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STUDIES ON PHOTOPHYSICAL PROCESSES IN

POLY(N-VINYLCARBAZOLE) AND RELATED COMPOUNDS

（ポリ（N-ビニルカルバゾール）及び その関連化合物の
光物理過程に関する研究 ）

AKIRA ITAYA

List of Publications

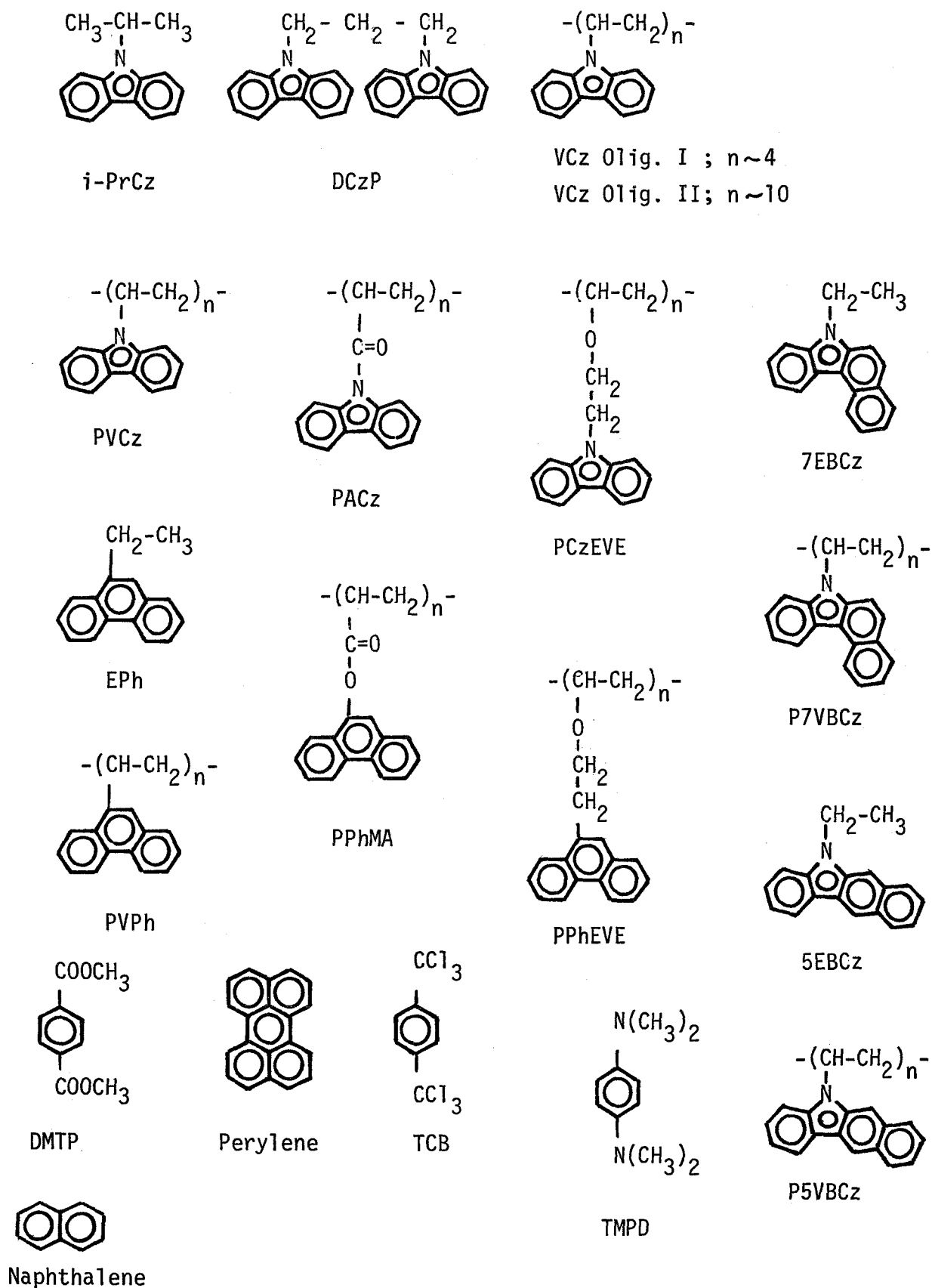The papers published by the author concerning this thesis are as follows.

(1) Heterogeneous Triplet-Triplet Annihilation in Poly-N-vinylcarbazole Films Doped with Naphthalene and Fluorene.

    A. Itaya, K. Okamoto, and S. Kusabayashi

    Chem. Lett., 1975, 833.

(2) Magnetic Field Effect on the Photoconductivity of Poly-N-vinylcarbazole.

    K. Okamoto, N. Oda, A. Itaya, and S. Kusabayashi

    Chem. Phys. Lett., 35, 483 (1975).

(3) Magnetic Field Effect on the Exciplex Fluorescence of Poly-N-vinylcarbazole.

    K. Okamoto, A. Itaya, and S. Kusabayashi

    Chem. Lett., 1976, 99.

(4) The Photoconductivity of Poly(N-vinylcarbazole). VII. The Effect of the Singlet and Triplet Quenchers on the Photoconductivity.

    K. Okamoto, N. Oda, A. Itaya, and S. Kusabayashi

    Bull. Chem. Soc. Jpn., 49, 1415 (1976).

(5) Triplet Excitation Energy Transfer in the Vinyl Polymers with Pendant Carbazolyl Groups.

    A. Itaya, K. Okamoto, and S. Kusabayashi

    Bull. Chem. Soc. Jpn., 49, 2037 (1976).

(6) Emission Spectra of the Vinyl Polymers with Pendant Carbazolyl Groups.

    A. Itaya, K. Okamoto, and S. Kusabayashi

    Bull. Chem. Soc. Jpn., 49, 2082 (1976).

(7) Polymerization of N-Vinylcarbazole, 5-Vinyl-benzo[b]carbazole, and 7-Vinyl-benzo[c]carbazole.

K. Okamoto, M. Yamada, A. Itaya, T. Kimura, and

S. Kusabayashi

Macromolecules, 9, 645 (1976).

(8) Singlet Excitation Energy Transfer in the Vinyl Polymers with Pendant Carbazolyl Groups.

A. Itaya, K. Okamoto, and S. Kusabayashi

Bull. Chem. Soc. Jpn., 50, 22 (1977).

(9) Emission Spectra of the Vinyl Polymers with Pendant Phenanthryl Groups.

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Bull. Chem Soc. Jpn., 50, 52 (1977).

(10) Emission Spectra of the Vinyl Polymers with Pendant Benzocarbazolyl Groups.

A. Itaya, K. Okamoto, and S. Kusabayashi

Bull. Chem. Soc. Jpn., 51, 79 (1978).

(11) Electronic Spectra of 1,3-Di(N-carbazolyl)propane in the Amorphous State

A. Itaya, K. Okamoto, and S. Kusabayashi

Chem. Lett., 1978, 131.

(12) Photo-oxidation Effect of Poly(N-vinylcarbazole) film on Photoconductivity and Electronic Spectra.

A. Itaya, K. Okamoto, and S. Kusabayashi

Bull. Chem. Soc. Jpn., 52, 2218 (1979).

(13) The Singlet-Excitation-Energy Migration in an Amorphous State Film of 1,3-Di(N-carbazolyl)propane.

A. Itaya, K. Okamoto, and S. Kusabayashi

Bull. Chem. Soc. Jpn., 52, 3737 (1979).

CONTENTS

CH₃-CH-CH₃ → $CH_3-CH-CH_3$

Structures with labels:

$CH_3-CH-CH_3$
i-PrCz

$CH_2-CH_2-CH_2$
DCzP

$-(CH-CH_2)_n-$
VCz Olig. I ; n∼4
VCz Olig. II; n∼10

$-(CH-CH_2)_n-$
PVCz

$-(CH-CH_2)_n-$
C=O
PACz

$-(CH-CH_2)_n-$
O
CH_2
CH_2
PCzEVE

CH_2-CH_3
7EBCz

CH_2-CH_3
EPh

$-(CH-CH_2)_n-$
C=O
O
PPhMA

$-(CH-CH_2)_n-$
P7VBCz

$-(CH-CH_2)_n-$
O
CH_2
CH_2
PPhEVE

$-(CH-CH_2)_n-$
PVPh

CH_2-CH_3
5EBCz

$COOCH_3$
$COOCH_3$
DMTP

Perylene

CCl_3
CCl_3
TCB

$N(CH_3)_2$
$N(CH_3)_2$
TMPD

$-(CH-CH_2)_n-$
P5VBCz

Naphthalene

List of chemical structures and abbreviations of compounds
used in this thesis.

INTRODUCTION

Recently, many kinds of organic compounds with special function have been developed. Among them, vinyl polymers with large pendant aromatic groups have received much attention because of high photoconductivity and interesting emission properties. Photoconductivity of this kind of polymers has been extensively studied with regard to poly(N-vinylcarbazole)(PVCz).[1] However, electrical properties of a PVCz film still remain to be clarified. For the basic understanding of photoconductive properties, it is essential to have the information on the processes from light-absorption to photo-carrier-generation (photophysical process).

Photophysical processes of aromatic hydrocarbons have been studied in detail and many phenomena have been found. They include excimer and exciplex formation, electron transfer, energy migration and transfer, and so on.[2] In the case of aromatic vinyl polymers, intramolecular excimer formation and energy migration along the polymer chain are particularly important and interesting.

Yanari et al.[3] were the first to suggest that the fluorescence emission of polystyrene(PSt) was excimeric in nature. The configurational basis of the intramolecular excimer formation was first described by Hirayama in his study on diphenyl and triphenyl alkanes.[4] His "n=3 rule" states that the intramolecular excimer formation occurs only when the aromatic chromophores are separated by a main chain segment of three carbon atoms. Vala et al. then studied on excimer formation in the diphenyl alkanes and paracyclophane series, atactic and isotactic PSt and atactic poly(1-vinylnaphthalene).[5] At the present time, the mechanism

for the excimer formation in aromatic vinyl polymers is considered as follows. In rigid or high viscous solution and solid film, a singlet exciton generated in the polymer by exciting-light migrates over the pendant chromophores along the polymer chain and is trapped at an excimer-forming site, whose the chain conformation is geometrically suitable for excimer formation. On the other hand, in fluid solutions with low viscosity, the excimer formation is controlled by a dynamic process of chromophores. A chain conformation changes to another one such as an excimer-forming chain conformation by collision with solvent molecules. Such a conformational change occurs within the residence time of the migrating exciton on a particular chromophore with some probability, resulting in a rotational formation of excimer. Therefore, the excimer formation is closely related with the dynamic processes of polymers in solution. Studies on the excimer fluorescence provide many information on the segmental motion of polymer chains and on molecular arrangement in solution.[6]

Singlet and triplet excitation energies migrate along the polymer chain because of a one-dimensional arrangement of pendant chromophores along the main chain in high density.[7] Singlet excitation energy migration in a polymer film was first investigated by Klöpffer.[8] He reported that the results of fluorescence quenching experiments in a PVCz film are consistent with a hopping model of monomer-exciton migration and that the singlet exciton migration is limited by excimer-forming sites.

Singlet exciton migration along the polymer chain in dilute and rigid solutions was ascertained by the experiment of energy transfer in homopolymer donor - low-molecular-weight acceptor

systems. In this case, a singlet exciton migrates by a series of random walk due to Förster interactions between nearest neighbors.[9]

From an observation of delayed fluorescence caused by triplet-triplet annihilation and quenching experiments, Fox et al. showed that a triplet exciton migrates along the polymer chain in poly(1-vinylnaphthalene) both in rigid solution and in the solid film at 77 K.[10] Thereafter, the triplet exciton migration has been observed for a number of aromatic vinyl polymers and values of the migration coefficient have been obtained by the quenching experiment.

Considering that photo-carrier-generation in the lowest $\pi-\pi^*$ absorption region is attributed to the interaction between a migrating excited state and any electron-accepting impurity,[11] it is suggested that phenomena of the excimer formation and the above-mentioned energy migration are closely related to photo-carrier-generation and charge-carrier migration, because excimer-forming sites act as traps for the electronic energy migration and might act as traps for charge-carrier migration. Since both the triplet energy migration and the charge-carrier migration are due to the short-range interaction (electron-exchange interaction), the study on the triplet energy migration might provide some information on the charge-carrier migration.

In recent years, studies on ionic photodissociation in dilute homogeneous solution have been carried out in detail.[12] The ionic photodissociation is the basis of the photo-oxidation-reduction reactions and closely related to the fields of solar cells and photosynthesis. In such fields, distribution of photo-excited species is non-uniform and the local concentration is high.

That is, their systems are considered to be a kind of molecular aggregate ones. Therefore, it is interesting to see whether the results obtained in dilute homogeneous solution hold also for molecular aggregate systems or not.[13] The basic information on the above-mentioned problem is also given by the study of the photophysical process in aromatic vinyl polymers, which are a kind of molecular aggregate systems with respect to pendant aromatic groups.

Furthermore, the photophysical process of polymers is also closely related to phenomena of photostabilization and photo-degradation of polymers.[14]

In this thesis, the author describes the photophysical process of aromatic vinyl polymers with different chemical and fine structures in solution and in film, and a few effects on the photo-carrier-generation process of a PVCz film.

Part I deals with fluorescence spectra of vinyl polymers with large pendant aromatic groups in solution.   In chapter 1, 5-vinyl-benzo[b]carbazole and 7-vinyl-benzo[c]carbazole, which have more bulky pendant groups than N-vinylcarbazole(VCz), were synthesized. These two monomers and VCz were polymerized under various conditions. Solubilities, glass transition tempera-tures, and NMR spectra of these polymers indicated that the stereoregularity of the polymers varies depending on the polymerization method. In chapter 2, a relation between the fluorescence spectra and the stereoregularity of polymers has been obtained. From this relation, the conformational structures of the second and sandwich-like excimers were discussed. In chapter 3, the emission spectrum of poly[2-(N-carbazolyl)ethyl vinyl ether] with carbazolyl chromophores widely spaced on the

main chain by -O-CH$_2$-CH$_2$- bonds has been investigated in comparing

with those of PVCz and its related compounds. In chapter 4,

emission spectra of the vinyl polymers with phenanthryl groups

have been investigated in solution. The fluorescence spectra

are of interest, because phenanthryl chromophore shows no excimer

fluorescence in concentrated solutions as in the case of

carbazolyl chromophore.

Part II deals with the photophysical process in polymer films.
In chapter 1, singlet-excitation-energy migration in films of the
vinyl polymer with pendant carbazolyl groups has been investigated
in connection with chemical structure and tacticity of the
polymers. The spectroscopic properties of an amorphous film of
1,3-di(N-carbazolyl)propane, which is a dimeric model compound
of PVCz, has also been investigated and compared with those of
the amorphous polymer films. In chapter 2, triplet-excitation-
energy migration in films of the vinyl polymer with pendant
carbazolyl groups has been investigated by measuring delayed
emission spectra in films and in rigid solutions at 77 K.

In the last part, part III, in order to clarify the photo-
carrier-generation mechanism considered most appropriate at the
present stage, the author has investigated the following effects
on the photoconductivity of a PVCz film. In chapter 1, it is
concluded, from the effects of triplet and singlet quenchers on
the photoconductivity of PVCz and brominated PVCz films, that
charge carriers are generated via the singlet exciton rather
than the triplet one. In chapter 2, it is concluded, from
magnetic field effects on the photoconductivity of PVCz films
undoped and doped with dimethyl terephthalate, that the carrier-
generation process with participation of a non-relaxed exciplex

state plays an important role in the photo-carrier-generation in the lowest $\pi-\pi^*$ absorption region. In chapter 3, in order to elucidate what kind compound acts as an electron-accepting impurity, the photo-oxidation effects on the photoconductivity and electronic spectra of PVCz films have been investigated. From the results, it is concluded that the photo-oxidation products formed near the surface of PVCz films act as an electron-accepting impurity in the photo-carrier-generation mechanism.

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PART I

EMISSION SPECTRA OF AROMATIC VINYL POLYMERS

IN SOLUTION

INTRODUCTION

It is known that aromatic vinyl polymers show excimer
fluorescence in dilute fluid solution due to the intramolecular
interaction between chromophores in a polymer chain. The excimer
fluorescence provides some information on molecular motion or
conformation of the polymer chain in solution. The excimer
fluorescence is closely related also to the photoconduction of
the polymers, because the excimer forming site acts as an energy
trap for the migration of a singlet exciton.

Considerable data on the emission properties of PVCz have
been accumulated because of an interest in high photoconductive
polymers.[1-33] However, no relation between the tacticity and
the fluorescence spectra of PVCz has been reported. Concerning
the vinyl polymers with small aromatic chromophores such as a
phenyl group, the relation has been reported in several
investigations.[34-41] However, such a relation has never
hitherto been studied for the vinyl polymers with large and
bulky aromatic chromophores such as carbazole and benzocarbazole.

In chapter 1, vinylcarbazole and vinyl monomer with benzo-
carbazolyl groups newly synthesized were polymerized under

various conditions. A relation between the stereoregularity of the vinyl polymers and polymerization methods was found at the first time in this kind of polymers with large pendant groups.

In chapter 2, the fluorescence spectra of the polymers obtained in chapter 1 have been investigated in solution and a relation between the fluorescence spectra and the stereoregularity of the polymers is discussed.

In chapter 3, the fluorescence spectrum of poly[2-(N-carbazolyl)ethyl vinyl ether] has been investigated in comparing with those of PVCz and its related compounds.

In chapter 4, fluorescence spectra of the vinyl polymers with phenanthryl groups, which show no excimer fluorescence in concentrated solutions as in the case of carbazolyl chromophore, have been investigated in order to elucidate characteristics of the excimer formation of aromatic vinyl polymers, model compounds of which show no excimer fluorescence.

Chapter 1

Polymerization of N-Vinylcarbazole, 5-Vinyl-benzo[b]carbazole,

and 7-Vinyl-benzo[c]carbazole

Introduction

The polymerization of N-vinylcarbazole(VCz) has widely been

investigated.[42] This monomer can be easily polymerized by many

kinds of initiators such as free-radical, cationic, Ziegler-

Natta, and electron acceptor ones. Heller et al. have pointed

out that VCz did not undergo a coordination polymerization with

Ziegler-Natta catalyst systems, but merely underwent a cationic

one.[43] The stereoregularity and the crystallinity of PVCz have

been reported to be independent of the polymerization method from

the NMR spectra and X-ray diffraction patterns.[44-47] Addition

of a monomer onto a growing chain end has, therefore, been

considered to be controlled sterically due to the bulkiness of

the carbazolyl group, irrespective of the nature of the growing

chain end.[44] This has been supported by the fact that

poly(trityl methacrylate) prepared free radically has a pronounced

isotacticity due to the steric hindrance of the pendant group.[48]

On the other hand, this is clearly different from the polymeriza-

tion behavior of N-acryloylcarbazole with a carbazolyl group

widely spaced on a vinyl bond; the stereoregularity of this

polymer has been reported to be dependent on the polymerization

method.[49] It is, therefore, of interest to re-investigate in

detail the relation between the stereoregularity of the vinyl

polymers containing large pendant π-electron groups and the polymerization method.

In this chapter, 5-vinyl-benzo[b]carbazole(5VBCz) and 7-vinyl-benzo[c]carbazole(7VBCz) were synthesized and polymerized by free-radical, cationic, and Ziegler-Natta initiators. The solubilities, glass transition temperatures, and NMR spectra of PVCz, poly(5-vinyl-benzo[b]carbazole)(P5VBCz), and poly(7-vinyl-benzo[c]carbazole)(P7VBCz) were examined.

Experimental

5-β-Chloroethyl-benzo[b]carbazole(5CEBCz) was synthesized from 5H-benzo[b]carbazole, which was prepared from sodium 2-naphthol-1-sulfonate.[50] To a suspension of 5H-benzo[b]carbazole in 400 ml of acetone were added 20 g of β-chloroethyl p-toluene-sulfonate and a solution of 10 g of NaOH in 7.5 ml of water with stirring. The mixture was stirred at 60 °C for 10 h; then another 10 g of β-chloroethyl p-toluenesulfonate and a solution of 4 g NaOH in 1.5 ml of water were added and stirring was continued for an additional 10 h. The resulting precipitate was filtered off. After the unreacted β-chloroethyl p-toluene-sulfonate was separated off, the filtrate was evaporated and the residue chromatographed on silica gel using benzene as an eluent to give 7 g (54%) of the product. Recrystallization from methanol gave colorless needles of 5CEBCz, mp 121—122 °C.

To a suspension of 5CEBCz(7.2 g; 0.026 mol) in 360 ml of ethanol was added 75 ml of a 25% KOH-methanol solution. The mixture was refluxed for 15 h and poured into water. After standing over a night, a precipitate obtained was filtered and

washed with water. Repeated recrystallizations from methanol gave

pale yellow needles of 5VBCz (4.0 g, 62%), mp 89.5—90.5 °C.

Colorless plates of 7VBCz was synthesized from 7H-benzo[c]-

carbazole by the procedure described in the synthesis of 5VBCz.

The product was recrystallized twice from methanol, 56% yield;

mp 88—89 °C.

These new materials (5CEBCz, 5VBCz, 7CEBCz, and 7VBCz) were

identified by elemental analysis, NMR and IR spectra.

All polymerization reactions were carried out using

standard procedures under nitrogen or under vacuum.[51,52]

Reagents were carefully purified and dried. Polymers were

isolated by precipitation with methanol and purified by repeated

reprecipitations followed by drying under vacuum.

The polymer molecular weights (M_n) were determined in ethylene

chloride solution at 40 °C using a vapor pressure osmometer.

Glass transition temperatures (T_g) were determined with a Shimadzu

DSC-20 differential scanning calorimeter at the heating rates of

10—15 °C/min. The T_g for each sample was taken as the average

of four or five determinations. NMR spectra were measured in

deuteriochloroform at 60 °C and in tetradeuterioethylene bromide

at 60—140 °C with a JEOL MH-100 spectrometer.

Results and Discussion

(1) Polymerization.

Representative polymerization results of VCz are shown in

Table I-1. All of the PVCz samples are soluble in ordinary

solvents irrespective of the polymerization method. Clear

differences in T_g are, however, observed among the samples

prepared free radically, cationically in a polar solvent, and

cationically in a nonpolar one; the T_g increases in this order. The T_g is supposed to be independent of the M_n in the range of $M_n > 100000$.[54] It is considered that there is no serious difference in molecular weight distribution among these samples.[55,56] Therefore, the differences in T_g are not attributable to the differences in M_n, but to some differences in the stereoregularity which will be discussed below.

5VBCz is easily polymerized by cationic initiators, as is shown in Table I-2. The yields, softening ranges (T_s), and M_n of the polymers increase with a decrease in polymerization

Table I-1.

Characterization of PVCz Prepared by Various Methods

Sample	Solvent	Polymerization method						$I_{H/L}$[b]	
		Concn, M	Initiator (mol %)	Temp, °C	T_g, °C	M_n,[a] ×10⁴		–CHR–	–CH₂–
A	Benzene	0.5	AIBN (1)	70	228	20		0.35	0.38
B	Bulk		Thermally	80	226			0.46	
C	Toluene	0.26	BF₃OEt₂ (1)	20	248	10		0.97	0.83
D	(CH₂Cl)₂	0.09	BF₃OEt₂ (1)	20	238	11		0.58	0.60
E	Toluene	0.09	BF₃OEt₂ (1)	−78	244	77		1.00	
F	Toluene	0.2	AlEt₃/TiCl₄ (2/2)	20	245	33		0.73	

[a] Determined from the specific viscosity.[53] [b] See text. The $I_{H/L}$ value for methylene signal could not be obtained from the spectra measured in CDCl₃ at 60 °C because of the broadness.

Table I-2.

