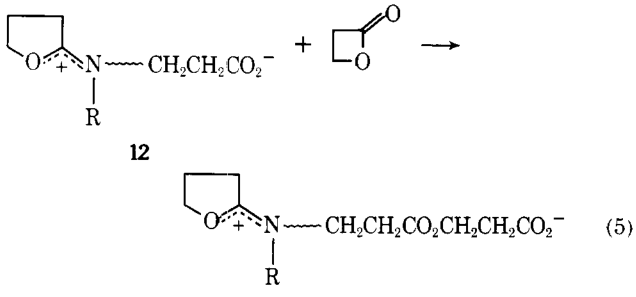
macrozwitterion[6] **12** (eq 4). The betaine **9** is a common key intermediate in both the BIT–BPL and BIT–AA alternating copolymerizations. Therefore, once **9** is formed the subsequent steps should proceed similarly in both cases (eq 3 and 4).

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



12

13

(5)

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°.

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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]

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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-

Table I

Photosensitized Reaction of VCZ in the Presence of the Electron Acceptor in Various Polar, Basic Solvents[a]

	Acceptor			
	CA		PTA	
Solvent	Product yield, mg	Mol wt of polymer	Product yield, mg	Mol wt of polymer
Acetone	371.5 (D)		392.3 (D)	
Acetonitrile	60.5 (D)[b]		360.9 (D)	
Methanol	23.1 (D)[c]			
N-Methyl-2-pyrrolidone	190.5 (D) + 69.5 (P)	9400	194.3 (D) + 95.4 (P)	6,200
DMF	112.1 (D) + 81.1 (P)	6900	95.1 (D) + 91.3 (P)	5,100
Me_2SO	41.9 (D) + 83.2 (P)	5800	97.4 (D) + 214.4 (P)	11,000
HMPA	80.4 (P)	4900	178.5 (P)	6,800

[a] The symbols D and P represent VCZ cyclodimer and VCZ polymer, respectively. $h\nu > 350$ nm in acetone, *N*-methyl-2-pyrrolidone, Me_2SO, and HMPA; $h\nu > 310$ nm in acetonitrile, methanol, and DMF. Reaction time 5 hr. Reaction temp 10–20° (in Me_2SO at 30°). [VCZ] = 482.5 mg/5 ml, [CA] = 6.2 mg/5 ml, and [PTA] = 3.7 mg/5 ml. [b] [VCZ] = 241.2 mg/5 ml and [CA] = 3.1 mg/5 ml. [c] [VCZ] = 96.5 mg/20 ml and [CA] = 6.2 mg/20 ml.

Table II

Correlation between the Strength of the Solvent Basicity and the Competing Cyclodimerization and Radical Polymerization of VCZ[a]

	Relative magnitude of basicity			Apparent yield ratio (P/D)		$p/(1-p)\phi_{CD}$[e]	
Solvent	$\Delta\nu_D$, cm^{-1} [b]	$\Delta\delta_\infty$ [$CHCl_3$], ppm		VCZ–CA system	VCZ–PTA system	VCZ–CA system	VCZ–PTA system
Acetonitrile	49	0.31[c]		D only	D only	D only	D only
Acetone	64		0.94[d]	D only	D only	D only	D only
Methanol				D only		D only	
N-Methyl-2-pyrrolidone				0.36	0.49	1.50×10^{-2}	3.06×10^{-2}
DMF	107	0.78[c]	1.30[d]	0.72	0.96	4.07×10^{-2}	7.28×10^{-2}
Me_2SO	141	1.05[c]	1.34[d]	1.99	2.20	1.31×10^{-1}	7.74×10^{-2}
HMPA		1.89[c]	2.03[d]	P only	P only	P only	P only

[a] In less basic solvents such as benzene, nitrobenzene, dichloromethane, or dichloroethane, cationic polymerization of VCZ occurs. The values of $\Delta\nu_D$ (cm^{-1})[b]: benzene (0), nitrobenzene (21), dichloromethane (−12), dichloroethane (2). [b] Taken from ref 5. [c] Taken from ref 6. [d] Taken from ref 7. [e] p and $(1-p)$ are the probabilities of II leading to radical polymerization and cyclodimerization, respectively. ϕ_{CD} is defined as the ratio of the number of moles of the cyclodimer formed to the number of moles of II available for the cyclodimerization.

ion radical (I). Cationic reactivity in I predominates in less basic solvents leading to cationic polymerization of VCZ, while in basic solvents the cationic reactivity is suppressed due to cation solvation by the basic solvent, hence radical reactivity in I becomes preferential, leading to the cyclodimerization or radical polymerization.[2]

