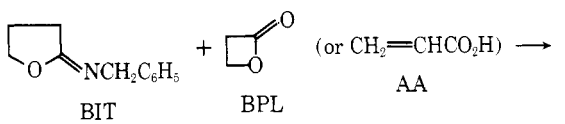
Polymerization *via* Betaine. IV.[1] Alternating Copolymerizations of 2-Benzyliminotetrahydrofuran with β-Propiolactone and with Acrylic Acid

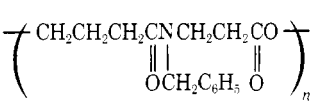
Takeo Saegusa,* Yoshiharu Kimura, Kiyonobu Sano, and Shiro Kobayashi

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan.
Received May 24, 1974

ABSTRACT: The present paper describes the alternating copolymerizations of 2-benzyliminotetrahydrofuran (BIT) with β-propiolactone (BPL) and with acrylic acid (AA). Copolymerization took place without any added initiator in chlorobenzene, acetonitrile, and dimethylformamide. Both systems of BIT–BPL and BIT–AA produced the alternating copolymers having the common structure of the amide–ester type **1**. These copolymerizations are reasonably explained by a scheme of macrozwitterion propagating species **12** involving a common key intermediate of betaine **9**. The apparent values of the monomer reactivity ratio were determined as $\gamma_{BIT} = 0.00$ and $\gamma_{BPL} = 0.20$ at 80° in chlorobenzene and as $\gamma_{BIT} = \gamma_{AA} = 0.00$ at 100° in acetonitrile, respectively.

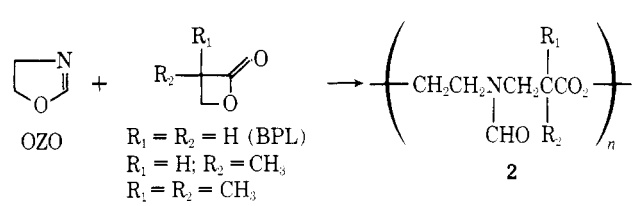
This paper describes the alternating copolymerizations of 2-benzyliminotetrahydrofuran (BIT) with β-propiolactone (BPL) and with acrylic acid (AA). Both copolymerizations took place without any added initiator. These findings constitute a significant development of the alternating copolymerization *via* betaine, a new type of ring-opening polymerization. Previously we reported that 2-oxazoline





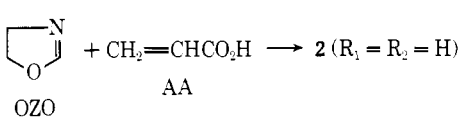
1

(OZO) and BPL[2] were copolymerized without any added initiator to give a 1:1 alternating copolymer **2**. In a similar way methyl-substituted propiolactones also copolymerized

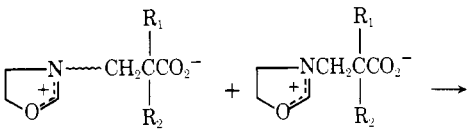


2

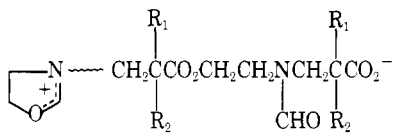
with OZO to yield copolymers of the structure **2**.[3] More interestingly the 1:1 alternating copolymer **2** ($R_1 = R_2 = H$) was obtained from OZO and AA in acetonitrile at 50–60°.[1]



In these copolymerizations a new concept of the "betaine propagation" has been proposed in which the propagation proceeds through the reaction of the macrozwitterion **4** with betaine **3**. Therefore, betaine **3** ($R_1 = R_2 = H$) is considered to be a common intermediate in the 1:1 copolymerizations of both OZO–BPL and OZO–AA systems. In the above copolymerizations, the propagation is a reaction between oxazolinium cation and carboxylate anion. In the present study, BIT was employed as the comonomer for the cyclic-onium part, which was combined with BPL and with AA as the comonomer for the carboxylate anion part. BIT has been homopolymerized by cationic initiators to produce poly(*N*-benzyl-γ-butyramide).[4]



4 3



Results and Discussion

Alternating Copolymerization of BIT with BPL. Copolymerizations were carried out in three solvents of chlorobenzene, DMF, and CH_3CN at temperatures as low as 15°. In all cases copolymerizations took place without added initiator. Table I summarizes results.