Polymerization Results of 5VBCz

No.	Initiator (mol %)	Concn, M[a]	Time, h	Temp, °C	Yield, %	T_s, °C	M_n
1	BF₃OEt₂ (2)	0.14	4	40	14	212–219	
2	BF₃OEt₂ (2)	0.14	4	−20	83	230–240	1750
3	BF₃OEt₂ (2)	0.42	3	−33	85	248–258	2000
4	BF₃OEt₂ (2)	0.42	3	−40	85	258–268	2030
5	BF₃OEt₂ (1)	0.14	4	−78	93	264–274	2120
6	BF₃OEt₂ (2)	0.10	6	−90	93	260–272	2030
7	AlEtCl₂ (2)	0.14	4	−78	86	243–253	1770
8	AlEt₃/TiCl₄ (2/2)	0.20	10	20	71	245–250	
9	BPO (2)	0.35	15	80	0		
10	BPO (2)	Bulk	24	100	37	200–208	
11	AIBN (2)	0.34	48	75	30	230–240	3060
12	AIBN (2)	0.40	35	80	47	240–248	
13	AIBN (2)	Bulk	48	100	56	290–300	12000
14	None	Bulk	48	100	Trace		

[a] Solvent: ethylene chloride for No. 3 and toluene for the others.

temperature. At the temperatures below -40 °C, the polymers are obtained almost quantitatively and the M_n values are constant at 2000—2100(DP=8—9). These polymers are readily soluble in ordinary solvents such as benzene and THF, and their T_s and T_g are 260—270 and 235 °C, respectively. Several attempts to obtain high molecular weight polymers by the use of cationic initiators have been unsuccessful. Ziegler-Natta initiators also give the low molecular weight polymers in high yields.

5VBCz is also polymerized by free-radical initiators, although the yields are very low as compared with those of cationic polymerizations. Benzoyl peroxide(BPO) gives the polymer having a low value of T_s only in bulk polymerization. Azobisiso-butyronitrile(AIBN) gives the polymers even in solution. The yields increase with an increase in the monomer concentration up to 50% in the saturated solution(0.4 M), but the T_s and probably the M_n also hardly increase. The AIBN-initiated bulk polymeriza-tion at 95—100 °C gives the fairly high molecular weight polymer (DP=50) in an about 50% yield. The polymer thus obtained is pale yellow, and soluble in THF, but not in benzene, and the T_g is 271 °C. It is noted that the T_s values of the cationically polymerized samples(cationic polymers) are much larger than those of the free-radically polymerized samples(radical polymers) with the corresponding M_n values.

5VBCz is not polymerized by anionic initiators. This is due to the same reason as the case with VCz.[57]

7VBCz is easily polymerized by free-radical initiators. Some polymerization results are shown in Table I-3. The yields and the M_n depend a little both on monomer concentration and on temperature. The M_n values are much larger than those of the PV5BCz samples prepared under the similar conditions, but much

-14-

smaller than those of the PVCz ones.

7VBCz is polymerized by cationic initiators in high yields with an exception of No. 7 in Table I-3. The T_g, M_n, and solubility of the cationic polymers vary remarkably with the polymerization condition. The M_n increases with an increase in the concentration of monomer or initiator, and there is an optimal polymerization temperature of the M_n at about -40 °C. The T_g increases with an increase in polymerization temperature and decreases with an increase in the solvent polarity. The T_g of the cationic polymers are much higher than those of the free-radical ones. These results are not explained by the differences in the M_n, although the T_g depends a little on the M_n even in the range of fairly high M_n. The polymers prepared at temperatures below -40 °C are readily soluble in ordinary solvents. However, the solubility becomes poor with an increase in the temperature, in spite of a decrease in the M_n. The polymers insoluble in all

Table I-3.

Polymerization Results of 7VBCz

| | Polymerization method | | | | Characterization of polymers | | | | | |
| | | | | | | | Solubility[b] | | $I_{H/L}{}^c$ | |
No.	Initiator (mol %)	Concn, M^a	Time, h	Temp, °C	Yield, %	T_g, °C	M_n	Bz	THF	–CHR–	–CH$_2$–
1	AIBN (2)	0.10	5	75	39		11 000	O	O		
2	AIBN (2)	0.28	5	75	65	271	14 000	O	O	0.32	
3	AIBN (2)	0.56	5.5	75	92	271	15 000	O	O	0.33	0.39
4	BF$_3$OEt$_2$ (2)	0.14	1.5	−78	99	283	>25 000	O	O	0.54	0.52
5	BF$_3$OEt$_2$ (2)	0.14	1	−55	98	288	>25 000	O	O		
6	BF$_3$OEt$_2$ (2)	0.14	1.5	−40	99	292		✕	△		
7	BF$_3$OEt$_2$ (2)	0.05	1	−78	19		10 000	O	O		
8	BF$_3$OEt$_2$ (2)	0.05	3	−50	92	280	16 000	O	O	0.63	
9	BF$_3$OEt$_2$ (2)	0.05	1	−40	99	287	20 000	O	O	0.68	
10	BF$_3$OEt$_2$ (2)	0.05	1	0	93	287	14 000	◐	O		
11	BF$_3$OEt$_2$ (2)	0.05	1	10	94		8 500	◐	O	0.99	
12	BF$_3$OEt$_2$ (2)	0.05	1	25	93	291		✕	△		
13	BF$_3$OEt$_2$ (1)	0.15	3	10	99	289		△	O	0.92	0.78
14	BF$_3$OEt$_2$ (1)	0.10	1	10	93	278		O	O	0.54	0.50
15	AlEt$_3$/TiCl$_4$ (1/1)	0.20	10	20	91	292		✕	△		
16	AlEt$_3$/TiCl$_4$ (3/2)	0.10	7	35	99			◐	O	0.56	
17	AlEt$_3$/TiCl$_3$ (1/1)	0.20	10	20	90	282		O	O	0.53	

^{a} Solvent: ethylene chloride for No. 14 and toluene for the others. ^{b} (O) soluble; (◐) soluble but opaque in cold benzene; (△) swollen; (✕) insoluble. ^{c} See Table I.

of the solvents examined are obtained at temperatures above a critical one, which is raised with an increase in the concentration of initiator or monomer. The solubility is also dependent on the solvent polarity; ethylene chloride gives the polymer having better solubility than toluene. Thus, there is a roughly parallel relationship between the T_g and the solubility.

7VBCz is easily polymerized by Ziegler-Natta initiators, but not polymerized anionically.

These three monomers are rich both in the electron-resonance stabilization and in the electron-donating character of the pendant groups. Their magnitudes are considered to be in the order of 5VBCz > 7VBCz > VCz. They were, therefore, predicted to be easily polymerized free radically and cationically to the high molecular weight polymers. In the case of free-radical polymerization, both the yields and the M_n are in the order of VCz > 7VBCz > 5VBCz. This is opposite to the order predicted from the electron resonance stabilization. The radical reactivity of these monomers seems to be controlled by the steric hindrance effect rather than by the resonance effect.

In the case of cationic polymerization, the yields are almost quantitative and the M_n is in the order of VCz > 7VBCz >> 5VBCz. The cationic reactivity of the growing chain end is predicted to be in the inverse order of that of the monomer, as is the case with vinyl ethers.[58] This may be a reason for the latter fact (the order of M_n), if the approach of an incoming monomer to the growing chain end followed by the separation of the counterion is not the rate-determining step of the propagation reaction. However, this assumption seems very unlikely for these monomers. Therefore, the order of M_n suggests that the cationic reactivity

of the growing chain end may be controlled by the steric

hindrance effect rather than by the electron-donating effect.

The cationic polymerization of 5VBCz, the most bulky monomer

among these used, gives only the low molecular weight polymer

in a high yield. This suggests that the cationic reactivity of

the growing chain end decreases drastically with increasing

sequence of the growing chain, resulting in the transfer reaction

to a counterion and/or a monomer.

(2) NMR Spectra.

The T_g and solubility data mentioned above suggest that the

stereoregularity and/or the crystallinity of the polymers vary

depending on the polymerization method. The IR, NMR, and X-ray

diffraction spectra of these polymers also were examined. The

IR and X-ray diffraction spectra are essentially the same,

irrespective of the polymerization method. All of the samples

which were precipitated from solution and have never experienced

heat treatment are of low crystallinity. The 100-MHz NMR spectra

are shown in Figs. I-1—I-3. The spectra of P5VBCz and P7VBCz

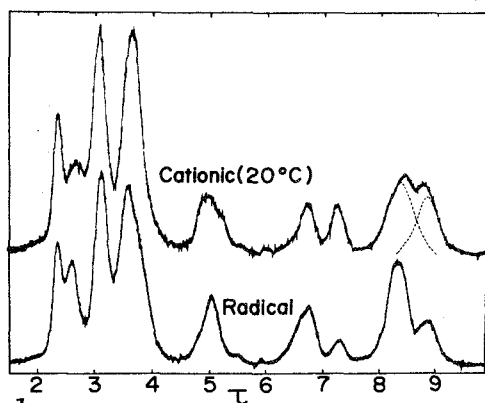were assigned according to the case of PVCz.[59] The assignment

Fig. I-1.
NMR spectra (100 MHz) of PVCz in tetradeuterioethylene
bromide at 125 °C. The upper and lower curves are for the samples
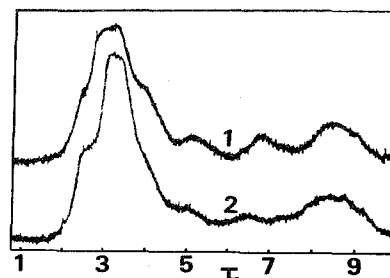of No. C and A in Table I-1, respectively.

Fig. I-2. NMR spectra(100 MHz) of
P5VBCz in deoteriochloroform at
60 °C. 1 and 2 are for the samples
of No. 13 and 5 in Table I-2,
respectively.

is listed in Table I-4. Both positions and relative intensities of all the signals are independent of temperature in the range of 60 to 140 °C, although the resolution of the signals of methylene protons are appreciably improved with an increase in temperature.

In the case of PVCz and P7VBCz, the aromatic regions of the spectra($\tau < 6.0$) vary only a little with the polymerization method. The intensity of a peak appearing at about 5τ always corresponds to about one proton. On the other hand, the methylene and methine regions of the spectra, which are composed of two peaks respectively, vary appreciably with the polymerization method; the intensity ratio of the higher field peak to the lower field one($I_{H/L}$) is dependent on the polymerization method, as is shown in the last columns in Tables I-1 and I-3, although the positions of the signals are hardly dependent on it. The $I_{H/L}$ value for methylene protons is in agreement with that for a methine proton, taking into consideration the error ($\pm$ 5%) in resolving a methylene signal into two components. In both PVCz and P7VBCz, the samples prepared cationically in a nonpolar solvent at room temperature have the largest $I_{H/L}$ value(unity) and the free-radical samples have the smallest value(one third). In the cationic polymerization, the $I_{H/L}$ value decreases appreciably in
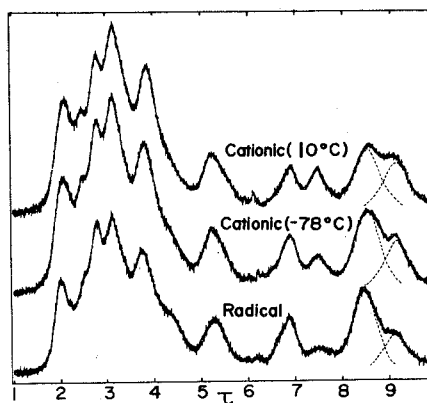

Fig. I-3.

NMR spectra (100 MHz) of P7VBCz in tetradeuterioethylene bromide at 125 °C. The upper, middle, and lower curves are for the samples of No. 13, 4, and 3 in Table I-3, respectively.

Table I-4.

Chemical Shifts (τ) of Protons [a]

Sample	Aromatic	Methine	Methylene
PVCz (cationic)	2.3–3.7, 4.95	6.7, 7.25	8.35, 8.83
PVCz (radical)	2.3–3.6, 5.0	6.73, 7.27	8.3, 8.85
P7VBCz (cationic)	2.0–3.8, 5.15	6.8, 7.4	8.4, 9.05
P7VBCz (radical)	1.9–3.7, 5.2	6.8, 7.4	8.36, 9.0
P5VBCz (radical)	2.3–3.9, 5.1	6.75	8.4

[a] The spectra were measured in tetradeuterioethylene bromide at 125 °C.

going from toluene to ethylene chloride. As the temperature

decreases, it decreases down to about 0.50 at -78 °C in the case

of P7VBCz, but does not vary in the case of PVCz. Thus, it varies

with the polymerization method in a manner similar to the case of

both the T_g and the solubility; the sample having a higher T_g and

poorer solubility has a larger $I_{H/L}$ value. However, this relation

is not held for the samples prepared by Ziegler-Natta initiators;

the $I_{H/L}$ values are relatively small, in spite of the high T_g and

the poor solubility.

In the case of P5VBCz, there seems to be a similar difference

in the $I_{H/L}$ value between the cationic and the free-radical

samples, but no quantitative discussion can be done because of

the highly unresolved spectra.

Both the doublet signals of methylene and methine protons

in the 100-MHz spectra are independent of measuring temperature

but dependent on the polymerization method. On the other hand,

Williams has reported that the 220-MHz NMR spectrum of PVCz shows

clearly the multiplicity of the signals of methylene and methine

protons and that the methylene signal in the 220-MHz spectrum

varies with temperature owing to temperature-dependent confor-

mational effects.[46] We have also measured the 220-MHz spectra

of PVCz in several solvents and at a series of temperatures.

The resolution of the spectrum of methylene protons varies with

both solvent and temperature. In some cases, the 220-MHz

spectra are unresolved rather than the 100-MHz spectra.

However, the highly resolved spectra of methylene protons are

composed of four peaks in both cases of the cationic and free-

radical samples; the two higher field peaks and the two lower

field ones correspond to the higher field peak and the lower

field one in the 100-MHz spectra, respectively. Moreover, the intensity ratios of the two higher field peaks to the two lower field ones (for example, 0.35 and 0.89 for samples A and C, respectively) are in good agreement with the $I_{H/L}$ values of the corresponding samples listed in Table I-1. Therefore, the differences in $I_{H/L}$ values are attributable to some difference in the stereochemical configuration of the polymer chain.

The splittings of both doublet signals of methylene and methine protons are too large to be attributable to some triad tacticity in a usual manner. Therefore, it may be necessary to assume the presence of two kinds of both methylene and methine protons having the magnetically different environments, that is, the stereoblock arrangements of isotactic 3/1 and syndiotactic 2/1 helixes, as have been proposed by Mikawa et al..[44]

Heller et al. investigated the NMR spectra of polyvinyl-aromatics such as polystyrene and poly(1-vinylnaphthalene)(P1VN) in connection with the stereoregularity, and found that the aliphatic protons of P1VN have the following unusual behaviors probably owing to the bulkiness of the pendant group.[60]   (1) Both the methylene and methine signals of the isotactic sample (9.02 and 7.52 τ, respectively) are remarkably shifted to the field higher than those of the atactic one (8.57 and 7.24 τ). (2) The methine signals of both the samples are shifted appreciably to the lower field as compared with those of polystyrene etc..

In the present case, the aliphatic protons have the behaviors similar to those of P1VN. Therefore, the higher field peaks of both methylene and methine protons may tentatively be assigned to the isotactic sequence, and the lower field peaks to the syndiotactic one. According to this assignment, the $I_{H/L}$ value

is a measure of the relative amount of isotactic sequence to syndiotactic one of the polymer. In both PVCz and P7VBCz, the samples prepared cationically in a nonpolar solvent at room temperature have the largest amount of isotactic sequence (50%) and the free-radical samples have the smallest amount (25%). The difference in the amount of isotactic sequence explains reasonably the high T_g and poor solubility of the former samples as compared with the case of the latter ones, because the isotactic 3/1 helix is considered to be less flexible rather than the syndiotactic 2/1 helix. This is another evidence for the present assignment.

Crystal[47] and Griffiths[61] have reported that in the lamellar type or rod type crystals of PVCz prepared by appropriate heat treatments a polymer chain is composed of an isotactic 3/1 helix but not of a syndiotactic 2/1 helix, although the PVCz sample used by Griffiths is considered to be a free-radical sample judging from the T_g (227 °C). This might suggest that the isotactic 3/1 helix segment is crystallized much more easily than the syndiotactic 2/1 helix segment, and the latter segment is primarily present in the poor crystalline and amorphous phases. The sample with the crystallinity of 60% has been obtained from the PVCz sample used by Griffiths.[61] This might support assigning the lower field peaks of both methylene and methine protons to the syndiotactic sequence rather than the atactic one.

Summary

5VBCz and 7VBCz having more bulky pendant groups than VCz were synthesized and polymerized. By cationic polymerization

at low temperatures, 5VBCz gave only the low molecular weight

polymer (DP ≤ 9) in a high yield. The high molecular weight

polymer (DP = 50) was prepared only by bulk polymerization

initiated with azobisisobutyronitrile. 7VBCz was easily

polymerized free-radically and cationically, as is the case

with VCz. From the NMR spectra, the glass transition tempera-

tures, and the solubility of the polymers, it was clarified

that the stereoregularity varies depending on the polymerization

method. Both methylene and methine protons of these three

polymers show doublet signals, of which the higher field peaks

were assigned to the isotactic sequence and the lower field

peaks to the syndiotactic one. According to this assignment,

it was estimated that the cationic polymers have the largest

amount of the isotactic sequence (50%), and that the free-radical

polymers have the smallest amount (25%).

Chapter 2

Fluorescence Spectra of the Vinyl Polymers with Pendant

Carbazolyl and Benzocarbazolyl Groups

Introduction

Poly(N-vinylcarbazole)(PVCz), both in solution and in film,

shows one broad fluorescence, which is not composed of only one

component, but of two components. The broad emission at the

longer wavelength(λ_{max}; ca. 23900 cm^{-1}) is assigned to the

sandwich-like excimer fluorescence. On the other hand, the

assignment of the broad emission in the shorter-wavelength region

(λ_{max}; ca. 27000 cm^{-1}) is controversial because of the absence

of the structure and of the large Stokes shift. David et al. and

Yokoyama et al. have assigned it to the monomer fluorescence for

PVCz in solution.[5,17] P. C. Johnson and Offen,[4] and Powell

and Venikouas[14] have assigned it to the emission from a dimer

trap for PVCz films. On the other hand, G. E. Johnson has

recently assigned it to the second excimer fluorescence for PVCz

in solution, and reported that the polymer conformation appro-

priate for the formation of this state exists prior to the

initial excitation step.[18] Thus, the structure of the species

emitting at ca. 27000 cm^{-1} has been ambiguous so far.

It is of interest to investigate how the difference in the

tacticity is reflected in the fluorescence spectra.

Concerning the vinyl polymers with small aromatic chromopho-

res, the relation between the tacticity of the polymer chain and

the fluorescence spectrum has been reported in several

investigations. For polystyrene(PSt),[34,35,40,41] poly(α-methyl-

styrene),[36] and poly(p-methylstyrene),[41] it has been reported

that the ratio of the sandwich-like excimer to the monomer

fluorescence intensity for the isotactic polymer is larger than

that for the atactic polymer, although an opposite experimental

result for PSt has been reported.[34] Y.-C. Wang and H. Morawetz

have found, from the NMR spectra of polyacenaphthylene, that

the polymers prepared by cationic and radical polymerizations

have different configurations, and that this is reflected in the

ease with which they form excimers.[39] However, such a relation

has never hitherto been studied for the vinyl polymers with large

and bulky aromatic chromophores such as carbazole and benzo-

carbazole.

Experimental

The polymers used are listed in Table I-5. The low-molecular-weight compounds were the same as used before[62] or were of commercial origin and they were purified by the appropriate methods.

The emission spectra were measured

Table I-5. Characterization of Polymers Used[a]

Sample	Polymerization temp/°C	Degree of polymerization	$I_{H/L}$
VCz Olig. I[b]	20	4	——
VCz Olig. II[b]	20	10	——
PVCz(r)	70	1040	0.35
PVCz(c)	20	520	0.97
PCzEVE [c]	-25	33	——
P7VBCz(r)	75	58	0.32
P7VBCz(c)-I	-78	103	0.51
P7VBCz(c)-II	-40	82	0.68
P7VBCz(c)-III	10	36	0.92
P5VBCz(r)-I	100	49	——
P5VBCz(r)-II	80	13	——
P5VBCz(c)	-78	8	——

a) Polymers prepared by the radical and cationic polymerizations are abbreviated as (r) and (c), respectively.
b) VCz oligomers were prepared by the methods described in the literature.[62]
c) PCzEVE was the same as used before.[62]

with a spectrophotofluorometer constructed using a stabilized

500 W xenon lamp, monochromators, and a PM-55 (S-20) photomulti-

plier. The spectra were calibrated for the detector response by

using a standard tungsten lamp. The fluorescence-decay times

were measured with a pulsed N_2 gas laser as the exciting light

source. Responses from the photomultiplier were led to a

sampling oscilloscope(Tektronix 661) and recorded on a X-Y

recorder, or led to a Tektronix 475 oscilloscope and the decay

curve was photographed.

Results and Discussion

(1) Fluorescence Spectra of PVCz.

The fluorescence spectra of the various PVCz samples in

aerated THF solution are shown in Fig. I-4. The ratio of the

fluorescence intensity in the shorter-wavelength region to that

in the longer-wavelength region (sandwich-like excimer fluores-

cence, λ_{max}; 23900 cm^{-1}) in PVCz(r) samples is remarkably

larger than that in PVCz(c) samples. Figure I-5 shows the

fluorescence spectra of PVCz(r) and PVCz(c), which have almost

the same concentrations in degassed THF-MTHF solution, and their

resolution spectra. The resolution was carried out on the

assumption that the location of the sandwich-like excimer

fluorescence band in solution was the same as that in film(see p.64).

The fluorescence at the shorter wavelength in the resolution

spectra (λ_{max}; 26900 cm^{-1}) is not assigned to the monomer one

because of the absence of the structure and of the large Stokes

shift (2200 cm^{-1}). The fluorescence is not assigned also to

the stable ground state dimer because of the absence of an

absorption due to such a dimer. The broad fluorescence seems
to be assigned to a second excimer on the basis of a conforma-
tional consideration in section 4. It may safely be considered
that the radiative rate constants of each fluorescence (second

and sandwich-like excimer bands) of
PVCz(r) are equal to those of
PVCz(c). Therefore, Fig. I-5 shows
that the concentration of the
sandwich-like excimer in PVCz(r) is
nearly equal to that in PVCz(c),
and that the concentration of the
second excimer in PVCz(r) is higher
than that in PVCz(c) by a factor of
about 2.4.

   In rigid glass at 77 K, a

Fig. I-4.

Fluorescence spectra of PVCz and VCz-
vinylnaphthalene(VN) copolymers polymerized by
various methods in THF aerated solutions at room
temperature. Excitation wavelength; 330 nm.
(1) VCz-VN(0.5 mol% in feed) copolymer polymerized
by AIBN (1 mol%) in benzene (1 M) at 70 °C for
2 h, (2) PVCz(r) polymerized by AIBN (1 mol%)
in benzene (1.3 M) at 70 °C for 4.5 h, (3) PVCz(r)
polymerized by AIBN (1 mol%) in benzene (0.5 M)
at 70 °C for 7 h, (4) PVCz(c) polymerized by
BF_3OEt_2 (1 mol%) in toluene (0.26 M) at 20 °C for
1 h, (5) VCz-VN (1 mol% in feed) copolymer poly-
merized by BF_3OEt_2 (1 mol%) in toluene (0.86 M) at
15 °C for 3 h, (6) PVCz(c) polymerized by BF_3OEt_2
(1 mol%) in toluene (0.09 M) at −78 °C for 1 h,
(7) PVCz(c) polymerized by BF_3OEt_2 (0.5 mol%) at
20 °C for 18.5 h.

Fig. I-5.