In order to gain more insight into the reaction course in basic solvents, cyclodimerization, or radical polymerization (?) and the correlation between the reaction course and the strength of the solvent basicity, the photosensitized reaction of VCZ in the presence of the electron acceptor was studied in various polar, basic solvents which differ greatly in the strength of the basicity.[3]

Experimental Section

Materials. VCZ, chloranil, and phthalic anhydride were purified as described in the previous paper.[2]

Acetone, acetonitrile, methanol, *N,N*-dimethylformamide, and dimethyl sulfoxide (Me_2SO) were purified and dried as described before.[2] *N*-Methyl-2-pyrrolidone was fractionally distilled three times over calcium hydride *in vacuo* immediately before use. Hexamethylphosphoric triamide was heated with small amounts of sodium metal for a long time in an atmosphere of dry nitrogen and fractionally distilled three times from it immediately before use.

Reaction Procedure. All reactions were carried out in the same manner as described in the previous paper.[2] The reaction system which was evacuated at 10^{-6} Torr was irradiated at 10–20° (in Me_2SO at 30°) for 5 hr with light of wavelength longer than 310 or 350 nm so as to avoid the excitation of the solvent at a distance of about 2 cm from a 500-W high-pressure mercury lamp (type PIH-500, Eikosha Co. Ltd.). An aqueous filter solution of $Cu(NO_3)_2 \cdot 3H_2O$ was used to obtain the latter light. The concentrations of the VCZ monomer and the electron acceptor were usually 0.5 *M* and 5.0×10^{-3} *M*, respectively.

Isolation and Analyses of Reaction Products. The reaction products were separated by fractionation with solvents and identified as described in the previous papers.[2,4] The ratio of the yields of the polymer to the cyclodimer was also checked by means of liquid chromatography (Japan Analytical Ind. Model LC-07). Number-average molecular weights of the polymers were determined with a Mechrolab VPO Model 302 in pyridine at 65°.

Results and Discussion

The photosensitized reaction of *N*-vinylcarbazole (VCZ) in the presence of the electron acceptor was studied in various polar, basic solvents which differ greatly in the strength of the basicity by use of chloranil (CA) or phthalic anhydride (PTA) as an electron acceptor. The results are summarized in Table I. It was found that the strength of the solvent basicity exerts a striking effect on the reaction course. While the cyclodimerization of VCZ occurred exclusively to give *trans*-1,2-dicarbazol-9-ylcyclobutane in such basic solvents as acetone, acetonitrile, or methanol,[2] simultaneous radical polymerization and cyclodimerization of VCZ took place in stronger basic solvents such as *N*-methyl-2-pyrrolidone, *N,N*-dimethylformamide (DMF), or dimethyl sulfoxide (Me_2SO). In hexamethylphosphoric triamide (HMPA), the strongest basic solvent used here, no more cyclodimerization of VCZ occurred and only radical polymerization of VCZ took place. That the photopolymerization of VCZ in these strongly basic solvents is radical in nature stems from the fact that the addition of catalytic amounts of 1,1-diphenyl-2-picrylhydrazyl greatly reduced the polymerization. Also, it has been confirmed that the results of the photocopolymerization of VCZ with styrene in the presence of CA or PTA as an electron acceptor in DMF

Table III
Effect of Additive (Me_2SO) on the Photosensitized Reaction of VCZ in VCZ–CA–Acetone System[a]

Additive concn, g/5 ml	Product yield, mg	Mol wt of polymer	Apparent yield ratio (P/D)	$p/(1-p)\phi_{CD}$[b]
0 (acetone only)	371.5 (D)		D only	D only
0.391	267.3 (D) + 10.1 (P)	2,400	3.78×10^{-2}	6.08×10^{-3}
0.781	224.8 (D) + 22.7 (P)	2,800	0.100	1.39×10^{-2}
1.172	167.4 (D) + 32.3 (P)	3,600	0.193	2.07×10^{-2}
1.562	104.7 (D) + 41.0 (P)	3,800	0.392	3.99×10^{-2}
1.953	60.3 (D) + 59.8 (P)	5,600	0.992	6.86×10^{-2}
Me_2SO only	41.9 (D) + 83.2 (P)	5,800	1.99	1.31×10^{-1}

[a] Reaction conditions and the symbols D and P are the same as described in Table I. [b] See footnote *e* in Table II.

Table IV
Summary of the Generalized Reaction Courses in the Photosensitized Reaction of VCZ in the Presence of the Electron Acceptor

Solvent	Reaction course
Less basic solvents *e.g.*, benzene, nitrobenzene, dichloromethane, dichloroethane	Cationic polymerization of VCZ
Basic solvents	
Increasing solvent basicity ↓	
Moderately basic solvents, *e.g.*, acetone, acetonitrile, methanol	Cyclodimerization of VCZ
Strongly basic solvents	
E.g., *N*-methyl-2-pyrrolidone, DMF, Me_2SO	Cyclodimerization of VCZ plus radical polymerization of VCZ
E.g., HMPA	Radical polymerization of VCZ

are in accordance with the radical mechanism.[2] The polymer yield was relatively lower with CA which may act as a radical trap than with PTA.