Figure 1 shows the nmr spectrum of the copolymer sample number 1 in Table I. Singlet-like signals at δ 7.23 (peak A) and 4.66 (B) are assigned to phenyl and methylene protons of $C_6H_5CH_2N$, respectively. Broad signals centered at δ 4.11 (peak C), 3.56 (D), 2.50 (E), and 1.98 (F) are due respectively to methylene protons of OCH_2, NCH_2, $C(O)CH_2$ and CCH_2C. From the integration value of peaks A and C, both the BIT and BPL units in the copolymer were calculated to be 50%.

In addition no peak is noticed in the vicinity of δ 4.45. The OCH_2 protons' signal of the BPL homopolymer appears at δ 4.45, a lower field of the OCH_2 protons' signal of this copolymer. Thus the absence of the BPL–BPL sequence has been shown, which is taken to support strongly the 1:1 alternating structure of **1**. In fact, the nmr spectrum of the number 9 copolymer containing 58 mol % of the BPL unit does show a broad peak at δ 4.4 (signal G, Figure 1) which is overlapping partly with peak C. The BIT content in the other copolymers in Table I was determined by the integration intensity of peak A *vs.* peaks C and G.

The ir spectrum of the copolymer number 1 (Figure 2) shows characteristic absorptions of amide (1650 cm^{-1}) and ester (1735 and 1180 cm^{-1}) groups of **1**.

The elementary analysis of the copolymer number 1 is well coincident with the calculated value of 1:1 composition of BIT and BPL. The analytical results of other copolymers (numbers 4, 5, 7, and 9) are in good agreement with nmr analyses (Table I).

The copolymer structure of **1** was further confirmed by an alkaline hydrolysis experiment in D_2O. The nmr spectrum of the hydrolysis product of copolymer number 1

Table I
Copolymerization of BIT with BPL[a]

No.	Solvent	Temp, °C	Time, hr	Copolymer yield, %	BIT unit in copolymer,[b] mol %	Mol wt[c]	Anal.[d] Found, % C	H	N
1	C_6H_5Cl	80	0.2	28	50[e]		67.80	7.17	5.76
2	C_6H_5Cl	15	100	81	50[e]	6520			
3	DMF	50	15	75	33				
4	DMF	15	120	53	33	8850	63.03	6.56	4.20
5[f]	CH_3CN	80	1.5	45	50[e]	5120	67.77	7.07	5.66
6	CH_3CN	70	3	75	46				
7	CH_3CN	50	15	82	45	8210	66.38	6.90	5.11
8	CH_3CN	27	40	63	40				
9	CH_3CN	15	120	62	42	8510	65.91	6.86	4.85

[a] [BIT] = [BPL] = 5.0 mmol in 1.5 ml of solvent unless otherwise indicated. [b] Determined by nmr spectroscopy. [c] Determined by vapor pressure osmometry. [d] Calcd for the 1:1 copolymer $(C_{14}H_{17}NO_3)_n$: C, 67.99; H, 6.93; N, 5.66. [e] 1:1 alternating copolymer. [f] [BIT] = 10.0 mmol and [BPL] = 5.0 mmol in 1.5 ml of CH_3CN.

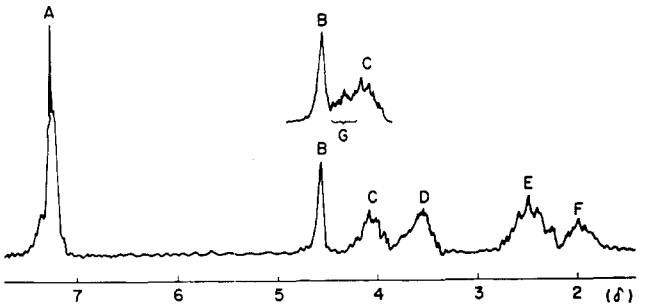


Figure 1. Nmr spectrum of copolymer in $CDCl_3$.

