R_p on the monomer feed ratios as observed for thermally catalyzed and photopolymerizations must be interpreted in term of the initiation process.   The enhanced rate of photoinitiation in the AN–IBVE system would therefore be due to the photoexcitation of the weak donor–acceptor pair.   The AN–IBVE pair is quite stable at 50°C if the mixture is kept in the dark.

The compositions of polymer obtained by photopolymerization and thermally catalyzed polymerization agree very well, as shown in Figure 3 and Table II.   On expectation of observing ionic propagation by analogy to that in radiation-induced polymerization,[3,4] the absolutely dry system was studied.   However, no ionic propagation could be detected.

The photochemistry of charge transfer pairs is not at all a single process and at least the following five modes of initial acts must be taken into account.
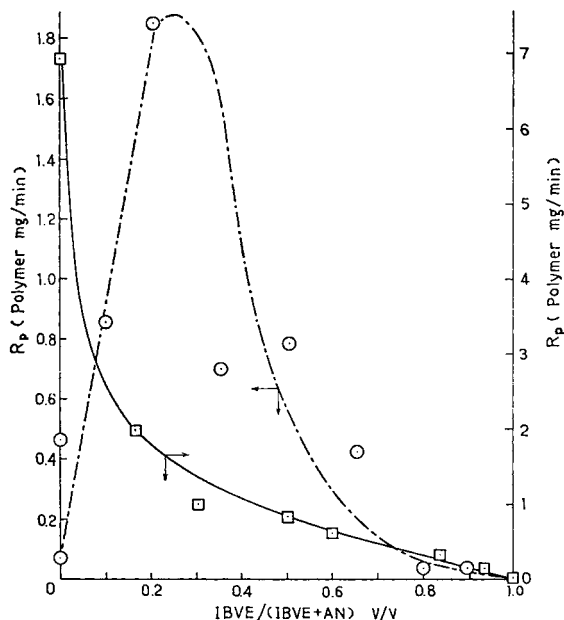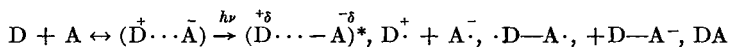
Fig. 1. Polymerization of AN–IBVE system at 50°C *in vacuo*:   (O) photopolymerization (absolutely dry system) IBVE + AN = 2 ml; (□) catalyzed polymerization in the dark [AIBN] = 10^{-2} M, IBVE + AN = 1.5 ml.

$$D + A \leftrightarrow (\overset{+}{D}\cdots \overset{-}{A}) \xrightarrow{h\nu} \overset{+\delta}{(D}\cdots \overset{-\delta}{-A})^*, \overset{+}{D}\cdot + A\overset{-}{\cdot}, \cdot D—A\cdot, +D—A^-, DA$$

The contribution of ionic species is unlikely in the present system, and radical active species alone have to be considered.   The aftereffect of photopolymerization of the donor–acceptor system does not differ much from that
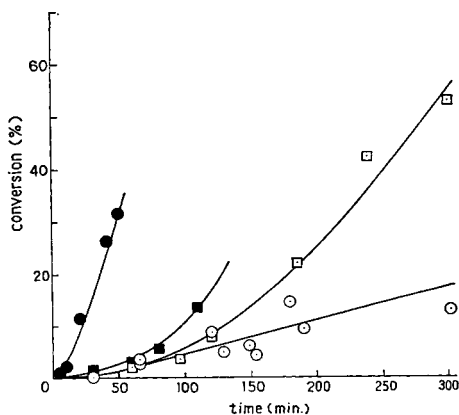
Fig. 2. Time–conversion curves of AN–IBVE system at 50°C *in vacuo*: (O) AN alone, photoirradiated; (●) AN alone, [AIBN] = 10^{-2} M, in the dark; (□) AN + IBVE (20 vol-%), photo-irradiated; (■) AN + IBVE (20 vol-%), [AIBN] = 10^{-2} M in the dark.