Fluorescence spectra and the resolution spectra
of PVCz(r) and PVCz(c) in MTHF-THF degassed
solutions at room temperature. Optical densities at
excitation wavelength (310 nm) are 0.132 and 0.131
for PVCz(r) and PVCz(c), respectively.
(1) ———; PVCz(r), (2) ————; PVCz(c), (3) ······;
the component of the sandwich-like excimer fluo-
rescence of PVCz(r) and PVCz(c), (4) ————; the
component of the second excimer fluorescence of
PVCz(r), (5) ······; the component of the second
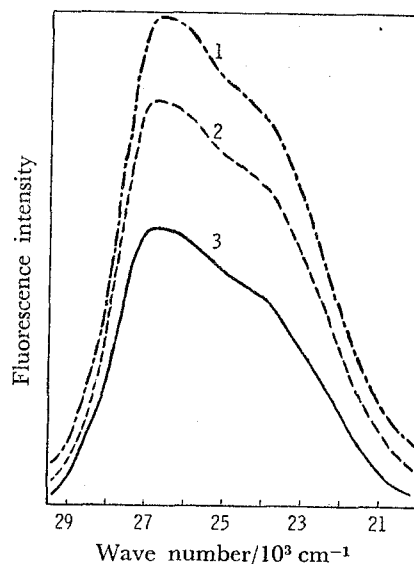excimer fluorescence of PVCz(c).

significant difference in the fluorescence spectra between PVCz(r) and PVCz(c) was found, as is shown in Fig. I-6. The PVCz(c) shows mainly a monomer structured fluorescence, while the PVCz(r) shows mainly the second excimer fluorescence, although weak monomer fluorescence is observed. The fluorescence spectra both in fluid and in rigid solutions are considered to reflect the difference in the tacticity of PVCz. That is, the concentration of the second excimer in syndiotactic-rich polymer(PVCz(r)) is higher than that in isotactic-rich polymer(PVCz(c)).

(2) Fluorescence Spectra of P7VBCz.

The fluorescence spectra of 7EBCz and P7VBCz are shown in Fig. I-7. The 7EBCz shows no excimer fluorescence even in concentrated solutions up to 0.1 M, as is the case of ECz. The polymers show one broad fluorescence composed of two components (λ_{max}; 21950 and 24900 cm^{-1}), as is the case of PVCz. The
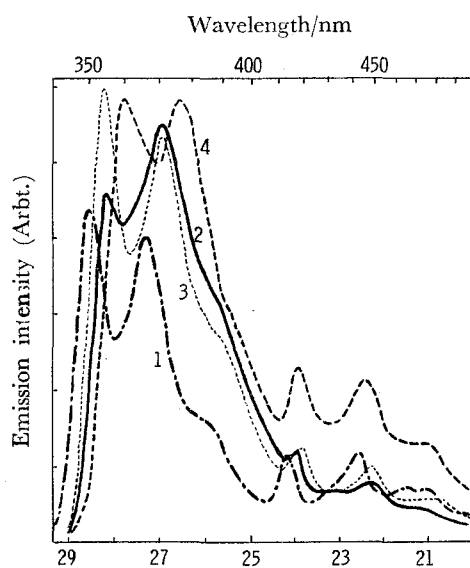
Fig. I-6. Wave number/10³ cm⁻¹
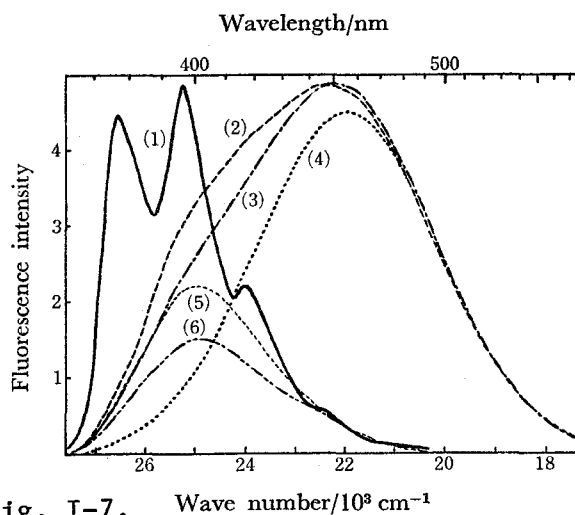Emission spectra of (1) ————; VCz Olig, II, (2) ————; PVCz(r), (3) ----; PVCz(c), and (4) —————; PCzEVE in MTHF-THF rigid glasses at 77 K.

Fig. I-7. Wave number/10³ cm⁻¹
Fluorescence spectra and their resolution spectra of 7EBCz, P7VBCz(r), and P7VBCz(c)-I in MTHF-THF degassed solutions at room temperature. Optical densities of both the polymers at excitation wavelength (350 nm) are 0.249. Fluorescence spectra: (1)————: 7EBCz, (2)————, P7VBCz(r), and (3)————: P7VBCz-(c)-I. Resolution spectra: (4)······: the component of the sandwich-like excimer fluorescence of P7VBCz(r) and P7VBCz(c)-I. (5)----, and (6)—————: the component of the second excimer fluorescence of P7VBCz-(r) and P7VBCz(c)-I, respectively.

energy differences between the peaks of these two bands and the

0-0 fluorescence band (26560 cm^{-1}) of 7EBCz are 4610 and 1660

cm^{-1}. These are almost the same as the corresponding energy

differences between PVCz and ECz (4630 and 1630 cm^{-1}). The

fluorescence excitation spectra of the polymers, obtained by

monitoring at several wavelengths (390—500 nm), duplicate the

absorption spectra of these solutions exactly. By analogy with

the fluorescence spectrum of PVCz, the fluorescence bands can be

assigned to the sandwich-like excimer fluorescence and the second

excimer one. Figure I-7 shows that the difference in the

fluorescence spectra between the radical and cationic polymers

is attributable to the difference in the concentration of the

second excimer.

The $I_{H/L}$ and $\overline{DP}$ of the cationic polymers vary remarkably

with the polymerization temperature (Table I-5). Thus, the

fluorescence spectra of P7VBCz samples in aerated solution

(5.9×10^{-5} M) were compared with one another in Fig. I-8. The

second excimer fluorescence intensities are in the order of

(r) > (c)-I > (c)-II >
(c)-III. This order is
not correlated to the
molecular weight of the
polymers, but to the
decrease in the $I_{H/L}$ value.
That is, the concentration
of the second excimer
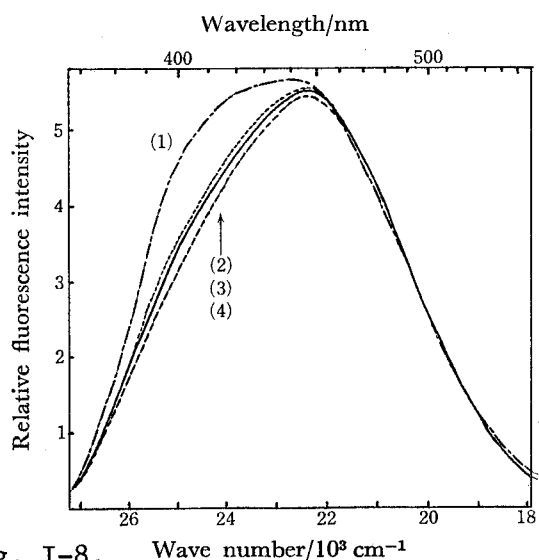increases with an increase
in the syndiotactic
sequence.

Fig. I-8. Fluorescence spectra of (1) P7VBCz(r), (2) P7V-BCz(c)-I, (3) P7VBCz(c)-II, and (4) P7VBCz(c)-III in MTHF–THF aerated solutions at room temperature. Excitation wavelength; 350 nm.

The sandwich-like excimer fluorescence of each P7VBCz

sample has a constant intensity at temperatures from ca. -110 to

20 °C, as is shown in Fig. I-9. At temperatures above ca. 20 °C,

the intensity of the sandwich-like excimer fluorescence decreases

and the intensity of the second excimer fluorescence increases

with an increase in the temperature. This phenomenon is observed

also for PVCz.[18] This behavior and the presence of the long-

lived component decay at the shorter wavelength (vide infra)

indicate the dissociation of sandwich-like excimer to give back

the second excimer.

The fluorescence-decay curves of the polymers at room

temperature are multi-component in the shorter-wavelength region

(36 ± 2 ns and initial fast decay), while they are one-component

(36 ± 2 ns) in the longer-wavelength region. The long-lived

component corresponds to the sandwich-like excimer fluorescence.

The spectral band of the polymers in rigid glass solutions

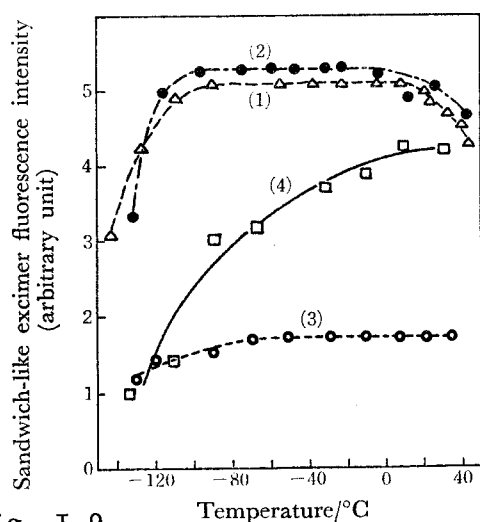at 77 K is shifted to a lower frequency and broadened as compared

Fig. I-9.
Temperature dependence of the sandwich-like excimer fluorescence intensity. (1)-△-: P7VBCz(r), (2)-●-: P7VBCz(c)-I, (3)-○--: P5VBCz(r)-II, and (4)-□-: P5VBCz(c).
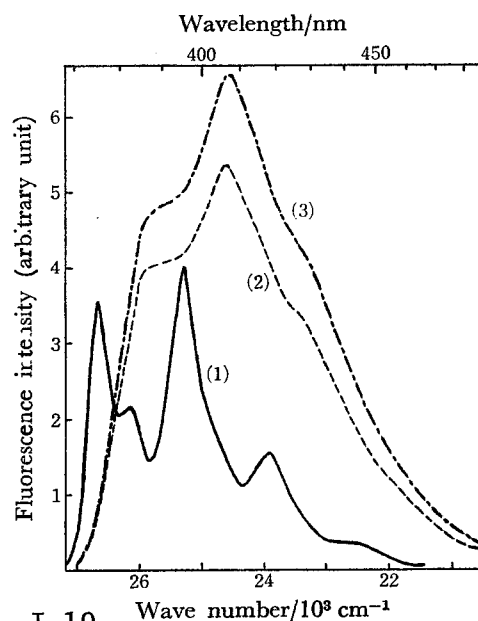

Fig. I-10.
Fluorescence spectra of (1) 7EBCz, (2) P7VBCz-(r), and (3) P7VBCz(c)-I in MTHF-THF rigid glasses at 77 K. Excitation wavelength; 350 nm.

with that of 7EBCz, as is shown in Fig. I-10. This deviation

from the monomer-like fluorescence band shape seems to be

attributable to a large contribution of the second excimer

fluorescence. In the case of the PVCz samples, the cationic

polymer shows a monomer-like structured fluorescence, while the

radical polymers show mainly the second excimer fluorescence.

The fluorescence decay times of both the PVCz samples (λ_{obsd} =

355—390 nm) are approximately the same as that measured for i-PrCz

(17 ± 2 ns), although a slight departure from a strict first-order

decay is observed (Table I-6). This fact indicates that the

lifetime of the second excimer fluorescence seems to be nearly

equal to that of the monomer-like fluorescence. In the case of

the P7VBCz samples, the fluorescence decay times of both the

polymers at 380 nm are ca. 18 ns, while those at the longer wave-

length($\lambda > 400$ nm) are 25 ± 2 ns. The decay curves are roughly

single-exponential. This lifetime(25 ns) is not in agreement with

those of the monomeric fluorescence of the model compound(13 ns)

and of the sandwich-like excimer fluorescence(36 ns), and is

attributed to the second excimer. The decay time(18 ns) at 380

nm seems to be an apparent value due to an overlap of the monomer-

like fluorescence and the second excimer one.

(3) Fluorescence Spectra
of P5VBCz.

The fluorescence

spectra of 5EBCz and P5VBCz

are shown in Fig. I-11.

The 5EBCz shows no excimer

fluorescence even in

concentrated solutions up

Table I-6. FLUORESCENCE LIFETIME[a]

Sample	Monomer[b]	Monomer-like[c]	Second excimer[c]	Sandwich-like excimer[d]
i-PrCz	17 ± 2	—	—	—
PVCz(c)	—	19 ± 2	—	45 ± 1
PVCz(r)	—	17 ± 2	17 ± 2	45 ± 1
7EBCz	13 ± 1	—	—	—
P7VBCz(c)	—	(13)[e]	25 ± 3	36 ± 2
P7VBCz(r)	—	(13)[e]	25 ± 1	36 ± 2
5EBCz	24 ± 1	—	—	—
P5VBCz(c)	—	23 ± 2	—	57 ± 3
P5VBCz(r)	—	26	65—75	57 ± 3

a) Unit; ns. Solvent: MTHF-THF degassed solution.
b) At room temperature and 77 K. c) At 77 K. d)
At room temperature. e) See text.

to 0.1 M, as is the case with ECz and 7EBCz. The radical

polymers show one broad fluorescence, the spectra of which were

successfully resolved into two broad bands, with peaks of 20350

and 22550 cm^{-1}, in a manner similar to that in P7VBCz. The

energy differences between the peaks of these two bands and the

0-0 fluorescence band (24330 cm^{-1}) of 5EBCz are 3980 and 1780 cm^{-1}

respectively. Therefore, the fluorescence bands can be assigned

to the sandwich-like excimer fluorescence and the second excimer

one .

The temperature dependence of the fluorescence spectrum of

the P5VBCz(r)-II sample is shown in Fig. I-12. As may be seen,

there is no evidence for the formation of an isoemissive point.

The sandwich-like excimer fluorescence has a constant intensity

over the temperature range from ca. -70 to 40 °C, as is shown in

Fig. I-9. These phenomena observed for the radical polymers are
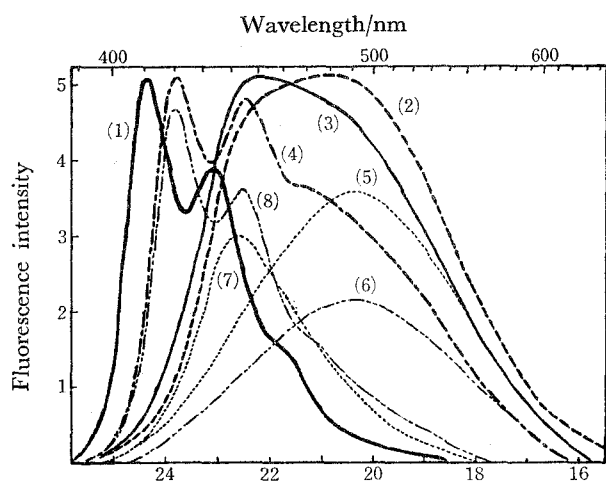

Fig. I-11. Normalized fluorescence spectra and their re-
solution spectra of 5EBCz, P5VBCz(r)-I, P5VBCz(r)-
II, and P5VBCz(c) in MTHF-THF degassed solutions
at room temperature. Excitation wavelength; 350
nm. Fluorescence spectra: (1)———: 5EBCz, (2)————;
P5VBCz(r)-I, (3)———; P5VBCz(r)-II, and (4)————;
P5VBCz(c). Resolution spectra: (5)······, and (6)
————: the component of the sandwich-like excimer
fluorescence of P5VBCz(r)-II and P5VBCz(c), respec-
tively. (7)······: the component of the second excimer
fluorescence of P5VBCz(r)-II, and (8)————; the
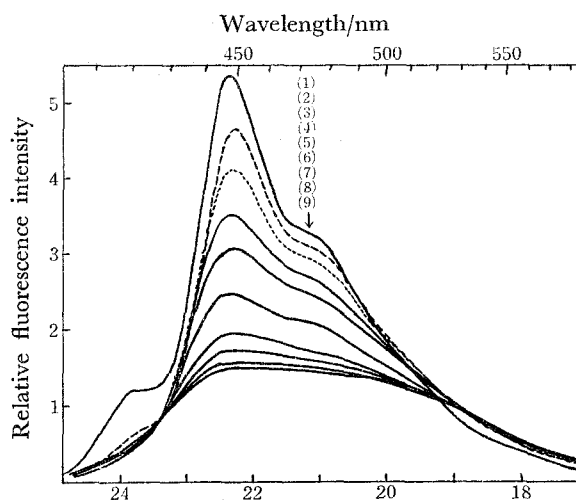component of the monomeric fluorescence of P5VBCz-
(c).

Fig. I-12. Temperature dependence of the fluorescence
spectra of P5VBCz(r)-II in MTHF-THF degassed solu-
tion. Excitation wavelength; 350 nm. (1) 143.5 K,
(2) 163 K, (3) 203.5 K, (4) 222 K, (5) 244 K, (6) 263
K, (7) 281 K, (8) 294.5 K, and (9) 308 K.

quite similar to those observed for the PVCz and P7VBCz.

On the other hand, the fluorescence spectrum of the cationic polymer differs markedly from those of the above-mentioned polymers: (1) The monomer-like structured fluorescence (0-0; 23800 cm^{-1}) in the shorter-wavelength region is observed clearly even at room temperature, while the second excimer fluorescence is not observed, as is shown in Fig. I-11. (2) An isoemissive point is clearly observed, as is shown in Fig. I-13. (3) The intensity of the sandwich-like excimer fluorescence in the longer-wavelength region increases with an increase in the temperature up to ca. 20 °C, as is also shown in Fig. I-9.

A dilute fluid solution of a VCz Olig. II at room temperature does not show any structured fluorescence at the shorter wavelength, but a broad fluorescence which is composed of two excimer fluorescences. Therefore, these three significant differences in the fluorescence spectra between the radical and cationic polymers are not attributable to any difference in the molecular weight, but to the difference in their tacticities. This explanation seems to be supported also by the polymerization results: the cationic polymer is considered to be composed of only an isotactic sequence. The radical polymers are composed of stereoblock arrangements of the isotactic and syndiotactic helixes. Therefore, the
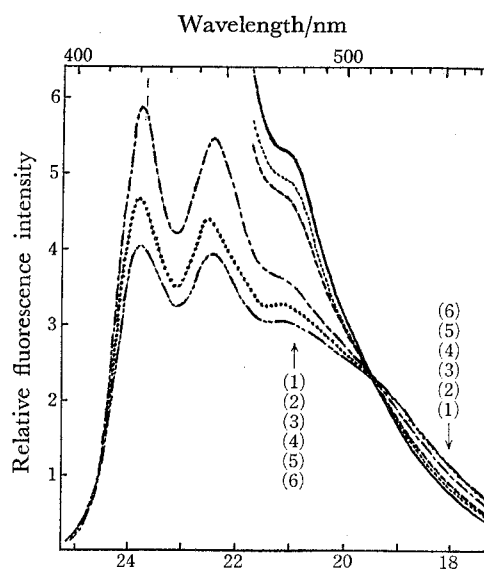

Fig. I-13. Temperature dependence of the fluorescence spectra of P5VBCz(c) in MTHF-THF degassed solution. Excitation wavelength; 350 nm. (1) 183.5 K, (2) 202.5 K, (3) 221 K, (4) 262.5 K, (5) 282 K, and (6) 304 K.

above-mentioned discussion supports the idea that the second

excimer site is not formed within the isotactic sequence, but

only within the syndiotactic sequence.

The fluorescence-decay curves of both the radical and

cationic polymers at room temperature are multi-component in the

shorter-wavelength region (57 ± 3 ns and an initial fast decay),

while there is only one component with a long lifetime (57 ± 3 ns)

in the longer-wavelength region. The long-lived component

corresponds to the sandwich-like excimer fluorescence.

Figure I-14 shows the fluorescence spectra of P5VBCz and

5EBCz in rigid glass solutions at 77 K. The fluorescence spectrum

of the cationic polymer is mainly composed of a monomer-like

fluorescence, the lifetime of which at 420 nm was 23 ± 2 ns. This

is the same value as the decay time of 5EBCz. On the other hand,

the fluorescence spectra of the radical polymers are markedly

broadened as compared with that of the cationic polymer. This

fluorescence is mainly emitted from the second excimer site,

although the fluorescences
from the excited monomer
state and the sandwich-like
excimer site are slightly
involved.

(4) Structure of the Second

Excimer.

In the conformations for

a three-skeletal carbon

rotational dyad of syndio-
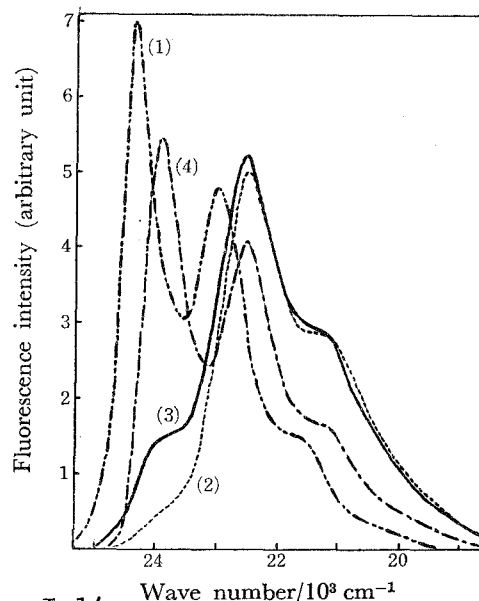
tactic and isotactic polymer

Fig. I-14.
Fluorescence spectra of (1) 5EBCz, (2) P5VBCz-(r)-I, (3) P5VBCz(r)-II, and (4) P5VBCz(c) in MTHF–THF rigid glasses at 77 K. Excitation wavelength; 350 nm.

chain sequences based on a threefold rotational potential,[37] the

conformational states with the lowest energy and those corre-

sponding to the sandwich-like excimer site are shown in Fig.

I-15 (a) and (b). In the syndiotactic case there are a doubly

degenerate ground state $(g^+g^+{}',\ tt)$ and a doubly degenerate

sandwich-like excimer state $(g^-t,\ tg^-)$. On the other hand, in

the isotactic case there are a doubly degenerate ground state

$(g^+t,\ tg^-)$ and a single sandwich-like excimer state (tt). The

formation of the sandwich-like excimer conformation from the

ground-state conformation requires rotational motion about the

carbon-carbon bond. In the ground-state conformations, the tt

conformation of the syndiotactic chain (Fig. I-15 (a)) has the

shortest distance between
neighboring carbazolyl
chromophores. Since the
carbazolyl chromophore is
bulky, it seems to be easy
to approach and mutually
overlap the one benzene
ring of the neighboring
carbazolyl chromophores in
the excited state, as is
shown in Fig. I-16. The
ground-state molecules
corresponding to this
reduced separation have a
repulsive interaction.

It has been reported
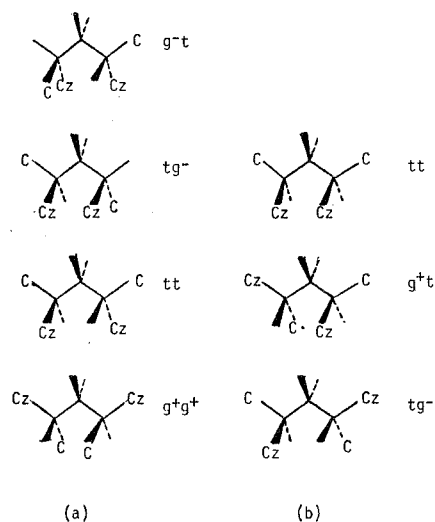that 1,2-di(1-anthryl)ethane

Fig. I-15.

The lowest energy conformations and excimer
forming site ones for a three skeletal carbon rotational
dyad of (a) syndiotactic and (b) isotactic polymer
chain sequences based on a three fold rotational
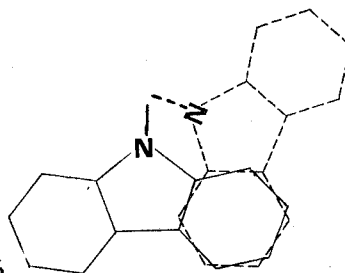potential. This figure is quoted from Fig. 10 in Ref.
37.

Fig. I-16.

The model of the second excimer of PVCz.