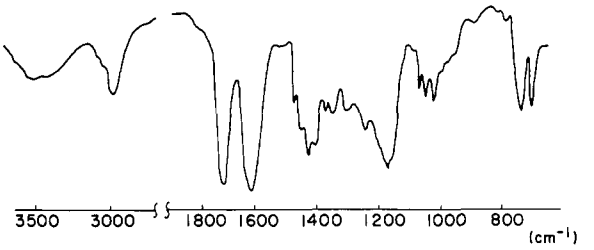
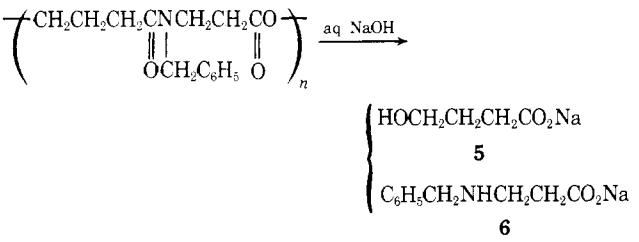
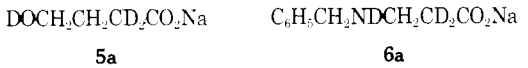


Figure 2. Ir spectrum of the alternating copolymer (sample number 1) (KBr).

(Figure 3) consists exclusively of the spectra of two species of γ-hydroxybutyric acid **5** (as Na salt) and β-alanine derivative **6** (as Na salt). After a prolonged reaction time (50



hr at 100°) active hydrogens of **5** and **6** were completely deuterated by D_2O (Figure 3). Therefore, **5** and **6** were identified as the deuterated forms, **5a** and **6a**, respectively.



CCH_2C of **5a**. Three singlets at δ 7.10 (peak A), 3.50 (C), and 2.65 (D) are due respectively to phenyl protons (5 H), benzyl methylene protons (2 H), and methylene protons (2 H) of NCH_2C of **6a**. Furthermore, the nmr spectrum of Figure 3 was identical with that of the 1:1 mixture of the authentic samples of **5** and **6** taken under the same conditions as those of an alkaline hydrolysis experiment in D_2O. In contrast to this, the alkaline hydrolysis of copolymer number 9 gave β-hydroxypropionic acid **8** (as Na salt) in addition to **5** and **6**. A sharp singlet at δ 3.80 (peak F in Figure 3) is ascribed to methylene protons of OCH_2C of **8a**. This indicates that the copolymer number 9 contains not only the BIT–BPL alternating units but also a small amount of the BPL–BPL sequence **7**. The BPL content in the copolymer could also be determined by the integration ratio of peak F and peaks B and C as 59%, which was in good agreement with the nmr determination of the copolymer composition.

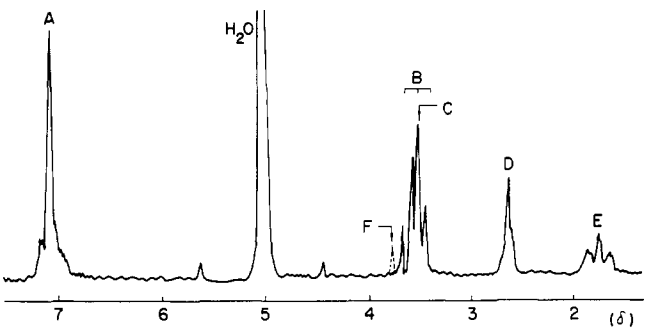
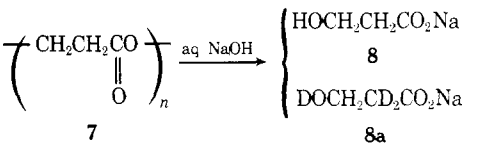


Figure 3. Nmr spectrum of alkaline hydrolysis product of copolymer in D_2O.



As seen in Table I, copolymerizations in chlorobenzene gave 1:1 alternating copolymer at the reaction temperatures of 80 and 15°. However, DMF and CH_3CN are not suitable solvents to yield alternating copolymers at a wide range of reaction temperatures. In CH_3CN solvent, an alternating copolymer was obtained at 80° with the initial feed ratio of BIT:BPL = 2:1 (number 5). In other cases of the 1:1 initial feed, the BIT unit was less than 50 mol %; *i.e.*, copolymers contain a small amount of the BPL–BPL sequence besides the alternating sequence.

All copolymers thus obtained were white gummy material whose molecular weight exceeded at least 5000. They are

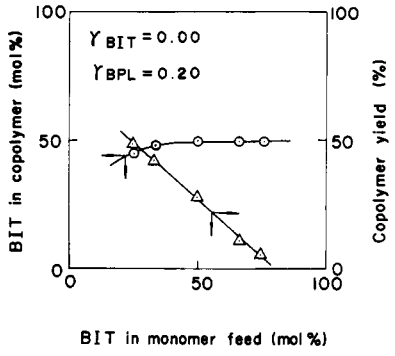


Figure 4. Copolymerization of BIT with BPL. Copolymer compositions and yields at various comonomer feeds (80° for 10 min in chlorobenzene): [BIT] + [BPL] = 10 mmol in 1.5 ml of chlorobenzene; $\gamma_{BIT} = 0.00$, $\gamma_{BPL} = 0.20$.