TABLE II
Copolymerization of Acrylonitrile—Isobutyl Vinyl Ether (M_1) at 50°C

M_1 in feed, mole fraction	N in copolymer, %	M_2 in copolymer, mole system
Photopolymerization (Absolutely Dry System)		
0.053	23.12	0.927
0.112	23.20	0.930
0.214	18.08	0.803
0.335	16.23	0.750
0.483	14.69	0.703
0.670	12.81	0.640
Photopolymerization (Ordinary Dry System)		
0.053	24.03	0.951
0.112	22.84	0.924
0.178	19.56	0.843
0.291	16.09	0.747
0.380	14.87	0.708
0.604	12.87	0.642
Thermal Polymerization Initiated by AIBN		
0.086	22.59	0.915
0.189	19.64	0.845
0.335	16.24	0.749
0.430	15.15	0.718
0.715	12.70	0.637
0.875	10.45	0.552

of photopolymerization of pure AN, as shown in Figure 4. In the case of biradical propagation, the aftereffect would be larger than that for the ordinary monoradical process unless termination by disproportionation or spontaneous linear termination predominates. Direct determination of biradical propagation by measuring the change in molecular weight during
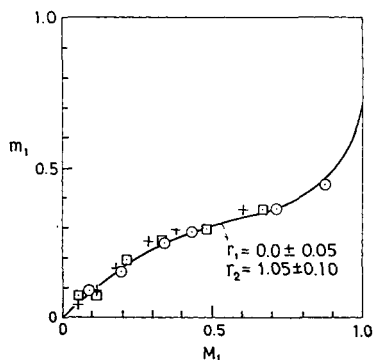

Fig. 3. Copolymer composition curve of AN–IBVE (M_1) system at 50°C: (O) thermal polymerization catalyzed by AIBN (10^{-2} M); (□) photopolymerization (absolutely dry system); (+) photopolymerization (ordinary dry system).
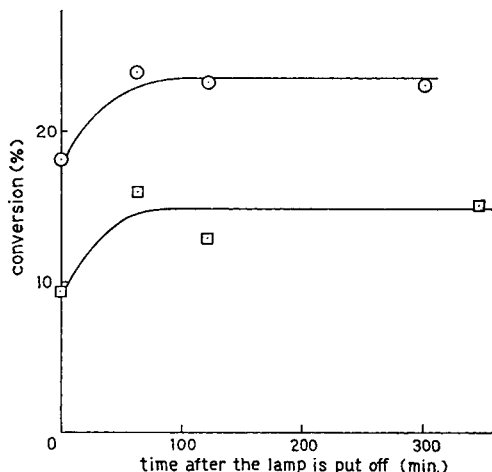
Fig. 4. Post polymerization at 50°C in the dark: (O) AN/IBVE = 4/1 (v/v), irradiated for 120 min. at 50°C *in vacuo*; (□) AN alone, irradiated for 150 min *in vacuo* at 50°C.

the post polymerization could not be done because of crosslinking of polymer.

Possibility of Side Reactions

Photosensitized reactions other than polymerization are possible. For example, cyclic dimerization of ethylenic donor–aceptor systems is known.[5] Also, homocyclic dimerization can be induced by photoirradiation under appropriate conditions as reported for AN.[6]

In the present reaction system, evidence of dimerization or of formation of small molecules could not be obtained, at least within the limit of accuracy of gas chromatographic determination. The mixture of AN–IBVE at mixing ratios varying from 1/10 to 9/10 was placed in one arm of a Y-type reaction vessel and sealed off after degrassing. After irradiating for a required time, another arm of the reaction vessel was cooled to liquid nitrogen temperature to transfer all volatile materials from the irradiated arm. The solid residue was a copolymer of AN with IBVE. The volatile material was analyzed by gas chromatography at 130°C with the use of a 3 m column packed with poly(ethylene glycol) 4000 supported on celite. Two peaks corresponding to unreacted AN and IBVE were the only ones recorded, and no other substance could be detected in the retention time of 30 min.