.ows a broad excimer fluorescence in solution at room temperature at wavelengths shorter than the fluorescence of a sandwich-like excimer formed by the decomposition of its photodimer in rigid glass at 77 K, and that the structure of the excimer seems to be the overlap of only one benzene ring in the mutual anthracene chromophores.[63] Therefore, it seems reasonable to consider that the structure of the second excimer state may be the overlap of only one benzene ring in the neighboring chromophores. This structure seems to be supported by the fact that the formation of the sandwich-like excimer from the second excimer requires a rotational motion about the carbon-carbon bond.[18]

(5) Formation of an Exciplex.

The fluorescence spectra of PVCz(r) and PCzEVE in solution in the absence and in the presence of DMTP (6 x 10^{-2} M) are shown in Fig. I-17. In the cases of PVCz(r and c) and VCz Olig. II, the fluorescence is nonuniformly quenched by DMTP. That is, the sandwich-like excimer fluorescence is quenched more effectively than the second excimer fluorescence. On the other hand, the fluorescence of PCzEVE is uniformly quenched by DMTP. In all cases, the exciplex fluorescence
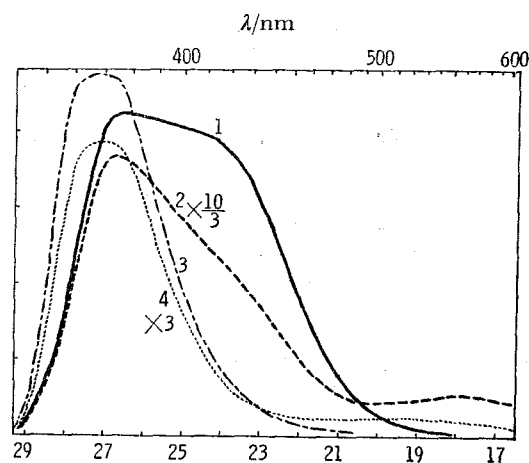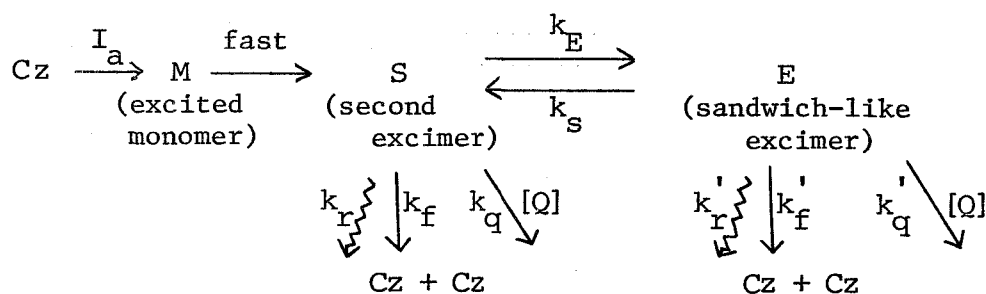

Fig. I-17. Wave number/10^3 cm^{-1}

Fluorescence spectra of PVCz(r) (3.9×10^{-4} M) and PCzEVE (1.9×10^{-4} M) in MTHF-THF degassed solutions in the absence and the presence of DMTP (1.9×10^{-2} M) at room temperature. The intensities of the spectra are not comparative for the different polymers.
(1) ——; PVCz(r) in the absence of DMTP, (2) ----; PVCz(r) in the presence of DMTP, (3) ————; PCzEVE in the absence of DMTP, and (4) ······; PCzEVE in the presence of DMTP.

appears in the longer-wavelength region. The quenching factor, Q, is defined by $Q = (I^0-I)/I$, where I^0 and I are the fluorescence intensity in the absence and in the presence of the quencher molecule(DMTP) in a concentration of [Q] (mol/l), respectively. As is shown in Fig. I-18, the second excimer band is linearly quenched and the sandwich-like excimer band is superlinearly quenched. This phenomenon is the same as the case of fluorescence quenching by acid.[13]

From the results mentioned in the previous sections, the following reaction scheme is the most conceivable.

$$Cz \xrightarrow{I_a} M \xrightarrow{fast} S \underset{k_s}{\overset{k_E}{\rightleftharpoons}} E$$

$$\text{(excited monomer)} \quad \text{(second excimer)} \quad \text{(sandwich-like excimer)}$$

$$k_r \quad k_f \quad k_q[Q] \qquad k_r' \quad k_f' \quad k_q'[Q]$$

$$Cz + Cz \qquad\qquad Cz + Cz$$

, where k_f, k_r, and k_q are the radiative, nonradiative, and quenching rate constants. respectively. The letters with nonprime and prime show the second and sandwich-like excimers, respectively. The k_E and k_s are the rate constants of the conversion between the second excimer and the sandwich-like one. The τ_s and τ_E are the lifetimes of the second and sandwich-like excimer fluorescences in the absence of DMTP. Under steady state conditions, the intensities
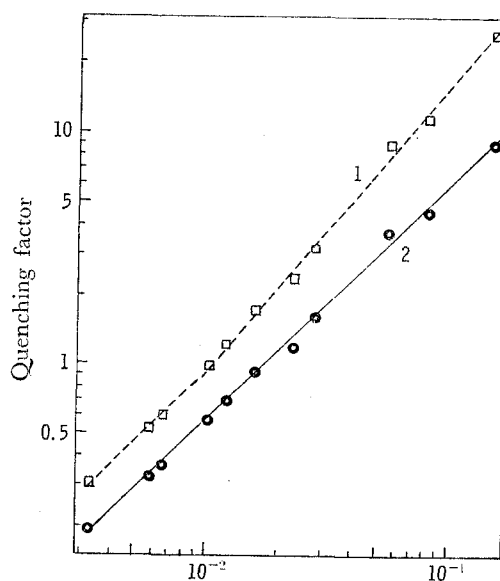

Fig. I-18. DMTP concentration/M⁻¹

Quenching of PVCz(r) by DMTP in THF aerated solutions at room temperature. Excitation wavelength; 345 nm.
(1) The sandwich-like excimer band, and (2) the second excimer band.

of the second and the sandwich-like fluorescence bands (I_s and I_E, respectively) are given by the following equations;

$$I_s = \frac{k_f \tau_s (1 + k_q' \tau_E [Q])}{(1 + k_q \tau_s [Q])(1 + k_q' \tau_E [Q]) - k_s k_E \tau_s \tau_E} \cdot I_a \tag{1}$$

$$I_E = \frac{k_f' k_E \tau_s \tau_E}{(1 + k_q \tau_s [Q])(1 + k_q' \tau_E [Q]) - k_s k_E \tau_s \tau_E} \cdot I_a \tag{2}$$

From these equations, the following equations are obtained.

$$Q_s = \frac{I_s^0 - I_s}{I_s} = \frac{\tau_s \{ k_q (1 + k_q' \tau_E [Q]) + k_q' k_s k_E \tau_E^2 \}}{(1 - k_s k_E \tau_s \tau_E)(1 + k_q' \tau_E [Q])} \cdot [Q] \tag{3}$$

$$\frac{Q_E}{[Q]} = \frac{I_E^0 - I_E}{I_E [Q]} = \tau_s (k_q + k_q' \tau_E \tau_s^{-1} + k_q k_q' \tau_E [Q]) \tag{4}$$

$$\frac{I_s}{I_E} = \frac{k_f}{k_E \tau_E k_f'} + \frac{k_q' k_f}{k_f' k_E} [Q] \tag{5}$$

The quantum yields of the second excimer (η_s) and the sandwich-like excimer (η_E) are given by equation (6);

$$\frac{\eta_s}{\eta_E} = \frac{k_f \tau_s}{k_f' \tau_E} \tag{6}$$

The plots of equations (4) and (5) are given in Figs. I-19 and I-20, respectively. The following values were measured for PVCz(r),[64] $\tau_s \sim 4 \times 10^{-9}$ s, $\tau_E \sim 17 \times 10^{-9}$ s, and $\eta_s / \eta_E = 0.88$. Then, by using the equations (4), (5), and (6), the rate constants listed in Table I-7 were evaluated. Judging from the linear relation between Q_s and [Q] in Fig. I-18, the following relation should be held: $k_q' \tau_E [Q] \ll 1$. The relation was approximately satisfied under this experimental condition.

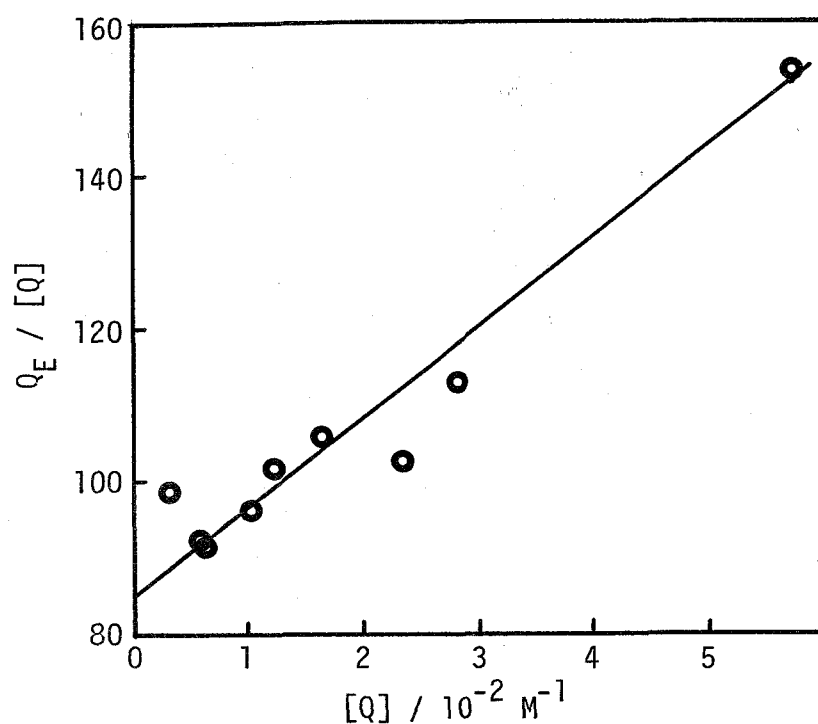The quenching reaction is more efficient for the second

Fig. I-19. The ratio of the quenching factor of the sandwich-like excimer to the concentration of DMTP vs. the concentration of DMTP.
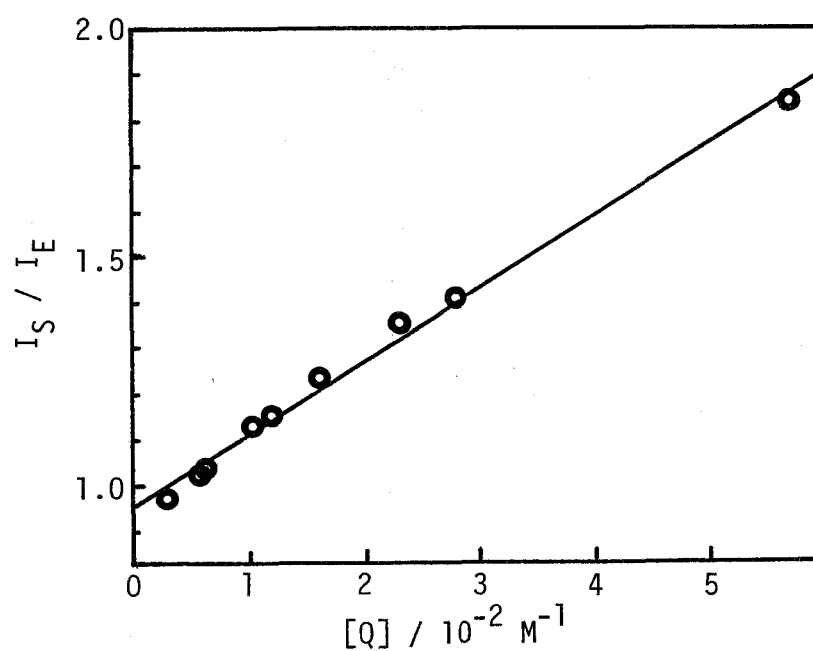

Fig. I-20. The fluorescence intensity ratio of the second excimer to the sandwich-like one vs. the concentration of DMTP.

excimer than for the sandwich-like one by a factor of ca. 4. The value of k_E is larger than that of k_s by a foctor of ca. 5, indicating that the sandwich-like excimer is formed easily from the second excimer. The value of k_E is the same order as that of the formation of the sandwich-like excimer from the monomer for DCzP in THF solution ($1 \times 10^8 \ s^{-1}$).[65]

Table I-7. Rate Constants for PVCz(r) in Aerated THF Solution.

$k_q/M^{-1}s^{-1}$	$k_q'/M^{-1}s^{-1}$	k_E/s^{-1}	k_s/s^{-1}	$(k_f+k_r)/s^{-1}$	$(k_f'+k_r')/s^{-1}$
4×10^9	1×10^9	2×10^8	4×10^7	5×10^7	2×10^7

Summary

The emission properties of PVCz, P7VBCz, and P5VBCz were investigated in solution in connection with the tacticity of the samples. PVCz(r and c), P7VBCz(r and c), and P5VBCz(r), which are composed of both the syndiotactic sequence and the isotactic one, showed one broad emission band composed of the second and the sandwich-like excimer fluorescences. The intensity of the second excimer fluorescence increased with an increase in the content of the syndiotactic sequence. P5VBCz(c), which is composed of only the isotactic sequence, showed structured emission composed of the monomer and the sandwich-like excimer fluorescences. These results indicate that the second excimer fluorescence is emitted from only the syndiotactic sequence. The conformational consideration suggests the structure of the second excimer that only one benzene ring in each neighboring carbazolyl chromophores overlaps with the other one (Fig. I-16).

The parameters of the photophysical process for PVCz(r) were evaluated by the quenching experiment. The sandwich-like excimer fluorescence was quenched more effectively than the second excimer fluorescence.

Chapter 3

Fluorescence Spectra of Poly[2-(N-carbazolyl)ethyl vinyl ether]

Introduction

It is known that 1-ethylpyrene and 1-ethylnaphthalene show

the excimer fluorescence in concentrated solutions. Poly(1-vinyl-

pyrene)[66,67] and poly(1-vinylnaphthalene)[34,68] show, almost

entirely, only the excimer fluorescence in dilute solutions.

Poly(1-pyrenylmethyl vinyl ether)(PPyMVE),[66,69] poly(1-naphthyl-

methyl vinyl ether)(PNMVE),[69] and poly(1-naphthyl methacrylate)

(PNMA),[70] in which the naphthyl and pyrenyl groups are widely

spaced on the skeletal chains by $-O-CH_2-$ and $-CO-O-$ bonds, show

both the structured monomeric fluorescence and the excimer one

in dilute solutions. On the other hand, ECz shows no excimer

fluorescence in concentrated solution.[17] However, PVCz shows

excimer fluorescence in dilute solution. Therefore, spectroscopic

studies on a vinyl polymer with carbazolyl chromophores widely

spaced on the skeletal chains are of interest in comparing with

those of the spectroscopic properties of PVCz.

In this chapter, the author investigated the spectroscopic

behavior of PCzEVE with carbazolyl chromophores widely spaced

on the main chain by $-O-CH_2-CH_2-$ bonds. It has already

been found, from the absorption and NMR spectra,[71] that PCzEVE

has no appreciable ground-state interaction among the carbazolyl

chromophores.

Experimental

The materials and the apparatus for measurments were the

same as those in the previous chapter.

For the fluorescence polarization, two polarizers were used,

and the data were corrected by the method described by Azumi and

McGlynn.[72]

Results and Discussion

The fluorescence spectra of the compounds with the

carbazolyl chromophores in MTHF-THF dilute solutions $(2.0 \times 10^{-4}$

M) are shown in Fig. I-21. The emission spectrum of DCzP

consists of a monomeric structured fluorescence and a sandwich-

like excimer one with a peak at ca. 23900 cm^{-1}, as is well-

known.[65,73-75] VCz Olig. I and II show both a structureless

fluorescence with a peak at 27000—27500 cm^{-1} and a sandwich-like

excimer fluorescence, as is the case of PVCz, although VCz

Olig. I also shows a monomer

fluorescence as a shoulder.

On the other hand, PCzEVE

shows only a broad, struc-

tureless fluorescence with

a peak at 27100 cm^{-1}. The

Stokes shift (1990 cm^{-1}) is

much larger than those of

i-PrCz and DCzP (380 cm^{-1}).

The fluorescence excitation

spectra of PCzEVE, obtained

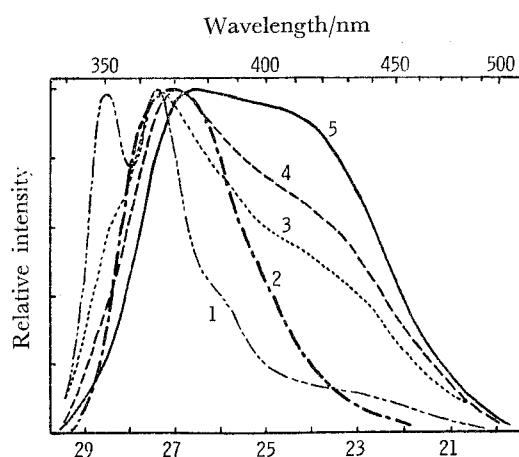Fig. I-21. Normalized fluorescence spectra of the model compound and vinylpolymers in MTHF–THF degassed solution at room temperature. Excitation wavelength; 310 nm.
(1) ——— ; DCzP, (2) ——— ; PCzEVE, (3) ----; VCz Olig. I, (4) ——— ; VCz Olig. II, (5) ——— ; PVCz(r).

-42-

by monitoring at several wavelengths (350—450 nm), duplicated exactly the absorption spectrum of this solution.

The fluorescence decay curve of PCzEVE in MTHF-THF solution clearly consists of two-component in all wavelength regions (370—430 nm), as is shown in Fig. I-22. The decay constant of the long-lived component observed at 370 nm (33 ± 1 ns) is longer than that of i-PrCz (17 ± 2 ns) and shorter than that of the sandwich-like excimer fluorescence of PVCz (45 ± 1 ns). The initial fast decay constant is 13 ± 2 ns. This two-component decay of PCzEVE is observed also in rigid glass at 77 K (35 ± 4 and 12 ± 2 ns). The intensity ratio of the short-decay component to the long one in rigid glass at 77 K is larger than that in fluid solution at room temperature.

Table I-7 shows the relative fluorescence quantum yields, taking the value of i-PrCz, which forms no excimer, as unity. The fluorescence quantum yield of PCzEVE is higher than that of DCzP, in which the sandwich-like excimer formation is minimum among the materials used, as is shown in Fig. I-21.

The fluorescence spectra of PCzEVE at various temperatures are shown in Fig. I-23. At lower temperatures, two peaks appear, and they approach
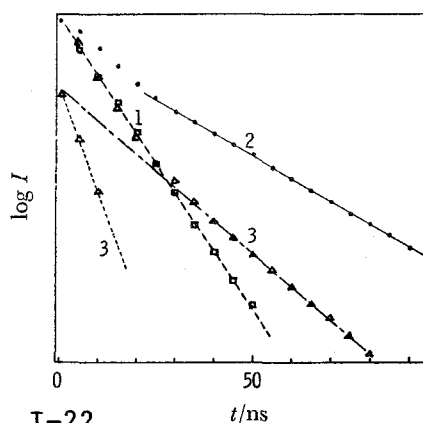

Fig. I-22.

Fluorescence decay curves of the model compound and vinylpolymers in MTHF-THF degassed solutions at room temperature.

(1) -□--□-; i-PrCz ($\lambda_{obsd}=370$ nm); $\tau_f=17$ ns.

(2) • • • ; PVCz(r) ($\lambda_{obsd}=380$ nm), —●--●—; the long-lived component; $\tau_f=46$ ns.

(3) △△△; PCzEVE ($\lambda_{obsd}=370$ nm), —△--△—; the long-lived component; $\tau_f=31$ ns, --△--△--; the short-lived compncnt; $\tau_f=11$ ns; the difference between the observed decay curve and the long-lived component.

Table I-7. RELATIVE FLUORESCENCE YIELDS

Substance	η
i-PrCz	1.00
PCzEVE	0.79
DCzP	0.57
VCz Olig. I	0.40
VCz Olig. II	0.37
PVCz(r)	0.33
PVCz(c)	0.27

each other with an increase in the temperature. At temperatures

higher than ca. 273 K, only a structureless fluorescence spectrum

is observed. The fluorescence intensity decreases with an

increase in the temperature. From the measurement of the

temperature dependence of the fluorescence spectra of PVCz, VCz

Olig. I and II, and DCzP, it was found that the sandwich-like

excimer fluorescence shows the maximum intensity at ca. 293 K.

On the other hand, in the case of PCzEVE, no appreciable change

in the fluorescence spectra near 23900 cm^{-1} is observed over a

wide temperature range, as is shown in Fig. I-23. These facts

indicate that PCzEVE does not form the sandwich-like excimer.

The emission spectrum of PCzEVE in rigid glass at 77 K also

is shown in Fig. I-23. The fluorescence spectrum of VCz Olig. II

has, roughly, a so-called "mirror-symmetry" relation between the

absorption and the fluorescence spectra (Fig. I-6 in chapter 2).

However, PVCz and PCzEVE do not have the mirror-symmetry

relation. In particular, the fluorescence spectrum of PCzEVE is

observed at a longer wavelength than that of PVCz and the shape is different from that of PVCz. The absorption spectra of PVCz and PCzEVE in rigid glass at 77 K are sharper than those in fluid solution at room temperature, but no appreciable new band is observed. The fluorescence excitation spectra of these polymers in rigid glass at 77 K are also in agreement
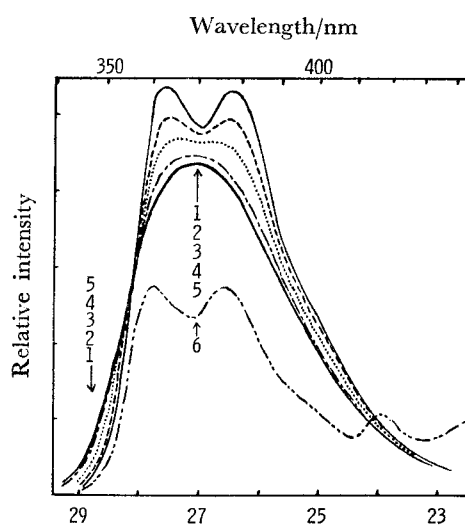

Fig. I-23. Temperature dependence of the fluorescence spectra of PCzEVE in MTHF–THF degassed solution. Concentration of PCzEVE; 2.0×10^{-4} M. Excitation wavelength; 310 nm.
(1) 168 K, (2) 208 K, (3) 249 K, (4) 298 K, and (5) 318 K. The fluorescence (6) at 77 K was also given for comparison.

with their absorption spectra. The resolution of the phosphorescence spectrum of PCzEVE is lower than those of i-PrCz and VCz Olig. I, and the spectrum is very similar to that of PVCz, although its lifetime (6.6±0.1 s) is shorter than that of PVCz (8.1±0.2 s). Therefore, the excited-state interactions are present among the carbazolyl chromophores in PCzEVE even at low temperatures, at which the solvent becomes rigid (ca. 102 K).

The degrees of polarization of the fluorescence are shown in Fig. I-24. The degrees are almost the same for PVCz and for PCzEVE. This fact indicates that the singlet energy migration in PCzECE occurs efficiently along the polymer chain, as is the case in PVCz.[17]

A concentrated THF solution of PCzEVE (0.5 M) shows the same spectrum as in dilute solutions near 223 K and above.