Table II shows the correlation between the reaction course and the strength of the solvent basicity, the relative magnitude of which has been determined in the literature by means of the ir[5] or nmr[6,7] method. It is evident that as the solvent basicity becomes stronger the cyclodimerization reaction which occurred exclusively in moderately basic solvents comes to be suppressed, being replaced by the radical polymerization. The extreme case is found with the strongest basic solvent HMPA, in which only the radical polymerization occurs. In such solvents as *N*-methyl-2-pyrrolidone, DMF, or Me_2SO in which simultaneous cyclodimerization and radical polymerization occurred, the apparent ratio of the yields of the polymer to the cyclodimer was found to increase in the increasing order of the solvent basicity. It should be noted, however, that these values do not directly reflect the effect of the solvent basicity on the reaction since the cyclodimerization as well as the polymerization is a chain reaction,[8] and the kinetic chain lengths are different in polymerization and in cyclodimerization. Now, let α denote the number of moles of the VCZ dimer cation radical intermediate (II) formed in the reaction system, and p $(0 < p < 1)$ the probability of II to lead to the radical polymerization, then $(1 - p)$ is the probability for the cyclodimerization (Scheme I). Since

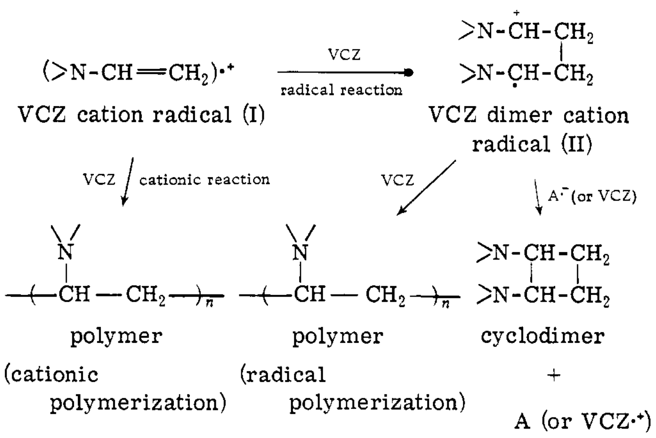
$$\alpha p = \frac{\text{polymer yield (g)}}{\text{mol wt of the polymer}}$$

and

$$\alpha(1 - p)\phi_{CD} = \frac{\text{cyclodimer yield (g)}}{\text{mol wt of the cyclodimer } (=193 \times 2)}$$

where ϕ_{CD} is defined as the ratio of the number of moles of the cyclodimer formed to the number of moles of II available for the cyclodimerization, one can calculate the value $p/(1 - p)\phi_{CD}$ in each solvent as is listed in Table II. As shown from Table II, the value $p/(1 - p)\phi_{CD}$ conspicuously increases with the increase in the magnitude of the solvent basicity. Although ϕ_{CD} might vary with the varying solvent, it is understood as most probable that p increases with the increase in the magnitude of the solvent basicity. The quantum yield for the photosensitized cyclodimerization of VCZ by, *e.g.*, CA in an acetone solution under N_2 atmosphere has been reported to be *ca.* 4.3.[8] ϕ_{CD} as defined in the present paper may naturally be greater than the quantum yield which represents the ratio of the number of moles of the cyclodimer formed to the number of photons absorbed. Now, when ϕ_{CD} is roughly estimated as, *e.g.*, *ca.* 10 in each solvent, then the probability p for the radical polymerization may vary from *ca.* 13% (in *N*-methyl-2-pyrrolidone) to *ca.* 29% (in DMF) and to *ca.* 57% (in Me_2SO) in the VCZ–CA system. On the whole it may be concluded that the radical polymerization is increasingly favored in competition with the cyclodimerization with the increase in the solvent basicity. The effect of the solvent basicity on the competing cyclodimerization and radical polymerization processes was further demonstrated in the binary solvent system, acetone–Me_2SO. While the cyclodimerization of VCZ took place exclusively in acetone, radical polymerization came to occur increasingly at the expense of the cyclodimerization reaction by the increasing addition of Me_2SO. The results are shown in Table III.