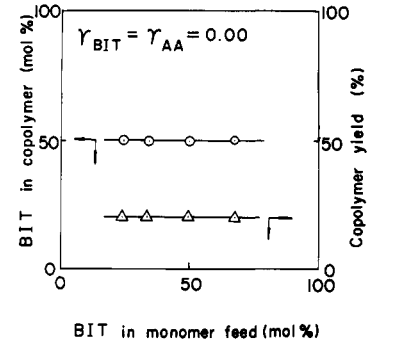


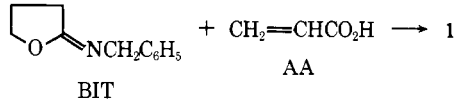
Figure 5. Copolymerization of BIT with AA. Copolymer compositions and yields at various comonomer feed (100° for 24 hr in CH_3CN): [BIT] + [AA] = 10 mmol in 1.5 ml of CH_3CN; $\gamma_{BIT} = \gamma_{AA} = 0.00$.

soluble in DMF, CH_3CN, and chloroform but not in benzene, acetone, diethyl ether, and water.

The relations between the composition of the comonomer feed and that of the product copolymer (determined by nmr) are shown in Figure 4. Under the conditions of 80° for 10 min in chlorobenzene the copolymer yield varied from 5 to 48% (Figure 4). The apparent copolymerization parameters were determined according to the integral method of Mayo and Lewis,[5] $\gamma_{BIT} = 0.00$ and $\gamma_{BPL} = 0.20$. These values of the monomer reactivity ratio are indicative of the high alternating tendency.

In CH_3CN solvent, on the other hand, the values of the monomer reactivity ratio were $\gamma_{BIT} = 0.00 \pm 0.03$ and $\gamma_{BPL} = 0.65 \pm 0.03$ at 50° for 3.0 hr. This result is compatible with the above observations that chlorobenzene is a more suitable solvent than CH_3CN to obtain the 1:1 alternating copolymer.

Alternating Copolymerization of BIT with AA. Copolymerization of BIT with AA was examined in CH_3CN. At higher temperatures than 90° the reaction took place without any initiator to give a 1:1 alternating copolymer whose structure was established to be identical with that of the BIT–BPL alternating copolymer **1** (Table II). In the BIT–AA copolymerization a hydrogen-transfer step of AA



is involved to provide the $-CH_2CH_2CO_2-$ unit in the copolymer, as in our recent finding of the alternating copolymerization between OZO and AA. The molecular weight of the copolymer from BIT and AA was somewhat lower than that from BIT and BPL.

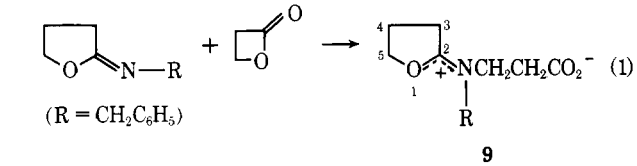
Table II
Alternating Copolymerization of BIT with AA[a]

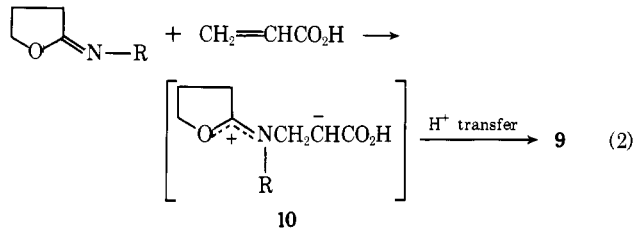
No.	Temp, °C	Time, day	Copolymer yield, %	BIT unit in copolymer,[b] mol %	Mol wt
10	120	14	25	50[c]	
11	110	20	21	50[c,d]	1650
12	100	1	19	50[c]	
13	90	4	4	50[c]	

[a] [BIT] = [BPI] = 5.0 mmol in 1.5 ml of CH_3CN. [b] Determined by nmr spectroscopy. [c] 1:1 alternating copolymer. [d] *Anal.* Calcd for the 1:1 copolymer $(C_{14}H_{17}NO_3)_n$: C, 67.99; H, 6.93; N, 5.66. Found: C, 67.80; H, 7.27; N, 5.66.