As has been mentioned above, PPyMVE, PNMVE, and PNMA show both the normal structured monomeric fluorescence and the sandwich-like excimer one in dilute solutions. On the other hand, poly[2-(9-phenanthryl)ethyl vinyl ether] (PPhEVE), with phenanthryl chromophores widely spaced on the main chain by $-O-CH_2-CH_2-$ bonds, shows only the monomeric structured fluorescence in dilute solution at room temperature, as will be described in the following chapter. The fluorescence structure and lifetime in a dilute solutions are almost the same as those of 9-ethyl-
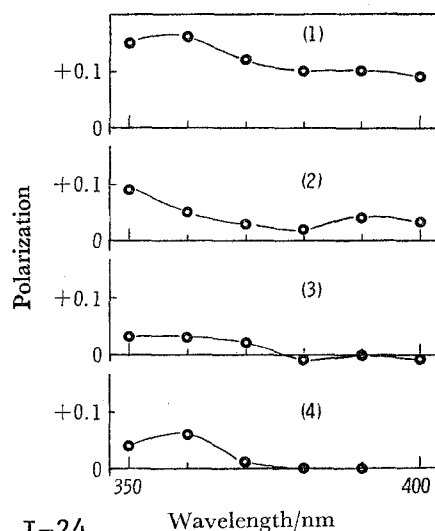

Fig. I-24. Fluorescence polarizations of MTHF–THF rigid glasses of (1) i-PrCz (6.7×10⁻⁵ M), (2) DCzP (7.3×10⁻⁵ M), (3) PCzEVE (9.6×10⁻⁵ M), and (4) PVC(r) (1.0×10⁻⁴ M) at 77 K. Excitation wavelength; 334 nm.

phenanthrene. It is well-known that the excimer fluorescence of phenanthrene is not observed at room temperature.[76] It is surprising that the normal structured monomeric fluorescence is not observed at all in the case of PCzEVE, in which aromatic chromophores are more widely spaced on the skeletal chain than PPyMVE, PNMVE, and PNMA. The fact that the sandwich-like excimer fluorescence of PCzEVE is not observed in either dilute or concentrated solution at room temperature also supports the idea that the sandwich-like excimer formation in PVCz is possible only between adjacent chromophores.[17]

The above-described results indicate that the excited-state interaction among the carbazolyl chromophores in PCzEVE is quite different from that in DCzP, VCz Olig. I and II, and PVCz , and that only PCzEVE is unique among the vinyl polymers with aromatic chromophores widely spaced on the main chain. This behavior of PCzEVE may reflect a characteristic of the bulky carbazolyl chromophore.

The position of the PCzEVE fluorescence band in solution at room temperature is almost the same as that of the fluorescence in the shorter wavelength regions of PVCz and VCz Olig. I and II, although the appearance of the structure below ca. 273 K is different. Therefore, one of the emitting species of PCzEVE in solution might be the second excimer. At the present time, there is no idea about the other emitting species of PCzEVE.

Summary

PCzEVE showed an interesting, new, structureless emission band with a peak at 27100 cm^{-1}. This is different from both

the monomeric structured fluorescence and the sandwich-like excimer one. The presence of two kinds of emitting species in this fluorescence was clarified by measuring the fluorescence decay curve. One of these emitting species is considered to be a second excimer. The emission properties of PCzEVE are unique among the vinyl polymers with aromatic chromophores widely spaced on the skeletal chain.

Chapter 4

Fluorescence Spectra of the Vinyl Polymers with Pendant

Phenanthryl Groups

Introduction

The monomeric model compounds of the vinyl polymers

investigated in the previous chapters show no excimer fluorescence.

It is of interest to investigate the excimer formation of another

aromatic vinyl polymer, whose the model compound shows no excimer

fluorescence.

Phenanthrene crystal has only two molecules per unit cell

arranged with their molecular planes almost perpendicular. It

does not normally exhibit an excimer emission. However, this

crystal under a high pressure exhibits a broad emission with a

peak at ca. 440 nm. This emission is assigned to the excimer

fluorescence.[77] Despite extensive studies of the prompt and

delayed fluorescences of phenanthrene, no excimer fluorescence

has been observed in this compound at room temperature.[75]

Studies on the emission of a phenanthrene sandwich dimer prepared

by photolytic dissociation have also shown that phenanthrene does

not form an excimer even under favorable condition.[78] Therefore,

it is of interest to investigate the emission spectra of the

vinyl polymers, where the phenanthryl(Ph) chromophores are

directly connected to or widely spaced on the skeletal chains.

In this chapter, the author describes the spectroscopic

behaviors of poly(9-vinylphenanthrene)(PVPh), poly(9-phenanthryl

methacrylate)(PPhMA), and poly[2-(9-phenanthryl)ethyl vinyl ether](PPhEVE); in the latter two polymers, the Ph chromophores are widely spaced on the skeletal chains by -CO-O- and -O-CH$_2$-CH$_2$- bonds, respectively.

Experimental

9-Ethylphenanthrene(EPh) and 9-vinylphenanthrene were prepared according to the literature.[79,80] The PVPh was prepared by a radical polymerization(AIBN). The degree of polymerization($\overline{DP}$) was about 18. This sample has sufficiently high molecular weight to examine the possibility of excimer formation, judging from the cases of DCzP and VCz Olig. I. 2-(9-Phenanthryl)ethyl vinyl ether was synthesized from 2-(9-phenanthryl)ethanol by the route similar to 2-(N-carbazolyl)-ethyl vinyl ether.[51,81] 9-Phenanthryl methacrylate was synthesized by the route similar to naphthyl methacrylate.[82,83] These monomers were identified by elemental analysis, NMR and IR spectra. The PPhEVE and the PPhMA used for spectral measurements were prepared by the cationic(BF$_3$OEt$_2$) and thermal polymerizations, respectively. The $\overline{DP}$ value of PPhEVE was about 87.

Results and Discussion

Fluorescence spectra of PVPh, PPhMA, PPhEVE, and EPh in solution are shown in Fig. I-25. The fluorescence spectrum of a concentrated EPh solution indicated that EPh forms no excimer, as is the case of phenanthrene. The fluorescence spectrum of PPhEVE is similar to that of EPh. Although the fluorescence

spectra of PVPh and PPhMA are broad as compared with the spectrum of EPh, no clear excimer fluorescence in the longer-wavelength region is observed for PVPh and PPhMA. Therefore, it is suggested that the interaction between neighboring chromophores in these polymers is much weaker than that observed for other aromatic vinyl polymers.

Fluorescence spectra of PVPh, PPhEVE, and EPh in rigid glasses at 77 K are shown in Fig. I-26. The fluorescence band is shifted to lower frequencies in the order of EPh, PPhEVE, and PVPh. The clear vibrational structure bands observed for PVPh and PPhEVE are similar to that for EPh and the fluorescence lifetimes of PVPh and PPhEVE are much the same as that of EPh at 77 K (Table I-8). These facts suggest that there is little interaction between neighboring Ph chromophores in PPhEVE and PVPh in rigid glass at 77 K.

Table I-8 shows the relative fluorescence quantum yields, taking the value of EPh as unity, and the fluorescence lifetimes. The fluorescence quantum yields and lifetimes of PVPh and PPhMA
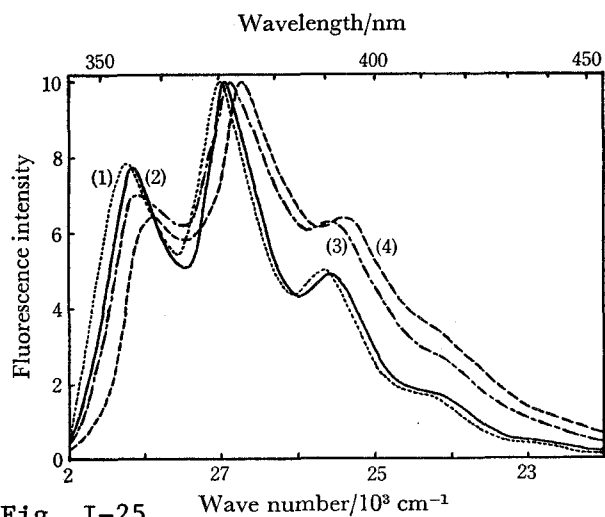

Fig. I-25.
Normalized fluorescence spectra of (1) ·······;
EPh, (2) ———; PPhEVE, (3) ·—·—; PPhMA, and (4)
------; PVPh in solutions at room temperature. Solvents;
(1), (2), (3); MTHF–THF (3:2) mixture, (3); chloro-
form containing 1.0% ethanol. Excitation wavelength;
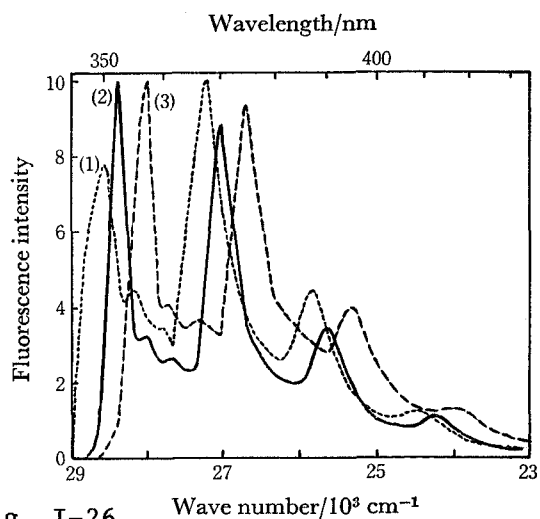345 nm.

Fig. I-26.
Normalized fluorescence spectra of (1) EPh, (2)
PPhEVE, and (3) PVPh in MTHF–THF rigid glasses
at 77 K. Excitation wavelength; 330 nm.

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at room temperature are much smaller than those of EPh and PPhEVE.

The decay curve of PVPh has an initial fast component. The

fluorescence spectra of PVPh in MTHF-THF solution at various

temperatures are shown in Fig. I-27. The fluorescence intensity

decreases and the vibrational bands broaden with raising

temperature. Temperature dependence of the fluorescence yields

are shown in Fig. I-28. The changes observed for EPh, PPhEVE,

and PPhMA are small and their magnitudes are nearly equal. On

the other hand, only PVPh shows a large decrease with raising

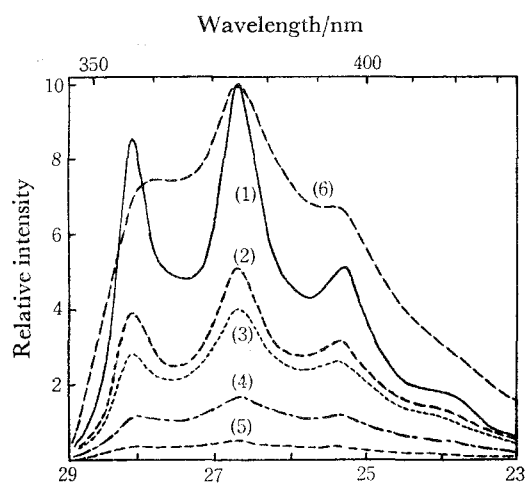temperature. The same tendency is observed for the temperature

Fig. I-27. Wave number/10^3 cm^{-1}
Temperature dependence of fluorescence spectra of PVPh (5.1×10^{-4} M) in MTHF–THF solution. Excitation wavelength; 310 nm. (1) -130, (2) -86.5, (3) -37.7, (4) 6, and (5) 63.5 °C. The fluorescence (6) is 1.95 times the fluorescence (5).
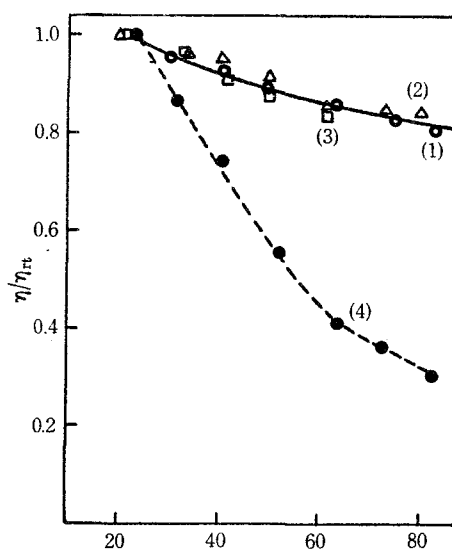

Fig. I-28. Temperature/°C
Temperature dependence of the fluorescence yields. The value of η/η_{rt} exhibits the ratio of the fluorescence yield at some temperature to that at room temperature. (1) ○; EPh, (2) △; PPhEVE, (3) □; PPhMA, and (4) ●; PVPh. Solvent: (1), (2), (4); 1,4-dioxane, (3); chloroform containing 1.0% ethanol. These values were uncorrected for decrease in density of solvents with an increase in temperature.

Table I-8. SPECTROSCOPIC DATA OF VINYL POLYMERS WITH PENDANT PHENANTHRYL CHROMOPHORES IN MTHF–THF

Polymer	Relative yield at 20°C	Fluorescence lifetime[b] /ns				Phosphorescence lifetime/s
		77 K	-40°C	24 °C	50 °C	
EPh	1.00	59	50	50	48	4.4
PPhEVE	0.85	59	49	47	46	3.4
PPhMA[a]	0.15	—	—	16[c]	15[c]	—
PVPh	0.17	58	40	21[c]	20[c]	2.8

a) Solvent: chloroform containing 1.0% ethanol.   b) The fluorescence was observed through Toshiba UV-DIC and UV-35 filters.   Error is ± 2 ns.   c) The initial fast decay component was observed.

dependence of the fluorescence lifetimes (Table I-8). Namely, the fluorescence lifetimes of EPh, PPhEVE, and PVPh in rigid glass at 77 K are all equal. Only the lifetime of PVPh, however, decreases unusually with an increase in temperature.

As mentioned above, the vibrational structure of fluorescence and its lifetimes of PVPh and PPhEVE are similar to those of EPh in rigid glass at 77 K. However, the phosphorescence of PVPh and PPhEVE is markedly different from that of EPh, as is shown in Fig. I-29. The phosphorescence band shifts to lower frequency and the vibrational structure broadens in the order of EPh, PPhEVE, and PVPh. The phosphorescence lifetime shortens in the same order (Table I-8). The red shift of the phosphorescence band is much larger than that of the fluorescence. PVPh and PPhEVE showed the delayed fluorescence resulting from a T-T annihilation between two migrating triplet excitons. These facts indicate that an interaction between neighboring Ph chromophores in the triplet state is much larger than that in the singlet state in rigid glass at 77 K.

PPhEVE resembles EPh very closely in fluorescence properties, forms no excimer, and does not show the anomalous fluorescence observed for PCzEVE. The fluorescence spectra of PPhMA is markedly different from that of EPh and its lifetime is very short. The temperature dependence of the fluorescence yield, however, is similar to those of EPh and
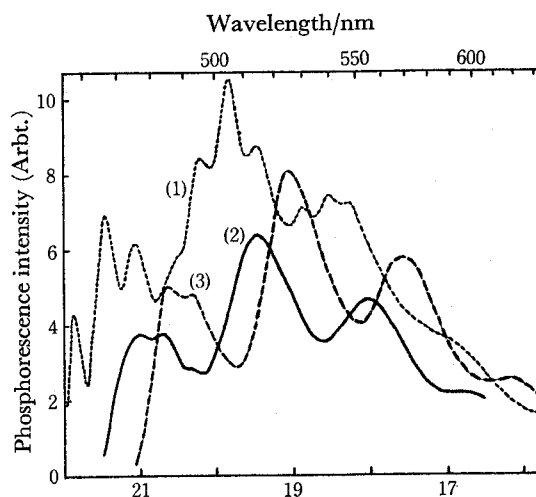

Fig. I-29. Phosphorescence spectra of (1) EPh, (2) PPhEVE, and (3) PVPh in MTHF–THF rigid glasses at 77 K. Excitation wavelength; 310 nm.

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PPhEVE. This indicates that PPhMA forms no excimer. The fluorescence properties observed for PPhMA are more likely to be affected by the substituent groups (-O-CO-). On the other hand, PPyMVE, PNMVE, and PNMA show the excimer fluorescence in dilute solution at room temperature. Therefore, the failure of PPhEVE and PPhMA to form an excimer is considered to be attributable to the nature of Ph, that is, Ph forms an excimer with difficulty.

Emission properties of PVPh clearly indicate that the interaction between neighboring Ph chromophores in PVPh is the strongest in the polymers studied. It has been reported, from fluorescence yield and decay curve measurements, that phenanthrene does not show concentration quenching of fluorescence at room temperature.[84,85] Therefore, if PVPh forms no excimer, the fluorescence yield of PVPh is expected to be as large as that observed for EPh. The present result is not so. Namely, the fluorescence yield of PVPh is much lower than that of EPh (Table I-8) and decreases largely with an increase in temperature (Fig. I-28). These facts suggest that PVPh forms an excimer which has a very low fluorescence quantum yield. This is compatible with the fact that the phenanthrene excimer in the crystalline state under a high pressure has a low fluorescence quantum yield.[77]

ECz, 5EBCz, 7EBCz, and EPh show no excimer fluorescence in concentrated solution at room temperature. PVCz, P5VBCz, and P7VBCz, however, show the excimer fluorescence in dilute solution at room temperature. It is suggested from the above-mentioned results that PVPh forms an excimer, although it shows no clear excimer fluorescence. Thus, the following conclusions were drawn: in the case of vinyl polymers with the aromatic chromophores

which form no excimer, an excimer is formed in the vinyl polymers in which the aromatic chromophores are directly connected to the skeletal chains, but it is not formed in the vinyl polymers in which the aromatic chromophores are widely spaced on the skeletal chains. PCzEVE is considered to be rather a special case.

Summary

The emission properties of EPh, PVPh, PPhMA, and PPhEVE were investigated in solution. These vinyl polymers showed no clear excimer fluorescence in the longer-wavelength region. Both the fluorescence quantum yield and lifetime of PVPh decreased largely with raising temperature in the higher temperature region, suggesting that PVPh forms an excimer which has a very low fluorescence quantum yield. The fluorescence properties of PPhMA and PPhEVE indicated little interaction between neighboring Ph chromophores in the singlet state. This originates from the nature of Ph, that is, Ph forms an excimer with difficulty. The phosphorescence spectrum and its lifetime of PPhEVE indicated a presence of a weak interaction between Ph chromophores in the triplet state.

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PART II

EMISSION SPECTRA OF AROMATIC VINYL POLYMER FILMS

AND EXCITATION ENERGY MIGRATION IN THE FILMS

INTRODUCTION

It is known that PVCz shows the largest photoconduction among the vinyl polymers investigated so far.[1] Okamoto et al. have suggested that the large photoconductivity of PVCz can be attributed both to the high efficiency of carrier generation due to the field-assisted thermal dissociation of an exciplex formed between the singlet exciton of PVCz and some electron-accepting impurity and to the ease of carrier migration due to the overlap of π-orbitals of neighboring Cz chromophores in one polymer chain.[2-6] Therefore, studies on singlet exciton migration in the aromatic vinyl polymer films are very important in understanding their photoconductivity, and also of interest in connection with the tacticity of the polymer chain.

It is known that triplet excitation energy also migrates very efficiently in aromatic vinyl polymers. The triplet excitation energy of PVCz is fairly high as compared with that of other aromatic vinyl polymers. Therefore, the photocarrier generation from the triplet excited state might be possible in PVCz.[7] Studies on the triplet exciton migration also are important, and of interest in connection with the singlet

exciton migration.

In order to reveal an origin of the high photoconductive properties of PVCz films, it is of interest and important to compare the spectroscopic properties of an amorphous film of the model compound with those of an amorphous PVCz film.

In this part, emission spectra of the vinyl polymer films with pendant carbazolyl groups and migrations of the singlet exciton (chapter 1) and the triplet one (chapter 2) in their films have been investigated. In chapter 1, fluorescence spectrum of an amorphous DCzP film and the singlet exciton migration in the films also have been investigated and compared with those of the amorphous vinyl polymer films.

Chapter 1

Singlet Excitation Energy Migration

Introduction

Klöpffer has reported that the results of fluorescence-quenching experiments in an amorphous PVCz film are consistent with a hopping model of monomer exciton migration, in which excitons can migrate in a polymer film and both excimer-forming sites and guest molecules act competitively as exciton traps.[8] From a lifetime quenching observed in a PVCz film doped with perylene, Powell et al. have recently proposed a model containing dimer sites besides guest molecules and the excimer-forming sites.[9] Concerning an undoped PVCz film, Johnson and Offen have suggested the presence of a dimer site as a result of measuring the fluorescence decay time of a PVCz film at 77 K.[10] Klöpffer and and Fischer have showed that the two different types of the spectra were observed in the prompt fluorescence and phosphorescence at 77 K, independent of the polymerization methods.[11]

It is of interest to investigate how the difference in the tacticity of the PVCz samples affects the singlet-excitation-energy migration. The study on singlet-excitation-energy migration in vinyl polymer films with carbazolyl(Cz) chromophores widely spaced on the skeletal chains is of interest in connection with that of a PVCz film.

The author has found that DCzP, a dimeric model compound of PVCz, forms an amorphous state by a fast evaporation of

solvent. It is of interest to investigate the spectroscopic properties of the amorphous DCzP(DCzP(a)) film and to compare them with those of an amorphous PVCz film. A few investigations have been carried out to ascertain how the efficiency of the singlet-excitation-energy migration changes when going from a crystalline to an amorphous state,[12-15] However, no comparison of the optical properties of an amorphous film of a model compound with those of the corresponding vinyl polymer has hitherto been performed.

In this chapter, the author describes the migration of the electronic-excitation energy in films of PVCz(r), PVCz(c), brominated PVCz(BPVCz), PCzEVE, poly(N-acryloylcarbazole)(PACz) and DCzP(a). DMTP, perylene, and p-bis(trichloromethyl)benzene (TCB) were used as the guest molecules. In the case of perylene, the long-range resonant energy transfer is somewhat possible.[16] However, the long-range resonant energy transfer from a Cz chromophore to a DMTP or TCB molecule is quite impossible, because DMTP and TCB have no absorption in the wavelength region where the fluorescence of the PVCz film is observed.[16] Therefore, DMTP and TCB are very useful in studying the phenomenon of the singlet exciton migration.

Experimental

PACz was the same as used in Ref. 17. BPVCz was prepared by the bromination of PVCz with N-bromosuccinimide and had one bromine atom per 1.1 Cz groups.[18]

Films of the model compounds were cast on quartz glass plates from a benzene solution followed by a fast evaporation of the

solvent at room temperature. Polymer films were cast on a quartz or pyrex glass plate from a benzene or 1,2-dichloroethane solution followed by slow evaporation of the solvent in a vessel nearly saturated with solvent vapor and dried in vacuo. The thickness of the film was about 0.1—0.06 μm for DCzP(a), about 4 μm for PCzEVE, and about 7 μm for other polymers. The apparatus for measurements were the same as those in the previous part.

Results and Discussion

(1) Fluorescence Spectra.

The fluorescence spectra of PVCz(r) and PVCz(c) films are shown in Figs. II-1 and II-2. The difference in the spectra between PVCz(r) and PVCz(c) films is similar to that observed in fluid solution. That is, the fluorescence intensity in the shorter-wavelength region of PVCz(r) films is larger than that of PVCz(c) films. Therefore, the emission band in the shorter-wavelength region was assigned to the second excimer fluorescence,
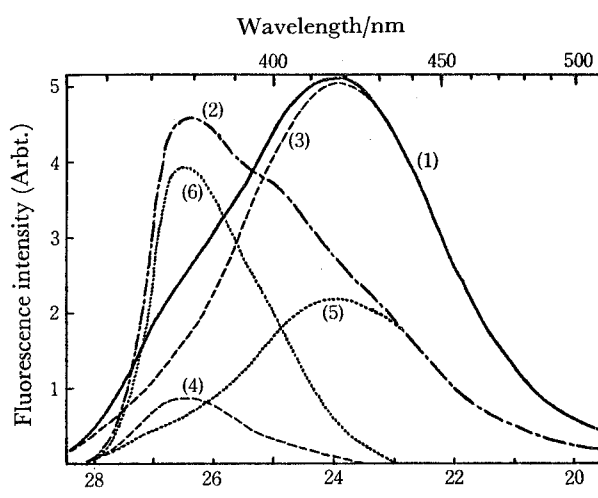
Fig. II-1. Fluorescence spectra and the resolution spectra of PVCz(r) films at 293 and 77 K.
(1) 293 K, (2) 77 K, (3) the component of the sandwich-like excimer fluorescence at 293 K, (4) the component of the second excimer fluorescence at 293 K, (5) the component of the sandwich-like excimer fluorescence at 77 K, (6) the component of the second excimer fluorescence at 77 K.
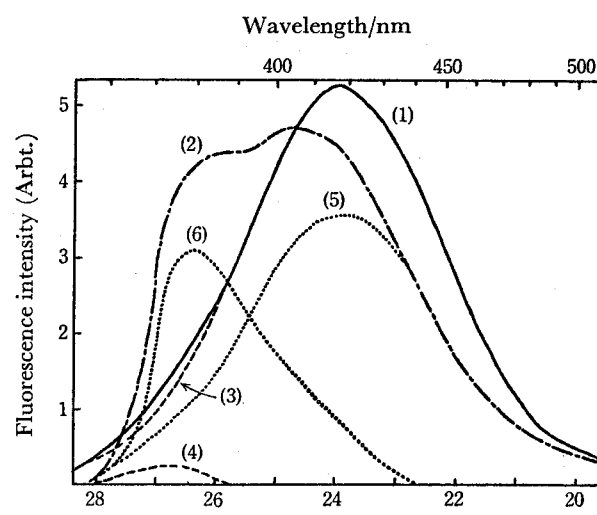
Fig. II-2. Fluorescence spectra and the resolution spectra of PVCz(c) films at 293 and 77 K.
(1) 293 K, (2) 77 K, (3) the component of the sandwich-like excimer fluorescence at 293 K, (4) the component of the second excimer fluorescence at 293 K, (5) the component of the sandwich-like excimer fluorescence at 77 K, (6) the component of the second excimer fluorescence at 77 K.

and that in the longer-wavelength region, to the sandwich-like excimer one. The fluorescence spectra of both polymer films were resolved into two components. The resolution spectra thus obtained also are shown in Figs. II-1 and II-2. The intensity of the second excimer fluorescence relative to the sandwich-like excimer one and the fluorescence yields are listed in Table II-1.