Spectroscopy

Although coloration was not observed visually when AN and IBVE were mixed, a clear shift of absorption spectra was detected in the ultraviolet region. The continuous variation method was applied to the mixture of AN and IBVE diluted by *n*-hexane. As shown in Figure 5, the optical absorp-
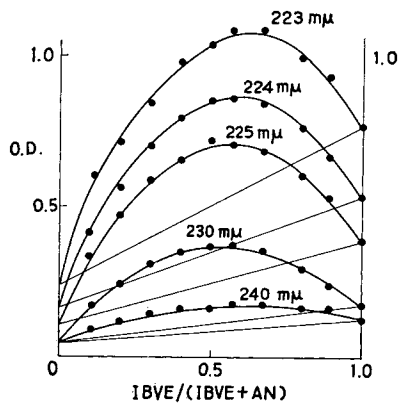
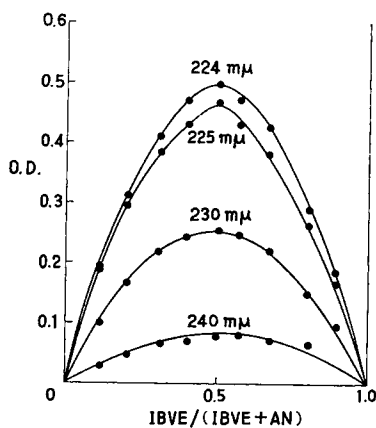Fig. 5. Optical absorption of AN–IBVE in n-hexane; [IBVE] + [AN] = 0.3M.

Fig. 6. Continuous variation method of AN–IBVE; [IBVE] + [AN] = 0.3 M, in n-hexane.
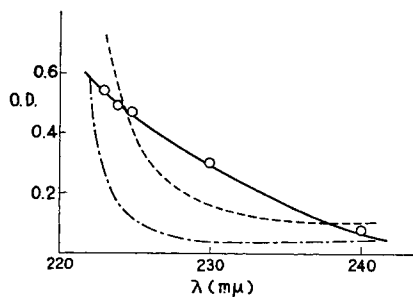

Fig. 7. Absorption spectra of AN, IBVE, and AN–IBVE complex.   IBVE–AN complex [IBVE] = [AN] = 0.15 M (the absorptions of uncomplexed IBVE and AN are subtracted); (—) [IBVE] = 0.3M; (—) [AN] = 0.3M. (optical length = 0.10 cm, solvent = n-hexane).
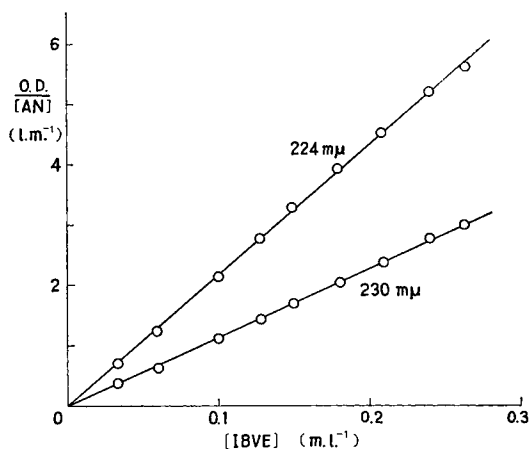
Fig. 8. Confirmation of contact charge-transfer complex formed between IBVE and
AN. Data are taken from Fig. 6.

tion of the mixture does not obey the Beer's law. The additional absorp-
tions after subtracting the absorptions of isolated AN and IBVE from the
observed values are plotted in Figure 6. The formation of 1:1 complex is
confirmed. The spectrum of the complex can be separated by plotting the
optical density at various wavelengths, as shown in Figure 6, although the
concentration of the complex could not be determined. Figure 7 indicates
that the spectra due to the interaction between AN and IBVE are quite
different from those of monomers. One may suspect that simple solvation
might cause the change in absorption spectra. However, the definite 1:1
relation between components as shown in Figure 6 could not be expected in
the case of solvation.

Interpretation of spectroscopic data on the basis of the Benesi-Hilde-
brand equation is not possible. As shown in Figure 8, this system is a good
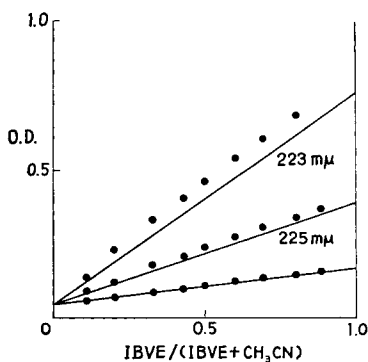example of contact charge transfer complex. The data in Figure 8 are

Fig. 9. Optical absorption of IBVE–acetonitrile in n-hexane. [IBVE] + [CH₃CN] =
0.3M.