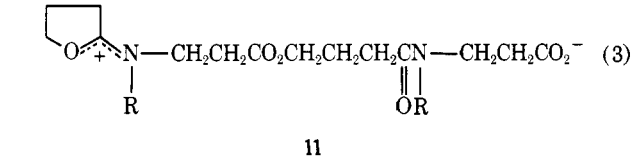
The values of the monomer reactivity ratio were determined to be $\gamma_{BIT} = \gamma_{AA} = 0.00$ in CH_3CN at 100° (Figure 5), indicating a complete alternation of BIT and AA monomers.

Mechanism of Alternating Copolymerization. All the above findings are well explained by the mechanism of "the polymerization *via* betaine" which has recently been proposed by us.[1-3] In the early stage of polymerization the betaine is formed in both BIT–BPL and BIT–AA copolymerizations (eq 1 and 2). In the latter case the Michael type adduct **10** is probably involved as an intermediate which is followed by the inter- and/or intramolecular proton transfer to produce the betaine **9** (eq 2). Then, the reaction of 2 mol of **9** leads to the formation of a dimeric zwitterion **11**,

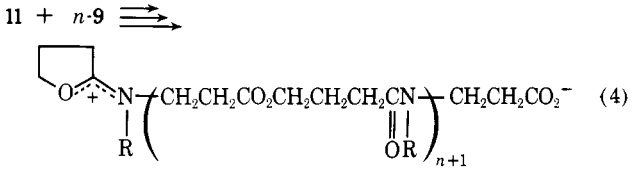




9 + 9 ⟶



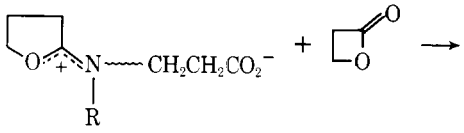
11 + *n*-9 ⟹



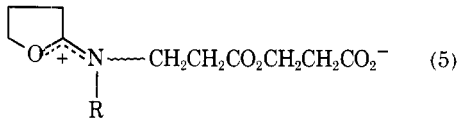
in which the carboxylate of one betaine attacks nucleophilically the five-carbon atom of the positively charged THF ring of another betaine to induce the ring opening of THF as well as the isomerization (eq 3). **11** is the smallest propagating species and copolymerization grows from **11** through the successive attack of the betaine **9** to yield the so-called

macrozwitterion[6] **12** (eq 4). The betaine **9** is a common key intermediate in both the BIT–BPL and BIT–AA alternating copolymerizations. Therefore, once **9** is formed the subsequent steps should proceed similarly in both cases (eq 3 and 4).

In the copolymerization of BIT with BPL, the carboxylate group of the macrozwitterion **12** reacts not only with the onium site of the betaine **9** to give the alternating units (eq 4) but also in some cases with BPL to give the BPL–BPL sequence (**13**) in the copolymer (eq 5). The occurrence of this reaction (eq 5) is responsible for the γ_{BPL} values larger than zero. With the equimolar feed of copolymerizations such a reaction (eq 5) becomes more noticeable in



12



(5)

13

DMF than in CH_3CN (Table I). In chlorobenzene the reaction of eq 4 took place exclusively.

In the propagation of the BIT–AA system, on the other hand, **12** cannot react with AA. Furthermore, the nucleophilic attack of BIT on the onium site of **12** does not occur.[2] Thus, **12** reacts only with the betaine **9** to give the alternating units **1** under a variety of reaction conditions. This is quite compatible with the values of $\gamma_{BIT} = \gamma_{AA} = 0.00$ showing a complete alternating tendency. The yield of alternating copolymer is decreased in the BIT–AA copolymerization (Table II). This is probably attributed to the slow betaine formation from BIT and AA (eq 2).