The presence of two kinds of emitting species in the fluorescence of PVCz(r) and PVCz(c) was clarified also by measuring the fluorescence decay curves of the polymers. The fluorescence decay curves of

Table II-1. THE INTENSITY OF THE SECOND EXCIMER FLUORESCENCE RELATIVE TO THE SANDWICH-LIKE ONE (I_S/I_E) AND THE QUANTUM EFFICIENCIES OF THE HOST FLUORESCENCE (η_H)

Host	I_S/I_E	η_H
PVCz(r)	0.083	0.045
PVCz(c)	0.013	0.041
PVCz(r)[a]	0.93	—
PVCz(c)[a]	0.55	—
PCzEVE	—	0.10
PACz	—	0.0002
BPVCz	—	0.001

a) At 77 K.

both polymer films in air at 293 K clearly involve two-component (20±3 and 6±1 ns) in the shorter wavelength region, but one-component (22±2 ns) in the longer wavelength region. The intensity of the short-lived component relative to the long-lived one for PVCz(r) films in the shorter wavelength region is larger than that for PVCz(c) films. Therefore, the long- and short-lived components correspond to the sandwich-like excimer fluorescence and the second excimer one, respectively. Similar results were obtained also at 77 K; the long- and short-lived components are 17±2 and 6±2 ns, respectively. These decay constants are roughly in agreement with the values reported by Powell et al. (20 and 10 ns).[9] The lifetime of the sandwich-like excimer fluorescence of PVCz films is shorter than that of PVCz in fluid solution (ca. 40—42 ns)[19,20] and that of PVCz films obtained by Johnson and Offen (43 ns).[10]

The fluorescence spectra of PCzEVE films undoped and doped with DMTP are shown in Fig. II-3. PCzEVE films show only a

broad, structureless fluorescence spectrum with a peak at ca. 26050 cm^{-1}. The fluorescence decay curve in air consists of one-component in both the shorter and longer wavelength regions (4—5 and 10—11 ns, respectively). Two component decay curve is observed in the medium wavelength region. This fact

Fig. II-3. Wave number/10^3 cm^{-1}

Fluorescence spectra of PCzEVE films doped with DMTP at 293 K. DMTP concentration; (1) 0, (2) 4.44 × 10^{-4}, (3) 8.88 × 10^{-4}, and (4) 1.18 × 10^{-2} (mol/ CzEVE unit mol). Fluorescence spectrum of the undoped film at 77 K is also given by a dotted line (5).

indicates that the two kinds of emitting species are present in PCzEVE films at 293 K. Although the fluorescence spectrum of PCzEVE films at 77 K has the structure, it does not seem to be the monomeric fluorescence of a Cz chromophore because of a large Stokes shift (1540 cm^{-1}).

The fluorescence spectra of PACz and BPVCz films undoped and doped with DMTP or perylene are shown in Fig. II-4. The fluorescence efficiency of PACz films is extremely low (Table II-1) because of the presence of intersystem crossing from the lowest $^1\pi$, π^* state to the lowest ^3n, π^* state due to a carbonyl group. PACz films show a fluorescence spectrum consisting of two components. The spectra of PACz and BPVCz films change rapidly under
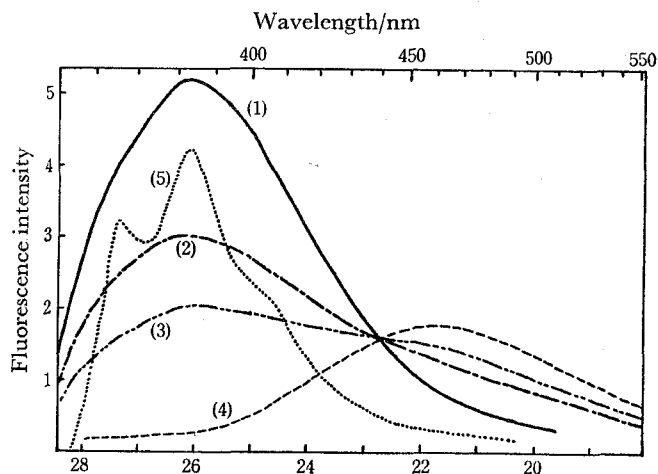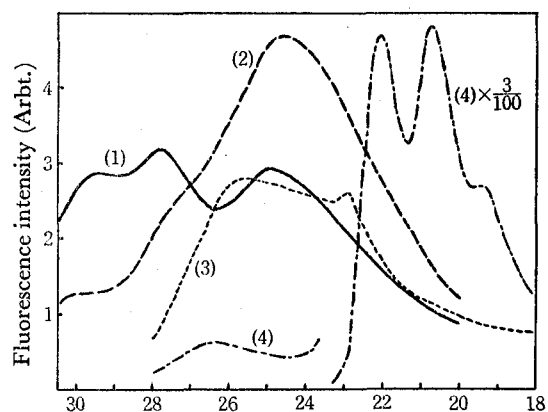

Fig. II-4. Wave number/10^3 cm^{-1}

Fluorescence spectra of PACz and BPVCz films at 293 K. PACz films; (1) undoped, (2) doped with DMTP (2.32 × 10^{-2} ACz unit mol). BPVCz films; (3) undoped, (4) doped with perylene (5.9 × 10^{-3} mol/ mol basic unit).

irradiation by an exciting light.

The fluorescence spectra of DCzP(a), polycrystalline DCzP (DCzP(c)), and polycrystalline i-PrCz films in air are shown in Fig. II-5. The spectrum of DCzP molecule in aerated benzene solution also is shown for comparison. The fluorescence spectrum of DCzP(a) films is remarkably different from those of amorphous PVCz and PCzEVE films. That is, DCzP(a) films show a structured fluorescence and a tailing in the long wavelength side of the band. The intensity of the second peak (26750 cm^{-1}) in the structured
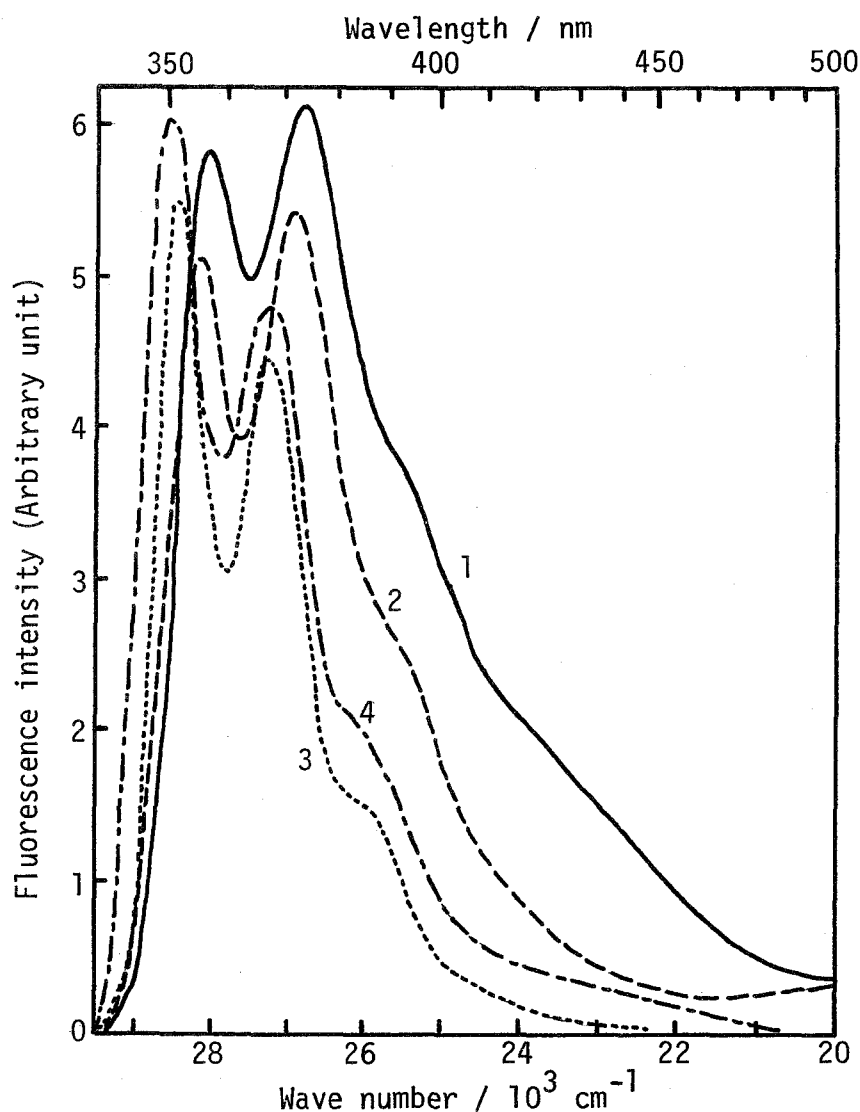

Fig. II-5. Fluorescence spectra of (1) DCzP(a), (2) DCzP(c), (3) i-PrCz films and (4) DCzP in aerated benzene solutions at 293 K.

band is anomalously large, compared with those observed for polycrystalline i-PrCz films and the DCzP molecule in solution. The position of the second peak is nearly equal to that of the second excimer fluorescence in PVCz films. The fluorescence-decay curve of DCzP(a) films involves multi-components (23±3 ns and an initial fast decay) in the longer-wavelength region (λ_{obs} >400 nm) and one component (ca. 7 ns) in the shorter-wavelength region. The long-lived component in the longer-wavelength region is nearly equal in the lifetime to the sandwich-like excimer fluorescence in PVCz films (22±2 ns). Excitation spectra of DCzP(a) films, obtained by monitoring at several wavelengths(355-500 nm), duplicated the absorption spectrum of the films exactly. Therefore, the fluorescence spectrum of DCzP(a) films seems to be composed of three components; monomer, second excimer, and sandwich-like excimer fluorescences.

As is shown in Fig. II-5, thin DCzP(c) films show no sandwich-like excimer fluorescence. This is supported also by the fact that the long-lived component (ca. 23 ns) in the longer-wavelength region was not observed. This is the same as the case of crystalline i-PrCz. However, the spectrum of thin DCzP(c) films is different from that of thin polycrystalline i-PrCz films. That is, the intensity of the second peak (ca. 26900 cm^{-1}) in the structured band is larger than that of the first peak, compared with the spectrum of i-PrCz films. The position of the second peak was the almost same as that observed for DCzP(a) films and that of the second excimer fluorescence in PVCz films. Therefore, thin DCzP(c) films may show both monomer and second excimer fluorescences. The presence of the second excimer site in DCzP(c) films seems to be also suggested by the fact that

formation of a microcrystal of DCzP in benzene matrix at low

temperature leads to formation of an excited state like that

observed for PVCz (second excimer).[19]

(2) Singlet Excitation Energy Migration.

The fluorescence spectra of PVCz(r), PVCz(c), and PCzEVE

films doped with DMTP or perylene at 77 K are shown in Fig. II-6.

In the case of all polymer
films studied at 293 and 77
K, by doping of DMTP,
TCB, or perylene, the host
fluorescence decreases and
is replaced by the exciplex
or guest fluorescence. The
exciplex is formed between
DMTP and a Cz chromophore.
As DMTP and TCB have no
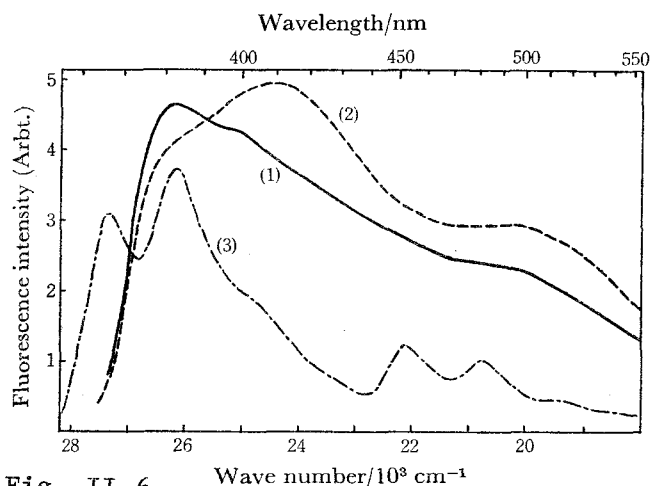absorption in the wavelength

Fig. II-6. Fluorescence spectra of PVCz(r), PVCz(c) and PCzEVE films doped with DMTP or perylene at 77 K. (1) PVCz(r) doped with DMTP (3.26×10^{-3} mol/VCz unit mol), (2) PVCz(c) doped with DMTP (3.02×10^{-3} mol/VCz unit mol), and (3) PCzEVE doped with perylene (1.15×10^{-4} mol/CzEVE unit mol).

region where the host fluorescence of these films is observed,

the dipole-dipole resonance cannot be responsible for the energy

transfer to DMTP and TCB molecules.[8,16] In fact, no decrease in

the fluorescence lifetimes of PVCz(r) films by doping of DMTP is

observed. That is, the fluorescence lifetimes of the PVCz(r)

film doped with a small amount of DMTP (ca. 3×10^{-3} mol/mol

basic unit) in the shorter-wavelength region are 17 ± 3 and 5 ± 2 ns

at 293 K and 19 ± 2 and 6 ± 1 ns at 77 K.

In the present case, therefore, the hopping model of monomer-

exciton migration is applicable at 293 and 77 K. We should

consider the case of the presence of two kinds of traps (for

example; the sandwich-like excimer-forming site, c_E [mol/mol basic unit], and the second excimer site, c_s [mol/mol basic unit], in the case of PVCz films) in a way similar to the treatment in Ref. 8. Then, the quenching factor of the host fluorescence, Q_H, is expressed by the following equations;

$$Q_H = (\eta_{H,0} - \eta_H)/\eta_H = 0.66nc/[1 + 0.66n(c_E + c_s)] = n'c \qquad (1)$$

$$n' = 0.66n/[1 + 0.66n(c_E + c_s)] \qquad (2)$$

$$n = n_s/(n_e + n_l) \qquad (3)$$

where n_s, n_e, and n_l are the relative probabilities (per unit time) of jumping, radiative, and nonradiative decay, $\eta_{H,0}$ and η_H are quantum efficiencies of the host fluorescence in the absence and in the presence of the guest molecule in a concentration of c [mol/mol basic unit], and n and n' are the number of jumps during the lifetime in the absence and in the presence of trap sites, respectively. The quenching factor of the monomer fluorescence, Q_M, may be expressed by;

$$Q_M = 0.66n(c_E + c_s) = 0.66nc_T \qquad (4)$$

In the case of polymer films, where no monomer fluorescence can be observed, $Q_M \gg 1$. Therefore,

$$n' = 1/(c_E + c_s) = 1/c_T \qquad (5)$$

$$Q_H = c/(c_E + c_s) = n'c \qquad (6)$$

The ratio of the fluorescence intensities guest/host (I_G/I_H) is;

$$I_G/I_H = c\eta_G/(c_E\eta_E + c_s\eta_s), \qquad (7)$$

where η_G is the quantum efficiency of the guest fluorescence in the host film under direct excitation. The relative intensity of the second excimer fluorescence to the sandwich-like excimer one is expressed by

$$I_s/I_E = c_s\eta_s/c_E\eta_E. \qquad (8)$$

On the other hand, in the case of DCzP(a) films, the value of

$1/c_T$ seems to be smaller than n', since the value of Q_M could not be determined. Although the experimental values of Q_H scatter a little, the measurement of Q_H at various concentrations of a guest gives the value of n' and c_T according to Eqs. 5 and 6, respectively. In the case of PVCz films, the measurement of I_G/I_H at various concentrations of the guest gives the values of $c_E\eta_E$ and $c_S\eta_S$ according to Eqs. 7 and 8, respectively, using the values of η_G and I_S/I_E in Tables II-1 and II-2. Figure II-7 shows the bilogarithmic plots of Q_H or I_G/I_H and c, as example, in the case of the PVCz(c)-DMTP system. The values thus obtained are listed in Table II-2.

In the case of the PVCz(r) and PVCz(c) films, the values of n', c_T $(=c_E+c_S)$, $c_E\eta_E$, and $c_S\eta_S$ are obtained by the method mentioned above. The value of c_E+c_S at 293 K is nearly equal to that of c_E obtained by Okamoto et al. in the PVCz(r)-DMTP system, on the assumption that the host fluorescence is emitted only from the sandwich-like excimer.[16] The values of n' and c_E+c_S are almost the same for PVCz(r) and PVCz(c) films. The value of $c_E\eta_E$ is almost the same for PVCz(r) and PVCz(c) films, while the value of $c_S\eta_S$ for PVCz(r) films is higher than that for PVCz(c) films. It can safely be considered that the efficiencies of each fluorescence (η_E and η_S) of PVCz(r) films are equal to those of PVCz(c) films.
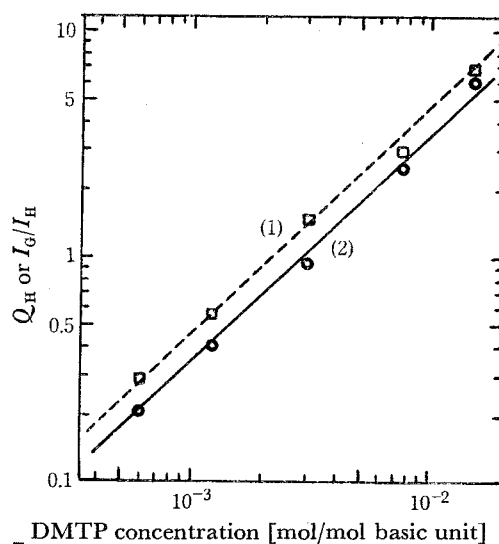

Fig. II-7. Ratio of fluorescence intensities guest/host I_G/I_H (1) and quenching factor of host fluorescence Q_H (2) as a function of guest concentration for PVCz(c)-DMTP system at 293 K.

Table II-2. Energy Transfer by the Exciton Diffusion Process in Amorphous Films at 293 and 77 K.

Host	Guest	η_G	$c_T \times 10^3$ (mol/mol basic unit)	n'	$c_E\eta_E \times 10^5$	$c_s\eta_s \times 10^5$	$L/\text{Å}$ [c]
PVCz(r)	perylene	—	0.83	1200	—	—	120
PCzEVE	"	—	0.27	3700	—	—	210
BPVCz	"	0.27	(19)[d]	(52)[d]	—	—	—
DCzP(a)	"	—	<0.17	5900	—	—	—
PVCz(r)	DMTP	0.043	2.7	370	10	0.83	67
PVCz(c)	"	0.039	2.2	450	(11)[b]	(0.11)[b]	74
PCzEVE	"	0.034	0.45	2200	—	—	—
PACz	"	0.004	24[e]	42[e]	—	—	—
			(25)[f]	(40)[f]	—	—	—
DCzP(a)	"	—	<0.77	1300	—	—	—
PVCz(r)[a]	"	0.17	3.5	290	40	37	60
PVCz(c)[a]	"	0.15	3.2	310	43	23	63
PVCz(r)	TCB	—	1.4	690	—	—	92
PCzEVE	"	—	0.5	2000	—	—	—
DCzP(a)	"	—	<0.28	3600	—	—	—

a) At 77 K. b) The values are less reliable because of the large error in I_s obtained by a resolution of the host fluorescence spectrum. c) $L = an'^{1/2}$, where L is the mean exciton migration length and a is the interchromophore sparation (3.5 Å). d) The values were obtained in a way similar to that used in the treatment in Ref. 8, on the assumption that the host fluorescence is emitted by one trap site. e) The values were obtained from Q_H, on the assumption that the fluorescences in the shorter and longer wavelength regions are emitted by some intrinsic traps and an excimer, respectively. f) The values were obtained from the ratio of (I_G/I_Hc), on the assumption that the fluorescences in the shorter and longer wavelength regions are emitted by a monomer and an excimer, respectively.

Therefore, the concentration of the sandwich-like excimer site (c_E) in PVCz(r) films is nearly equal to that in PVCz(c) films. On the other hand, the concentration of the second excimer (c_s) in PVCz(r) films is higher than that in PVCz(c) films by a factor

of about 1.6. This difference in the value of c_s does not clearly appear in the value of $c_E + c_s$. This fact suggests that the value of c_E is larger than that of c_s in both films.

The values of $c_E \eta_E$ for PVCz(r) and PVCz(c) films obtained at 77 K are larger than those obtained at 293 K by a factor of 4. It may safely be considered that the values of η_E and η_s for PVCz(r) films change with the temperature in a manner similar to that for PVCz(c) films. The values of c_E and c_s are determined by the casting temperature of the film because of the high glass-transition temperature of PVCz. Therefore, this increase in the value of $c_E \eta_E$ seems to be caused mainly by a change in the value of η_E. On the other hand, the value of $c_s \eta_s$ obtained at 77 K is much larger than that obtained at 293 K. This increase in $c_s \eta_s$ with a decrease in the temperature is too large to be caused only by an increase in η_s. The value of c_s should be considered to vary apparently with temperatures. This suggests that the second excimer site is a shallow trap and acts more effectively as a trap at low temperatures.

The value of c_T for PCzEVE films is much smaller than those for the PVCz(r) and PVCz(c) films. This suggests that it is difficult for Cz chromophores to form intrinsic trap sites because of the large distance between neighboring Cz chromophores. The value of n for PCzEVE films might be smaller than the values of n for PVCz(r) and PVCz(c) films, judging from the large distance between neighboring Cz chromophores. However, even in the case of PCzEVE films, $Q_M \gg 1$, that is, the singlet exciton migration is limited by the intrinsic trap sites. Thus, the value of n' for PCzEVE films is larger than that for PVCz films by a factor of ca. 5.

In the case of the PACz and BPVCz films, the emitting species of the host fluorescence are ambiguous. Judging from the profile of the fluorescence spectrum of PACz films, the broad fluorescence band with a peak at ca. 25000 cm^{-1} might be assigned to the excimer fluorescence. The fluorescence band in the shorter wavelength region might be attributable to a monomer or to some intrinsic trap sites. The host fluorescence of BPVCz films is considered to be emitted from some trap sites. Irrespective of the treatments used to obtain the value of n' (Table II-2), the values of n' for both polymer films are very small. This may be attributable to the short exciton lifetime because of the enhanced intersystem crossing and the presence of extrinsic trap sites(photoproducts and/or impurities introduced during a bromination reaction).

The concentration of the trap sites for DCzP(a) films was smaller than those for the polymer films, irrespective of the guest molecule, except for PCzEVE films doped with DMTP. This suggests that the excimer sites are formed with greater ease in a polymer film than in an amorphous film of the model compound, even if carbazolyl chromophores are widely spaced on the skeletal chain.