Scheme I
Photosensitized Reaction of VCZ in the Presence of the Electron Acceptor



>N–: carbazolyl group

A: electron acceptor

The entire picture of the photosensitized reaction of VCZ in the presence of the electron acceptor has now been brought to light, which is summarized in Table IV and

Scheme I. The reactions are systematically explained as initiated by the VCZ cation radical intermediate (I) formed by the photochemical electron transfer from VCZ to the electron acceptor, the direct evidence of which has been obtained by means of flash spectroscopy.[9,10] The present results concerning the correlation between the reaction course in basic solvents and the strength of the solvent basicity are consistent with the mechanism shown in Scheme I. That is, cation solvation toward I in the basic solvents leads to the formation of II by the radical reaction of I with the VCZ monomer and then the electron back-transfer to II and the cyclization produces the cyclodimer.[2] When the solvent basicity becomes very strong, the electron back-transfer to II comes to be impeded due to the very strong cation solvation; hence subsequent radical additions of the VCZ monomer occur leading to the formation of the polymer. In the previous paper[2] we have shown that whether I shows cationic or radical reactivity is mainly determined by the strength of the solvent basicity. In addition, the present study shows that the direction of the succeeding reaction following the initial radical reaction of I, *i.e.*, cyclodimerization or radical polymerization (?), is also determined by the strength of the solvent basicity most probably at the stage of II. Thus, photosensitized reactions of VCZ in the presence of the electron acceptor are entirely regulated by the solvent basicity.

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(3) Preliminary results concerning this problem have been obtained in the VCZ–oxygen system where oxygen acts as an electron acceptr toward the excited VCZ.[4] However, it is by all means necessary for the systematic and more detailed understanding of the nature of the reaction to clarify this problem by carrying out the investigation under high vacuum system using a typical organic electron acceptor since in the VCZ–oxygen system the amounts of dissolved oxygen may possibly be different with each solvent.

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A Resolution of the State of Association of Poly(dienyl)lithium Chain Ends in Hydrocarbon Solvents

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ABSTRACT: The association states of the poly(dienyl)lithium species in cyclohexane have been reexamined. This study was undertaken in view of a recent report which purports to show that, in cyclohexane solution, poly(butadienyl)lithium is associated as a tetramer while poly(isoprenyl)lithium possesses average degrees of association ranging from 3 to 4. It is shown here that these conclusions are in error and result from artifacts arising from faulty experimental procedures. The errors in the above-mentioned report are discussed and new data presented which confirm the fact that the poly(dienyl)lithium chains are associated *in pairs* at concentrations appropriate for polymerization. These results are derived, in part, from concentrated solution viscosity measurements of the polydiene solutions before and after linking with $(CH_3)_2Si(Cl)_2$, $(CH_3)Si(Cl)_3$, and $SiCl_4$. The use of the latter two chlorosilanes brought about the nearly quantitative formation of "star" branched polymers and a concurrent *increase* in solution viscosity whereas the use of $(CH_3)_2Si(Cl)_2$ brought about virtually *no* change in viscosity. This behavior is consistent with an association state of two for the poly(dienyl)lithium chains.

The degree of association of the chain ends of poly(styryl)-, poly(isoprenyl)-, and poly(butadienyl)lithium was originally determined[1-4] from measurements of the viscosity of concentrated solutions, using the well-known equation

$$\eta = KM^{3.4} \tag{1}$$

which relates the viscosity to the molecular weight in the "entanglement region." These measurements consistently and reproducibly showed that all of the above polymeric species are associated *in pairs.* Such results, though, have apparently met with dismay or have been ignored on the part of those[5-13] who wished to ascribe much higher states of association to the poly(dienyl)lithium chain ends (up to 4 or 6), based purely on considerations of polymerization kinetics, rather than on direct molecular weight measurements. More recently, a publication[14] has appeared which purported to present direct evidence for the tetrameric state of association of poly(dienyl)lithium.

The motivation behind assigning an association number of 4 or higher to the poly(dienyl)lithium chain ends results from the observed ¼–⅙ dependency of polymerization rate on chain end concentration and the acceptance of the proposition that only unassociated chain ends are reactive toward monomer. However, the convenient concept that only unassociated organolithium compounds are the reactive species in initiation and propagation reactions need not, necessarily, be correct. In fact, quite plausible mechanisms have been presented[15-25] which show that the fractional orders of these reactions can be accounted for quite satisfactorily by involving associated organolithium species (hexamer, tetramer, dimer) as reactive entities. The vast majority of the balanced appraisals and observations reveal that one must consider a wide range of possibilities in defining the active participant *or* participants in any organolithium reaction and that the establishment of any reaction order with respect to each participant is by no means a trivial operation.

The purpose of this article is to offer a critique of the publication[14] mentioned above and to present new data which support the original findings[1-4,25] that the poly(dienyl)lithium species are associated in dimers, in hydrocar-