Experimental Section

Materials. Solvents of CH_3CN and DMF were purified as previously reported.[2] Chlorobenzene and BPL were commercial reagents and purified by distillation before use. BIT was prepared according to Mukaiyama, *et al.*,[4] and purified by fractional distillation: bp 87–89° (1.0 mm) (lit.[4] 88° (1 mm)); nmr ($CDCl_3$) δ 7.26 (s, 5 H, C_6H_5), 4.45 (s, 2 H, CH_2N=), 4.10 (t, 2 H, OCH_2), 2.46 (t, 2 H, CCH_2CO), 1.88 (m, 2 H, $-CCH_2C-$). *N*-Benzyl-β-alanine **6** was prepared by the reaction of BPL and benzylamine according to Gresham, *et al.*:[7] mp 181° (lit.[7] 182–183°); nmr (D_2O) δ 7.23 (s, 5 H, C_6H_5), 3.92 (s, 2 H, $C_6H_5CH_2$), 2.92 (t, 2 H, NCH_2CH_2), 2.30 (t, 2 H, CH_2CO_2). γ-Hydroxybutyric and β-hydroxypropionic acids were commercial reagents.

Copolymerization. A typical example was as follows. A mixture of 5.0 mmol of BIT and 5.0 mmol of BPL in 1.5 ml of DMF solvent was allowed to copolymerize under nitrogen at 15°. After 120 hr the mixture was poured into a large excess amount of diethyl ether to precipitate the polymeric product. The product was isolated by filtration, dissolved in chloroform, and again poured into a large amount of diethyl ether. The polymer was isolated by filtration and dried *in vacuo*. The polymer structure was determined by ir and nmr spectroscopy and elemental analysis as well as by the alkaline hydrolysis products of the polymer.

Alkaline Hydrolysis of Copolymer. To 0.050 g of copolymer was added 0.5 ml of a 15% NaOH aqueous solution of D_2O. The mixture was kept in a sealed tube at 100° for 50 hr. The reaction product was directly subjected to nmr measurement.

Molecular Weight Determination. The molecular weight of the copolymer was measured by a vapor pressure osmometer (Hitachi Perkin-Elmer Model 115) in DMF at 55°.

References and Notes

(1) For part III of this series, see T. Saegusa, S. Kobayashi, and Y. Kimura, *Macromolecules*, **7**, 139 (1974).
(2) T. Saegusa, H. Ikeda, and H. Fujii, *Macromolecules*, **5**, 354 (1972).
(3) T. Saegusa, S. Kobayashi, and Y. Kimura, *Macromolecules*, **7**, 1 (1974).
(4) T. Mukaiyama and K. Sato, *Bull. Chem. Soc. Jap.*, **36**, 99 (1963).
(5) F. R. Mayo and F. M. Lewis, *J. Amer. Chem. Soc.*, **66**, 1594 (1944).
(6) N. Mathes and V. Jaacks, *Makromol. Chem.*, **142**, 209 (1971).
(7) T. L. Gresham, J. E. Jansen, F. W. Shaver, R. A. Bankert, and F. T. Fiedorek, *J. Amer. Chem. Soc.*, **73**, 3168 (1951).

Mechanism of Charge-Transfer Polymerization. VII. Effect of Solvent Basicity on the Competing Cyclodimerization and Radical Polymerization in the Photosensitized Reaction of *N*-Vinylcarbazole in the Presence of the Electron Acceptor[1]

Kazuhiro Tada, Yasuhiko Shirota, and Hiroshi Mikawa*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadakami, Suita, Osaka 565, Japan.

Received January 25, 1974

ABSTRACT: Photochemical reactions of *N*-vinylcarbazole (VCZ) in the presence of the electron acceptor were studied in various polar, basic solvents in order to clarify the effect of the basicity of solvent on the reaction. It was found that radical polymerization of VCZ was increasingly favored in competition with cyclodimerization of VCZ to give *trans*-1,2-dicarbazol-9-ylcyclobutane with the increase in the solvent basicity. It was suggested that whether the reaction in polar, basic solvents leads to the cyclodimerization or radical polymerization is determined by the magnitude of the solvent basicity at the stage of the VCZ dimer cation radical intermediate. The whole picture of the photosensitized reaction of VCZ in the presence of the electron acceptor is discussed in view of the effect of the solvent basicity on the reaction.

The photosensitized charge-transfer polymerization has currently been the subject of great interest. In the previous paper[2] we have clarified the general features of the photosensitized charge-transfer reaction of *N*-vinylcarbazole (VCZ) in the presence of the organic electron acceptor. The reaction involves cationic and radical polymerizations of VCZ, radical copolymerization of VCZ with the electron-accepting monomer, and cyclodimerization of VCZ to give *trans*-1,2-dicarbazol-9-ylcyclobutane, the reaction course being strongly solvent dependent. These multireaction courses are systematically explained in terms of dual cationic and radical reactivities of the intermediate VCZ cat-