It has been reported that the singlet exciton migration length in crystalline films is more than one order of magnitude larger than that in amorphous films.[12-15] In the present case, the value of n' in the crystalline film(DCzP(c)) was smaller than that in the amorphous film by a factor of about 3. The reasons for the poor energy transfer to a guest molecule in DCzP(c) films are probably as follows: (1) DCzP(c) has a trap site (second excimer site), and (2) the guest molecule may

segregate in a DCzP(c) film and so may not be dissolved in the film uniformly.

The number of Cz chromophores covered by a singlet exciton during the lifetime decreases in the following order; DCzP(a) > PCzEVE > PVCz(r) ~ PVCz(c) > PACz ~ BPVCz.

Summary

The migration of electronic excitation energy in films of PVCz(r), PVCz(c), PCzEVE, BPVCz, PACz, and DCzP(a) has been studied by means of fluorescence-quenching experiments, using DMTP, perylene, or TCB as a guest molecule.

PVCz(r and c) films showed a broad structureless fluorescence composed of the second and sandwich-like excimer fluorescences. The second excimer fluorescence intensity was larger for PVCz(r) films than for PVCz(c) films. The lifetime of the second and sandwich-like excimer fluorescences were ca. 6 and ca. 21 ns, respectively. PCzEVE films showed only a broad, structureless fluorescence composed of two unknown components. DCzP(a) films showed fluorescence composed of three components; monomer, second excimer, and sandwich-like excimer fluorescences.

In the case of all films studied, the hopping model of monomer-exciton migration was applicable at 293 and 77 K. The concentration of the sandwich-like excimer site (c_E) in PVCz(r) films was nearly equal to that in PVCz(c) films, while the concentration of the second excimer site (c_S) in PVCz(r) films was higher than that in PVCz(c) films. The value of c_E was much larger than that of c_S for both films. The value of c_S increased apparently with a decrease in the temperature, suggesting that

the second excimer site is a shallow trap. Even in PCzEVE films, the singlet exciton migration was limited by the intrinsic trap sites. DCzP(a) films had the lowest concentration of the trap sites ($\sim 3 \times 10^{-4}$ mol/mol basic unit), suggesting that the excimer sites are formed with greater ease in a polymer film than in an amorphous film of the model compound, even if Cz chromophores are widely spaced on the skeletal chain.

The number of carbazolyl chromophores covered by a singlet exciton during the lifetime decreases in the following order: DCzP(a) > PCzEVE > PVCz(r) $\sim$ PVCz(c) > PACz $\sim$ BPVCz. This order was explained by the concentration of the intrinsic trap sites depending on the distance between neighboring Cz chromophores, and by the substituent effect determining the lifetime of the singlet exciton.

Chapter 2

Triplet Excitation Energy Migration

Introduction

The triplet energy migration and transfer in vinyl polymers with large aromatic rings, such as naphthyl and carbazolyl groups, in rigid solution at 77 K have been studied in detail.[21-23] The result indicates that the triplet excitons can migrate along the polymer chain, and that delayed fluorescence is caused by a homogeneous triplet-triplet (T-T) annihilation between two intramolecular migrating triplet excitons. David et al. reported the triplet energy transfer in vinyl polymers with small aromatic rings in solid film, which emit only phosphorescence and no delayed fluorescence.[24,25] They showed that the triplet exciton migration frequencies in such polymer films were smaller than those in the corresponding crystals. Concerning the vinyl polymer films with large aromatic rings, Fox at al., and Klöpffer and Fischer have qualitatively studied poly(1-vinylnaphthalene) and PVCz, respectively.[11,26] Klöpffer and Fischer showed that the phosphorescence of PVCz films is governed by two kinds of traps, whose concentration was estimated to be 5×10^{-3} (mol of trap/mol of basic unit) from the saturated concentration of the sensitized dopant phosphorescence, and that PVCz films emitted no delayed fluorescence. However, the triplet energy migration in solid film has never hitherto been studied quantitatively on such vinyl polymers.

Therefore, it would be interesting to investigate

quantitatively the spectroscopic behavior of triplet excitons

in the vinyl polymers with large aromatic rings and to compare

the difference between in rigid solution and in solid film.

Experimental

Commercial naphthalene(NAPH) and fluorene of a scintillation

grade were purified by zone-refining. Commercial 1,3-pentadiene

(1,3-PD), a well-known triplet quencher, was used after

distillation.

The apparatus and technique for measuring the emission

spectra were described in the previous part. All the samples

were excited by 345 nm light, which is not absorbed by the

triplet quenchers. It was confirmed that the application of a

phosphoroscope factor[27] was not necessary in the case of film.

In the case of rigid solution, the delayed fluorescence spectra

were, however, corrected by using a phosphoroscope factor.

Phosphorescence decay curves were recorded on a X-t recorder

and delayed fluorescence lifetimes were determined from

oscilloscope traces.

Results and Discussion

(1) Delayed Emission Spectra in Rigid Solution and in Film.

The delayed emission spectra of PVCz(r), PVCz(c), and PCzEVE

in rigid solution and in film at 77 K are shown in Figs. II-8 and

II-9, respectively. Concerning PVCz(r and c) in rigid solution,

Yokoyama et al.[7] and Klöpffer[11] have reported as follows : (1)

the delayed emission spectrum
consists of a delayed
fluorescence and a phospho-
rescence; (2) the intensity
and the lifetime of the
delayed fluorescence are
dependent on the molecular
weight, and the delayed
fluorescence is not observed
for PVCz with a low molecular
weight ($\overline{DP} \leqq 50$); (3) the
phosphorescence is emitted
from a trap site in the
polymer chain because the
phosphorescence (0-0 band;
420 nm) is located at a lower
energy than that of i-PrCz
(0-0 band; 412 nm). However,
they have not reported on the
relation between the spectra
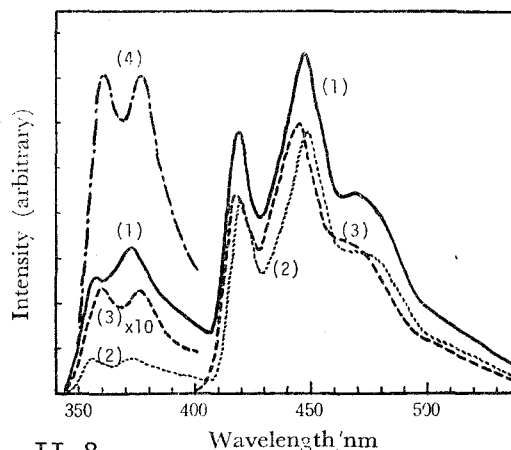and the tacticity of the
samples. In the present

Fig. II-8.
Delayed emission spectra of (1) PVCz(r), (2)
PVCz(c), and (3) PCzEVE in MTHF-THF rigid
solutions at 77 K (uncorrected). The prompt
fluorescence (4) of PCzEVE in MTHF-THF rigid
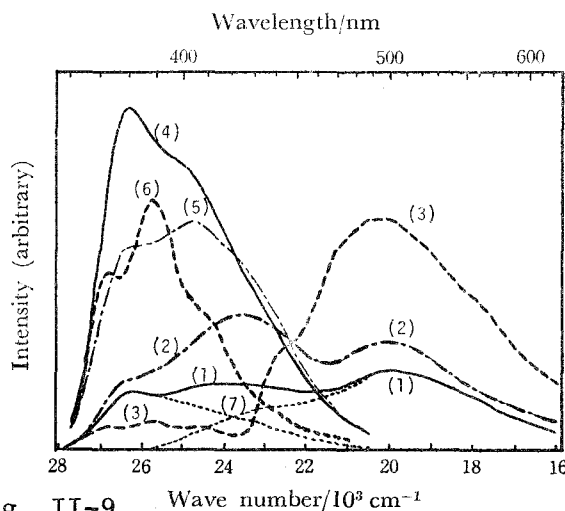solution at 77 K was also given for comparison.

Fig. II-9.
Delayed emission spectra of (1) PVCz(r), (2)
PVCz(c), and (3) PCzEVE films at 77 K. The
prompt fluorescence spectra of (4) PVCz(r), (5)
PVCz(c), and (6) PCzEVE films at 77 K were also
given for comparison. The resolution spectra (7) of
delayed emission spectum of PVCz(r) (1) were also
given.

results, the delayed fluorescence spectra are a little different
between PVCz(r) and PVCz(c), as is shown in Fig. II-8, although
the lifetimes (τ_{df}^0) are almost the same (11 ms for PVCz(r) and
12 ms for PVCz(c)). The phosphorescence spectra are almost the
same between PVCz(r) and PVCz(c). The lifetime (τ_{ph}^0) is 8.1 $\pm$
0.2 s for PVCz(r and c).

In the case of film, Klöpffer[11] showed that PVCz(r and c)

films emitted only a phosphorescence governed by two traps (two

component decay; 7.9±1 and 1.4 s), and no delayed fluorescence,

and that two different types of spectra were observed in the

phosphorescence and in the prompt fluorescence at 77 K,

independent of the polymerization methods.   In the present results,

the delayed emission spectra of PVCz(r and c) consist of two

emission bands, as is shown in Fig. II-9.   The prompt fluorescence

spectra of the films and the example of the resolution spectrum

are also shown in Fig. II-9.   The further purification of the

polymer (for example; reprecipitation up to ten times and/or

extraction with hot methanol) gave no change in the spectra.

The broad delayed emission in the longer wavelength region is

invariably monophotonic in origin, and this lifetime consists

of two components (7.9±0.7 and 1.6±0.5 s).   Therefore, this

emission is considered to be the phosphorescence emitted both

from Trap I (the sandwich-like excimer forming site) and from

Trap II, as has been reported by Klöpffer.[5]   Both the position

and profile of the delayed emission band in the shorter wavelength

region are the same as those observed for the normal fluorescence

at 77 K, as is shown in Fig. II-8, and the emission intensity

depends quadratically on the excitation light intensity.   The

lifetime of this emission is about 50 ms for PVCz(r and c).

These facts indicate that this emission band can be assigned to

the delayed fluorescence resulting from a homogeneous T-T

annihilation between two migrating triplet excitons in film, as

is the case with rigid solution.   The delayed fluorescence of

PVCz(r) differed from that of PVCz(c) in the similar manner

observed for the prompt fluorescence.

The delayed emission spectra of PCzEVE in rigid solution

and in film at 77 K also consist of two bands, as is shown in

Figs. II-8 and II-9. Both the positions(λ_{max}; 360 and 376 nm in

rigid solution and 371, 388, and 409(shoulder) nm in film) and

the profile of the emission band in the shorter-wavelength region

are nearly the same as is observed for the normal fluorescence,

and the emission intensity depends quadratically on the exciting-

light intensity. Therefore, the emission bands of PCzEVE are

identified as the delayed fluorescence. The τ_{df}^{0} of PCzEVE films

is 45 ms, while that in rigid solution has not been determined

because of low intensity. On the other hand, the delayed

emission band at a longer wavelength (λ_{max}; 418, 446 nm in rigid

solution and about 495 nm in film) is monophotonic in origin.

Therefore, this emission band is identified as the phosphores-

cence emitted from the trap site, by analogy with PVCz(r and c).

The τ_{ph}^{0} in rigid solution is 6.6$\pm$0.1 s, while that in film

consists of two components (3.5$\pm$0.2 and 0.7$\pm$0.05 s), which is

smaller than that of PVCz(r and c) by a factor of ca. 2.

(2) <u>Triplet Energy Migration in Film and in Rigid Solution.</u>

The delayed emission spectra of PVCz(r) and PCzEVE films

doped with NAPH of various concentrations are shown in Figs. II-

10 and II-11. The prompt fluorescence spectra of the polymer

films also are shown for the sake of comparison. In all the

polymer films studied, by the doping of NAPH, the Cz chromophore-

phosphorescence(I_{ph}) decreases significantly and is replaced by

a sensitized NAPH phosphorescence(I_{sph}). Although the Cz

chromophore-phosphorescence lifetime(τ_{ph}) in PVCz(r and c) films

has not been determined because of the overlapping of I_{ph} and I_{sph},

τ_{ph} in PCzEVE films was found, by observing the decay curve at

444 nm, not to decrease by the doping of NAPH, Therefore, in these films, the triplet energy seems to transfer from the freely migrating triplet exciton to the dopant, and I_{ph} seems to be emitted from the trapped triplet state.
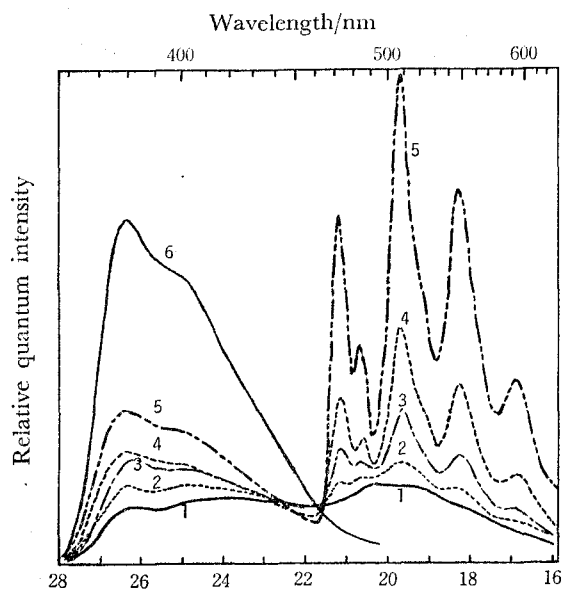
Wavelength/nm

Fig. II-10. Wave number/10^3 cm^{-1}
Delayed emission spectra of PVCz(r) films doped with NAPH at 77 K. NAPH concentration; (1) 0, (2) 1.41×10^{-4}, (3) 7.04×10^{-4}, (4) 1.41×10^{-3}, and (5) 7.04×10^{-3} mol/VCz unit mol. The prompt fluorescence (6) of a PVCz(r) film was also given for comparison.
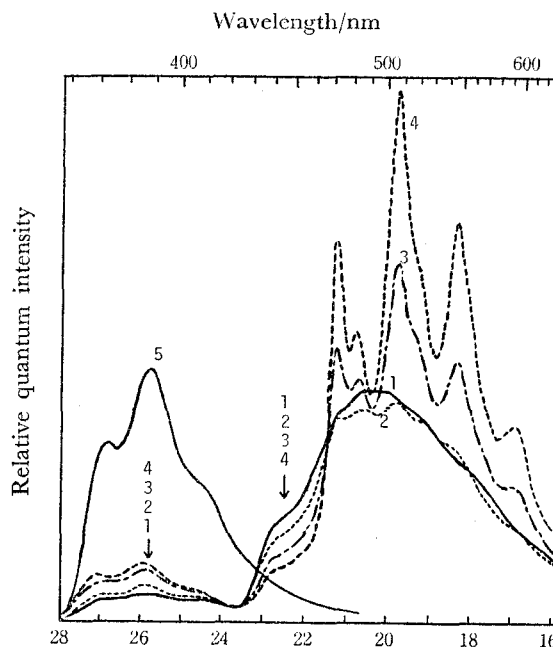
Wavelength/nm

Fig. II-11. Wave number/10^3 cm^{-1}
Delayed emission spectra of PCzEVE films doped with NAPH at 77 K. NAPH concentration; (1) 0, (2) 2.62×10^{-4}, (3) 1.64×10^{-3}, and (4) 8.18×10^{-3} mol/CzEVE unit mol. The prompt fluorescence (5) of a PCzEVE film was also given for comparison.

The Cz chromophore-delayed fluorescence (I_{df}) increases with an increase in the concentration of NAPH. The changes in I_{df} anf I_{sph} as a fraction of the NAPH concentration in films are given in Fig. II-12. In the case of the highest concentration of NAPH, the I_{ph} is quenched completely and I_{sph} reaches saturation,
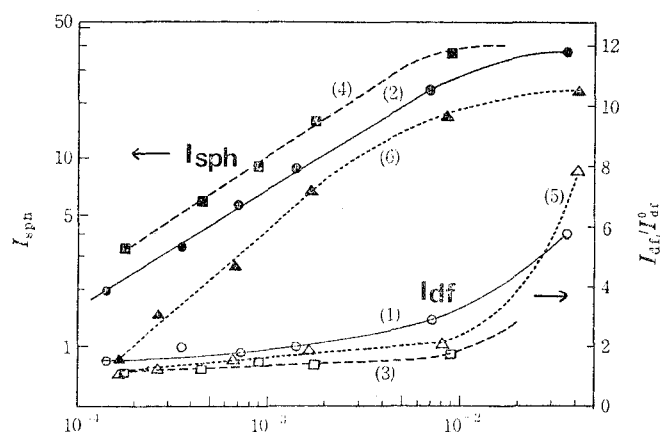

Fig. II-12 Naphthalene mol/VCz unit mol
Dependence of I_{df} and I_{sph} on concentration of NAPH in solid films at 77 K. (1), (2) ——; PVCz(r), (3), (4) ----; PVCz(c), and (5), (6) ······; PCzEVE.

whereas I_{df} increases

steeply and there was

seen a second-order

dependence of I_{df} on

the exciting light

intensity. The

lifetime of the delayed

fluorescence(τ_{df}) is

Fig. II-13. Naphthalene mol/VCz unit mol
Dependence of τ_{df} on concentration of NAPH in solid films at 77 K. (1) —O—; PVCz(r), (2) --□--; PVCz(c), and (3) ···△···; PCzEVE.

gradually lengthened with an increase in the concentration of

NAPH, as is shown in Fig. II-13. Similar phenomena are observed

for the PVCz(c and r) and PCzEVE films doped with fluorene.

It is clear from the above-mentioned results that the dopants

act as an effective triplet quencher for Cz chromophores in the

films. The increase in I_{df} by doping of these triplet

quenchers, therefore, strongly suggests that a heterogeneous T-T

annihilation process occurs with a fairly good efficiency between

freely migrating triplet excitons and the triplet state of the

dopant.

In the case of PVCz(r

and c) doped with NAPH in

rigid solution (Fig. II-14),

I_{ph} decreases and is replaced

by I_{sph}. On the other hand,

I_{df} shows an anomalous

phenomenon, a little differ-

ent from that in solid film:

it increases at low NAPH
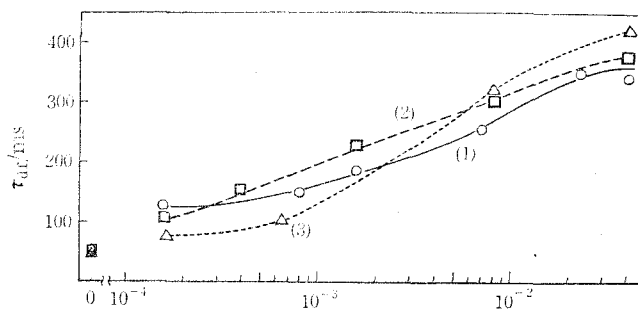
concentrations (up to 5 x

10^{-3}M) and decreases at
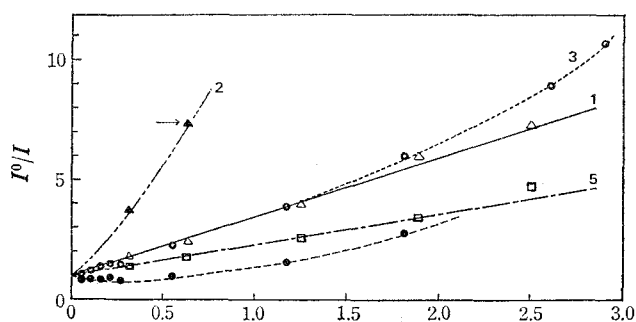

Fig. II-14. Quencher concentration/10^{-2} M
Stern-Volmer plots (I^0_{ph}/I_{ph} and I^0_{df}/I_{df}) for the quenching of the delayed emission of PVCz(r) and PVCz(c) by NAPH and 1,3-PD in MTHF-THF rigid solution at 77 K.
(1) —△—; Phosphorescence in the PVCz(r)-1,3-PD system. (2) —▲---; Delayed fluorescence in the PVCz(r)-1,3-PD system. (3)···O···; Phosphorescence in the PVCz(r)-NAPH system. (4) --●--; Delayed fluorescence in the PVCz(r)-NAPH system. (5) —□··-; Phosphoresceence in PVCz(c)-1,3-PD system. The point with arrow was corrected by the phosphoroscope factor which was estimated by assuming the lifetime to be 2 ms.

higher concentrations. The change in the τ_{df} corresponds approximately to the change in the intensity; for example, the τ_{df} values of PVCz(r) are about 11, 12, 10, and 3 ms for 0, 8.40 x 10^{-4}, 2.10 x 10^{-3}, and 1.45 x 10^{-3} M, respectively. In the case of PVCz(r and c) doped with NAPH, the heterogeneous T-T annihilation, therefore, seems to be present even in rigid solution at 77 K.

In the case of PVCz(r and c) doped with 1,3-PD, a well-known triplet quencher in rigid solution, both I_{df} and I_{ph} decrease significantly with an increase in the concentration of 1,3-PD, as is shown in Fig. II-14, where I^0 and I are the Cz chromophore emission intensity in the absence and in the presence of the dopant, respectively. The τ_{df} is decreased steeply(τ_{df}^0/τ_{df} = 4–5 for 0.25 x 10^{-2} M). However, the τ_{ph} is hardly decreased by the doping of 1,3-PD (τ_{ph}^0/τ_{ph} = 1.0–1.1 for 2.0 x 10^{-2} M). Therefore, it is considered that the triplet energy transfers mainly from freely migrating triplet excitons to the dopant, as is the case of solid films. The degree of quenching is much larger for I_{df} than for I_{ph}. This is the behavior usually observed for poly(1-vinylnaphthalene) and poly(1-naphthyl methacrylate).[18,19] When 1,3-PD is used as a triplet quencher, the heterogeneous T-T annihilation is not present

The I_{ph}^0/I_{ph} ratios are given in Fig. II-15 as a function of the NAPH mole ratio in polymer films. Since the density of the vinyl polymers was measured to be 1.19 g/cm^3, a conversion of the unit on the abscissa in Fig. II-15 from mole ratio to molarity results in the Stern-Volmer plot:

$$I_{ph}^0/I_{ph} = 1 + k_t \tau [Q]$$

Here, k_t is the bimolecular quenching rate constant, τ is the

excited state lifetime in the absence of a quencher, and [Q] is the quencher concentration in the molarity unit. In the case of PVCz(r and c) doped with 1,3-PD in rigid solution, Stern-Volmer polts also are obtained, as is shown in Fig. II-14. In the case of
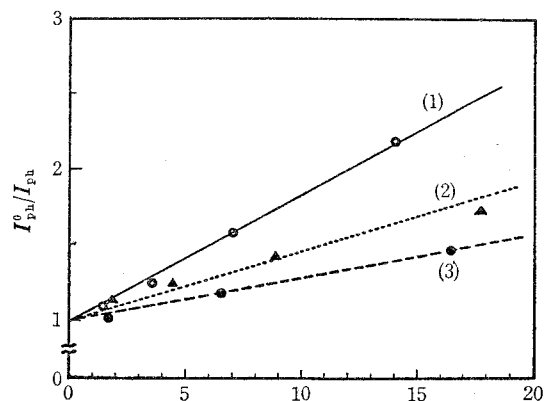

Fig. II-15. Stern-Volmer type plots (I_{ph}^0/I_{ph}) for the quenching of the Cz chromophore phosphorescence of (1) PVCz(r), (2) PVCz(c), and (3) PCzEVE films by NAPH at 77 K.

most aromatic vinyl polymers containing the present polymers, the phosphorescence is emitted not from the freely migrating triplet but from the trapped triplet state, so that the lifetime (τ_{ph}) is considered to be that of the trapped triplet state. Two times the τ_{df} value should, therefore, be used as the value of τ_{ph}. The values of k_t were thus obtained from the slopes of the Stern-Volmer polts. Here, k_t is related to the migration coefficient, λ, in the following equation;

$$k_t = 4\pi N_0 \lambda R_0 \times 10^{-3} \ M^{-1}s^{-1}$$

where N_0 is Avogadro's number and R_0 is the critical transfer distance between donor and acceptor. The value of 15 $\overset{\circ}{A}$ is used for R_0.[28] The migration frequency, k'_{mig}, was estimated from the following equations;

$$k'_{mig} = 2\lambda/a^2 \quad \text{(for one-dimensional random walk)}$$

$$k'_{mig} = 6\lambda/a^2 \quad \text{(for three-dimensional random walk)}$$

where a is the interchromophore separation (3.5 $\overset{\circ}{A}$). From the values of k'_{mig}, the number of Cz chromophores covered by the triplet exciton during its lifetime, n', and the mean exciton migration length, L, were obtained. These values are listed in

Table II-3. Triplet Energy Transfer in Film and in Rigid Solution.