derived from Figure 6 using the following equation where ϵ is the average molar absorption coefficient of the complex and γ is the probability of formation of the complex.[7]

$$OD/[AN] = \overline{\epsilon\gamma} \text{ [IBVE]}$$

The presence of a vinyl group seems to play an important role. When acrylonitrile is replaced by acetonitrile, the charge transfer interaction is very weak (Fig. 9). Also no interaction is observed between AN and tetrahydrofuran (THF), which is an saturated ether (Fig. 10). The combinations AN–THF or IBVE–acetonitrile are thermally as well as photochemically stable.
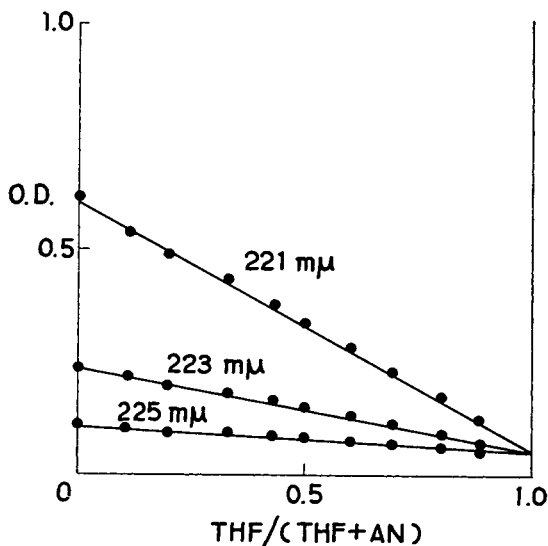

Fig. 10. Optical absorption of AN–tetrahydrofuran (THF) in n-hexane. [THF] + [AN] = $0.3M$.

Comparison of the Present System with the VCZ–AN System

The major difference between the present system and the VCZ–AN system[1,2] is the absence of ionic propagation in the present system. Both VCZ and IBVE are easily polymerized by cationic mechanism. The ion-radicals, if formed by the charge-transfer process, would have higher stability for VCZ than for IBVE. The different contribution of conjugation in these two monomers would reflect on the choice of reaction path. Although the interaction between AN and VCZ is certain, at least in the excited state, from the results of polymerization, the complex formation in the ground state could not be confirmed by spectroscopy, since the strong absorptions of VCZ nearly up to the visible region disturb the measurement. In the region of measurable wavelength, the absorptions of VCZ–AN or VCZ–acetonitrile obey Beer's law, as shown in Figure 11.
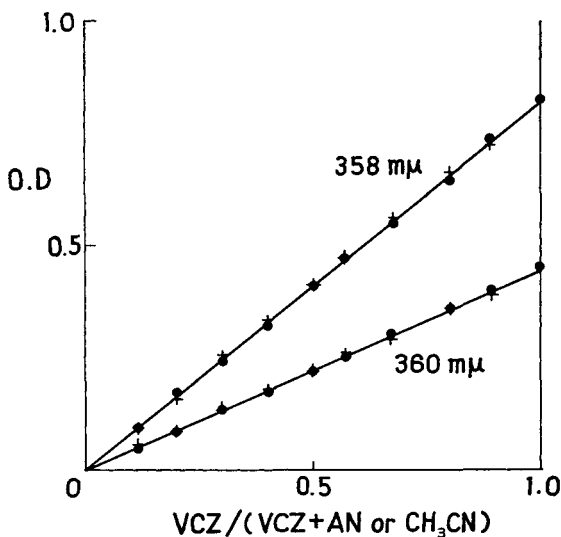
Fig. 11. Optical absorption of VCZ–AN or acetonitrile in benzene, [VCZ] + [AN] or [CH₃CN] = 0.3M: (●) [VCZ] + [AN]; (+) [VCZ] + [CH₃CN].

CONCLUSION

The confirmation of a contact charge-transfer complex between AN and IBVE shows that the spontaneous photopolymerization is initiated by the interaction of two monomers. The absorption of a charge-transfer band is possible only when the charge-transfer band does not overlap with the original absorptions of components. The photoexcitation of AN–IBVE system leads exclusively to radical polymerization; no other reactions were detected.

References

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