Substance	$k_t\tau/M^{-1}$	τ_{ph}^0/s	τ_{df}^0/ms	$k_t/M^{-1}s^{-1}$	λ/cm^2s^{-1}	k'_{mig}/s [b)]	n'	$L/\text{Å}$ [c)]
PVCz(r)	134	7.9±0.7 1.6±0.5	50±3	1300	1.2×10^{-12}	5.9×10^3	590	85
PVCz(c)	74	7.9±0.7 1.6±0.5	50±5	740	6.5×10^{-13}	3.2×10^3	320	63
PCzEVE	57	3.5±0.2 0.7±0.05	45±5	630	5.6×10^{-13}	——	—	—
PVCz(r) [a)]	245	8.1±0.2	10±3	12000	1.1×10^{-11}	1.8×10^4	360	66
PVCz(c) [a)]	128	8.1±0.2	11±2	5800	5.1×10^{-12}	8.3×10^3	180	47

a) In rigid solution. b) Three-dimensional random walk in film.

c) $L = an'^{1/2}$ (a = 3.5 Å for PVCz).

Table II-3.

The values of n' and L for PVCz(r) are higher than those for PVCz(c) both in film and in rigid solution. As described in the previous chapter, the singlet exciton migration is limited by the intrinsic trap sites (excimer-forming sites).[8,12] Similarly, the triplet exciton migration seems to be limited by the intrinsic trap sites, such as excimer-forming sites in the polymers, because the observed phosphorescence was emitted only from the trap sites. Therefore, the differences in n' and L between PVCz(r) and PVCz(c) seems to be attributable to the difference in the concentration of the intrinsic trap sites for the triplet exciton. That is, the concentration of the trap sites for a triplet exciton in PVCz(c) films is somewhat larger than that in PVCz(r) films. On the other hand, as has been described in the previous chapter, the concentration of the trap sites for a singlet exciton in PVCz(r) films is nearly equal to that in PVCz(c) films. This suggests that the confor- mation of the intrinsic trap sites is not necessarily the same between the singlet and triplet excitons. This explanation might be supported by the presence of a conformational difference between the singlet and triplet excimers of 1,3-di(1-naphthyl)propane.[30]

Although the conformation of the intrinsic trap sites seems to be difference between the singlet and triplet excitons, the number of the Cz chromophores covered by both excitons in the PVCz(r and c) films during the lifetimes ranges from 300 to 600 and the mean exciton migration length ranges from 60 to 80 Å.

As mentioned above, the phosphorescence of PCzEVE films is emitted from the trap sites. Judging from the presence of a shoulder at about 440 nm in the phosphorescence of PCzEVE films

and the small degree of polymerization ($\overline{DP}$ = 33), one of the emitting species seems to be assigned to a monomeric trap such as the Cz chromophore at the chain end. Therefore, the small value of λ in PCzEVE films may be explained by the assumption that a part of Cz chromophores at chain ends acts as an energy trap for a triplet exciton.

Summary

The triplet excitation energy migration in PVCz(r), PVCz(c), and PCzEVE has been investigated by measuring the delayed emission spectra composed of the delayed fluorescence and the phosphorescence in film and in rigid solution at 77 K.

The delayed fluorescence was attributed to a homogeneous T-T annihilation between two migrating triplet excitons. The phosphorescence was emitted from the trap sites. The delayed fluorescence spectra of PVCz(r) and PVCz(c) are different from each other as observed for the prompt fluorescence, because of the different tacticity.

In films of these polymers, the delayed fluorescence increased with an increase in the concentration of a triplet quencher, suggesting the presence of a heterogeneous T-T annihilation. Both the quenching of the Cz chromophore phosphorescence by doping with naphthalene in film and that by doping with 1,3-pentadiene in rigid solution obeyed the Stern-Volmer equation. The migration coefficient was in the following order; PVCz(r) > PVCz(c) > PCzEVE in film and PVCz(r) > PVCz(c) in rigid solution.

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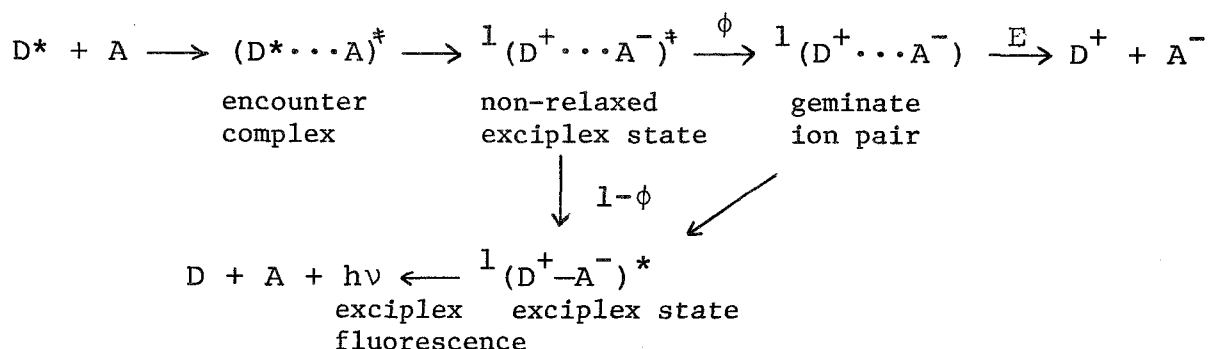14) K. P. Seefeld, H. Müller and H. Bässler, ibid., $\underline{16}$, 395

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PART III

PHOTO-OXIDATION EFFECT ON THE PHOTOCONDUCTIVITY

IN POLY(N-VINYLCARBAZOLE) FILMS

INTRODUCTION

The photo-carrier-generation process in a PVCz film has
widely been investigated in the last few years.[1-4] In the case
of the higher $\pi-\pi^*$ excitation, it is considered that photo-
carriers are generated from the singlet excited state via the
intrinsic charge transfer exciton state.[3] In the case of the
lower $\pi-\pi^*$ excitation, the following mechanism is considered to
be most appropriate.

$$D^* + A \longrightarrow (D^* \cdots A)^{\ddagger} \longrightarrow {}^1(D^+ \cdots A^-)^{\ddagger} \xrightarrow{\phi} {}^1(D^+ \cdots A^-) \xrightarrow{E} D^+ + A^-$$

encounter   non-relaxed   geminate
complex   exciplex state   ion pair

$$\downarrow 1-\phi$$

$$D + A + h\nu \longleftarrow {}^1(D^+ -A^-)^*$$
exciplex   exciplex state
fluorescence

The singlet excited state (D^*) of PVCz migrates effectively
through the Cz chromophores and encounters some electron-
accepting impurity (A) during its lifetime to form an encounter
complex $(D^* \cdots A)^{\ddagger}$. The complex goes through a rapid electron
transfer and changes to a non-relaxed exciplex state ${}^1(D^+ \cdots A^-)^{\ddagger}$.

The non-relaxed exciplex state has an excess kinetic energy and undergoes a thermalization of the excess energy to give either an electron-hole ion pair $^1(D^+\cdots A^-)$ at a separation r_o or a relaxed fluorescent exciplex state $^1(D^+-A^-)^*$. The electron-hole pair will either recombine geminately to give the relaxed fluorescent exciplex state or dissociate into free carriers (D^+, A^-) under an external electric field E. In this part, in order to confirm the mechanism described above, the following investigations have been done.

As described in the previous part, the triplet exciton has fairly high energy and migrates very efficiently in a polymer film as well as the singlet exciton. The effect of singlet and triplet quenchers on the photoconductivity in PVCz films has been described in chapter 1.

The use of magnetic fields is expected to be an invaluable tool for elucidating the mechanisms of photoconductivity.[5] Such investigations have been done successfully for molecular crystals such as anthracene and tetracene.[6-9] Therefore, it is interesting and practically important to investigate how the magnetic field affects the photoconductivity in a PVCz film. In chapter 2, the magnetic field effects on the photoconductivity in a PVCz film and on the prompt exciplex fluorescence of PVCz films doped with DMTP and N,N,N',N'-tetramethyl-p-phenylene-diamine (TMPD) have been described.

In the last chapter, in order to elucidate what kind of compound acts as an electron-accepting impurity, the photo-oxidation effects on the photoconductivity and the electronic spectra of PVCz films have been investigated.

Chapter 1

Effect of the Singlet and Triplet Quenchers on the Photoconductivity of Poly(N-vinylcarbazole)

Introduction

The triplet exciton of PVCz has a fairly high energy (E_T = 3.02 eV; cf. the energy of the singlet exciton, E_S = 3.55 eV), as compared with other aromatic vinyl polymers, such as poly(1-vinylnaphthalene) (E_T = 2.5 eV, E_S = 3.8 eV).[10] Therefore, the photo-carrier-generation via the triplet exciton may be possible in PVCz films. In order to examine this possibility, the effect of the triplet and singlet quenchers on the photoconductivity in PVCz and brominated PVCz (BPVCz) films was examined.

Experimental

The copolymer of VCz with 1-vinylnaphthalene (VN) was prepared by free-radical polymerization. Naphthalene and fluorene were used as triplet quenchers of the Cz chromophore, while anthracene and perylene were used as both singlet and triplet quenchers. Gold-polymer-nesa sandwich-type cells were used and the electrical measurements were made by the DC method in a vacuum of 10^{-5} Torr.[2]

Results and Discussion

BPVCz has photoconductive properties similar to those of PVCz.[11] The magnitude of the photocurrent of BPVCz is twice as large as that of PVCz in the case of the hole current and is almost the same as that of PVCz in the case of the electron current.

In both PVCz and BPVCz, the triplet quencher does not affect the photoconductive properties at all. Anthracene and perylene acting as both singlet and triplet quenchers significantly reduce the photocurrent in magnitude, but do not affect other photoconductive properties, such as the voltage and temperature dependences of the photocurrent. Table III-1 shows a comparison of the magnitude of the photocurrent among the films undoped and doped with triplet or singlet quenchers. From this table, it is clear that, in the quencher concentrations of 1.5—5 mol%, the singlet quenchers reduce the photocurrent by a factor of ca. 5, while the triplet quenchers do not.

From the results in the previous part, it is clear that the concentration of the freely migrating triplet exciton in the films doped heavily (more than 1 mol%) with the triplet quencher is remarkably reduced as compared with that in the undoped films. The situation is the same as for the case of the singlet quencher. Therefore, the present effect of the singlet and triplet quenchers on the photoconductivity excludes the possibility of the photocarrier generation via the triplet state in these polymers under ordinary experimental conditions.

It is noted that the photocarrier generation via the singlet

Table III-1. COMPARISON OF MAGNITUDES OF THE PHOTOCURRENT[11]

Material Polymer	Dopant	mol %	Number of samples	Hole current/10^-10 A cm^-2 350 nm	330 nm	Electron current/10^-11 A cm^-2 350 nm	330 nm
PVCz	None	0	7	(4.0±0.2)	(3.7±0.3)	(4.3±0.4)	(3.0±0.2)
	Fluorene	1.5	3	1.1±0.1	1.1±0.1	—	—
	Naphthalene	1.5	3	1.1±0.1	1.2±0.3	1.1±0.3	0.93±0.23
	Naphthalene	5.0	3	0.81±0.08	0.99±0.19	—	—
	Copolymerized	VN[b]	2	1.4±0.1	1.5±0.1	1.5±0.3	1.4±0.2
	Anthracene	3.0	2	0.18±0.07	0.23±0.09	0.09±0.01	0.14±0.01
	Perylene	2.0	3	0.20±0.06	0.22±0.09	0.13±0.05	0.25±0.08
VCz–VN (5 mol %) copolymer		0	2	(5.5±0.2)	(5.6±0.1)	(6.3±0.9)	(4.1±0.4)
	Anthracene	3.0	2	0.29±0.01	0.36±0.01	0.29±0.06	0.40±0.07
BPVCz	None	0	3	(7.2±0.2)	(7.0±0.2)	(3.2±0.2)	(2.6±0.1)
	Naphthalene	5.0	3	0.95±0.06	1.1±0.2	0.77±0.21	0.81±0.06
	Anthracene	3.0	2	0.16±0.03	0.19±0.02	0.37±0.03	0.54±0.06

a) The relative photocurrent values in the doped films taking the photocurrent values in the corresponding undoped films as unity. The values in parentheses are the photocurrent values in the undoped films measured under the condition of 35000 V/cm, 1×10^{13} photons/cm^2 s, 20 °C, and 1×10^{-5} Torr.　　b) VCz–VN (5 mol % in feed) copolymer.

excited state is predominant even in BPVCz, which has a low efficiency of the singlet exciton migration. A similar example has been reported of the photoconductivity in tetracene crystals, where the low efficiency of the singlet exciton migration is attributed to the enhanced singlet fission into two triplet excitons. [8] In tetracene crystals, the photocarrier generation via the triplet excited state is possible only in the presence of a strong electron acceptor like p-chloranil.

Under the present experimental conditions, the two photon processes are negligible because of the weak light intensity. In the case of the lower singlet π-π^* excitation, the extrinsic photocarrier generation process with the participation of some electron-accepting impurities must be considered. From the simple energetic calculation, this process is considered to be endothermic in the case of a weak electron acceptor such as some photooxidation products of the Cz chromophore, the most conceivable acceptor. In such an endothermic process, the energy

difference between the singlet and triplet excitons (0.5 eV) seems to determine the choice between the singlet and triplet channels, although it is much smaller than those of other aromatic vinyl polymers. This is the reason for the lack of the photocarrier generation process via the triplet exciton in these polymers.

Summary

The singlet quenchers significantly reduced the photo-currents of PVCz and BPVCz, but the triplet quenchers did not, regardless of the high efficiency of the polymer-to-quencher triplet energy transfer. This result excluded the possibility of the photocarrier generation via the triplet exciton in these polymers. Since the extrinsic photo-carrier-generation process is considered to be endothermic, the energy difference between the singlet and triplet excitons (0.5 eV) seems to determine the choice between the singlet and triplet channels.

Chapter 2

Magnetic Field Effect on the Photoconductivity of

Poly(N-vinylcarbazole)

Introduction

Recently, Groff et al. and Frankevich et al. have, independently, found a new type of magnetically-sensitive process involving an intermediate charge-transfer (exciplex) state formed on the crystal surface, from observations of the magnetic quenching of the dye-sensitized delayed fluorescence in anthracene crystals[12] and of the prompt exciplex fluorescence in finely-divided ruburene crystals[13] and in tetracene-adsorbed anthracene crystals,[14] respectively. This new type of magnetically-sensitive process has been considered to be due to a change in the rate of transformation between singlet and triplet states of the exciplex by a weak magnetic field. However, the sign of the change in the transformation rate is in controversy; the sign has been shown to be negative by Groff et al.[12] and conversely to be positive by Frankevich et al..[13,14] Groff et al. have also suggested that a similar mechanism is responsible for the positive magnetic field effect on the dye-sensitized photoconductivity in anthracene crystals.[12,15] However, details concerning this positive magnetic field effect on the photoconductivity has never been reported. Frankevich et al. have also suggested that a similar mechanism might be appropriate to the positive magnetic field effect which had been reported

previously by these authors,[16] on the surface photoconductivity in anthracene crystals and on the low-temperature photoconductivity in a sandwitch-type cell of a sublimed tetracene film.[14] In these cases, the situation is, however, considered to be complicated, because of the possibility that the singlet·fission may partly be responsible for this positive magnetic field effect. It has been confirmed by the observation of a small quenching of the prompt fluorescence by a magnetic field that the singlet fission is present both in anthracene crystals at 300 K and in tetracene crystals at 77 K.

In this chapter, the author examined magnetic field effects on the photoconductivity and on exciplex fluorescence in PVCz films, where the singlet fission is completely impossible energetically (E_S = 3.55 eV, E_T = 3.02 eV).

Experimental

An gold-PVCz-nesa sandwich-type cell was set in a cryostat, mounted between the poles of an electromagnet, and excited by monochromatized light from a stabilized 500 W xenon lamp. The photocurrent was measured with a vibrating reed electrometer. The emission passed to a 1P28 photomultiplier through a light guide and appropriate filters. The photomultiplier current was measured with a differential electrometer. The current at zero magnetic field was compensated and only the variation of the current caused by magnetic field was measured. Small current changes up to 0.2 % could be detected by means of this measuring system. The results to be presented below were obtained for the arrangement of the magnetic field vector perpendicular to

the electric field vector.

Results

(1) Photocurrent.

When a magnetic field H of up to 4000 G is applied to a
PVCz film, the photocurrent, i, in the wavelength region shorter
than 400 nm is increased by a quantity, Δi, although there is no
change both in the dark current and in the photocurrent in the
wavelength region longer than 400 nm. In all cases, $\Delta i/i$
increases monotonically with H and reaches saturation at about
500-1000 G, as is shown in Fig. III-1. The $\Delta i/i$ reaches a half
value of the saturated one at 200–300 G. As is shown in Fig.
III-2, $\Delta i/i$ increases with applied voltage, V, and reaches
saturation. Judging from the i–V relationship,[2] this means that
the relation $i \propto V^n$ (n = 1.5 - 2.0) is valid over the whole range
up to 100 V (10^5 V/cm) for the hole current and in the low appli-
ed voltage range up to 40 V (3.3×10^4 V/cm) for the electron
current.
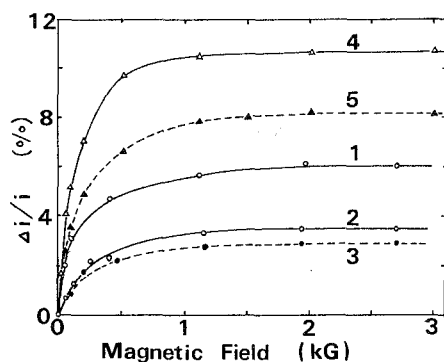
Fig. III-1.

Magnetic field dependence of the relative increase in
the photocurrent under 35000 V/cm at 20°C. Undoped PVCz
film: (1) 350 nm, hole current; (2) 260 nm, hole current; (3)
350 nm, electron current. PVCz film doped with DMTP (4
mol%): (4) 350 nm, hole current; (5) 350 nm, electron current.
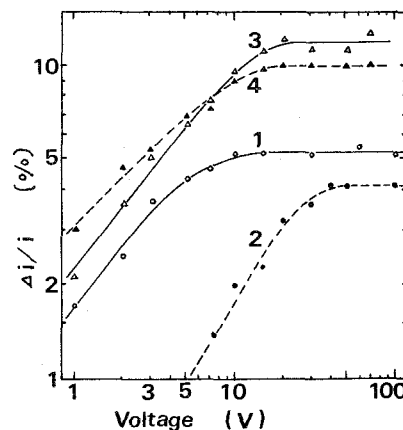
Fig. III-2.

Applied voltage dependence of the relative increase in
the photocurrent at 1500 G and 20°C. Undoped PVCz film:
(1) 350 nm, hole current; (2) 340 nm, electron current. PVCz
film doped with DMTP (2 mol%): (3) 350 nm, hole current;
(4) 340 nm, electron current.

The $\Delta i/i$ hardly depends on light intensity, L, in the range below about 2×10^{13} photons/cm^{2}s ; the relation $i \propto L^1$ is valid. On the other hand, $\Delta i/i$ decreases with increasing L in the range above 2×10^{13} photons/cm^{2}s with an exception of the case of illumination of the weakly-absorbed light (370—400 nm). In the case of illumination of the 370—400 nm light, $\Delta i/i$ does not depend on L over the whole range up to 5×10^{14} photons/cm^{2}s.

Spectral dependence of $\Delta i/i$ is shown in Fig. III-3. In both cases of the hole and electron currents, $\Delta i/i$ is comparatively large in the ^1L_a and ^1L_b absorption regions (or the higher energy region above 4.6 eV). The $\Delta i/i$ is larger for the hole current (5—6 %) than for the electron current (3.5—4 %).
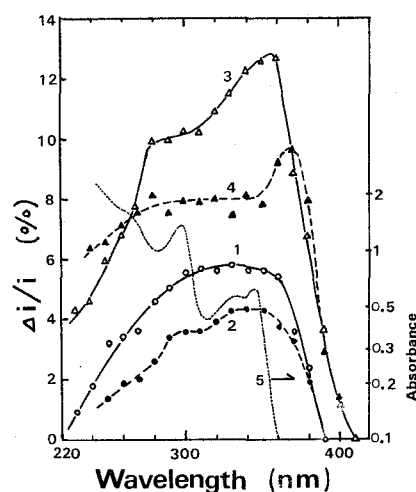

Fig. III-3.
Spectral dependence of the relative increase in the photocurrent at 1500 G, 33000 V/cm, and 20°C. Undoped PVCz film: (1) hole current; (2) electron current. PVCz film doped with DMTP (2 mol%): (3) hole current; (4) electron current. The UV absorption spectrum of a PVCz film about 1 μ thick is shown by a dotted line (5).

The $\Delta i/i$ depends considerably on temperature. The positive magnetic field effect on the photoconductivity disappears below -30 °C. With increasing temperature above -30 °C, $\Delta i/i$ first increases sharply and then decreases gradually.

The DMTP-doped films show similar results to the undoped films mentioned above, with an exception that the magnitude of $\Delta i/i$ is enhanced by a factor of two with doped DMTP, as is shown in Figs. III-1 — -3.

(2) Exciplex Fluorescence.

The prompt excimer fluorescence of undoped PVCz films was not affected by magnetic field up to 4000 G at all. However, the prompt exciplex fluorescences of PVCz films doped with DMTP and TMPD were enhanced in intensity by magnetic fields. The ratio of this increment to the total prompt fluorescence intensity ($\Delta F/F$) increased monotonically with an increase in magnetic fields, H, and reached a saturation at about 400 G, as is shown in Fig. III-4. The $\Delta F/F$ reached a half value of the saturation at about 100 G. The data presented below were obtained for the saturated values.

The $\Delta F/F$ was independent both of the wavelength (280-360 nm) and of the intensity (10^{13-14} photons/cm^{2}s) of the exciting light. The $\Delta F/F$ apparently depended on the emission-wavelength, as is shown in Fig. III-5. In both doped systems, the $\Delta F/F$ for 400 nm was about 0.6 times as large as for 450-600 nm. This is because the excimer fluorescence is superimposed considerably on the exciplex fluorescence in the wavelength region shorter than 400 nm. For instance, in the PVCz film doped with 3.3 mol% DMTP, the ratio of the exciplex fluorescence to the total one was about 0.55 at 400 nm, and then the ratio of ΔF to the exciplex fluorescence intensity was evaluated to be about 2.1 % at 400 nm, being equal to the $\Delta F/F$ value for
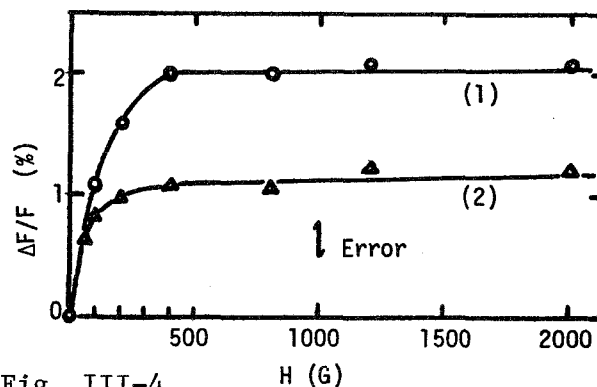

Fig. III-4.

Magnetic field dependence of relative increase in the exciplex fluorescence of PVCz films doped with (1) 3.3 mol% DMTP and (2) 4.3 mol% TMPD; λ_{ex}= 330 nm, λ_{em}= 500 nm, at 25 °C.
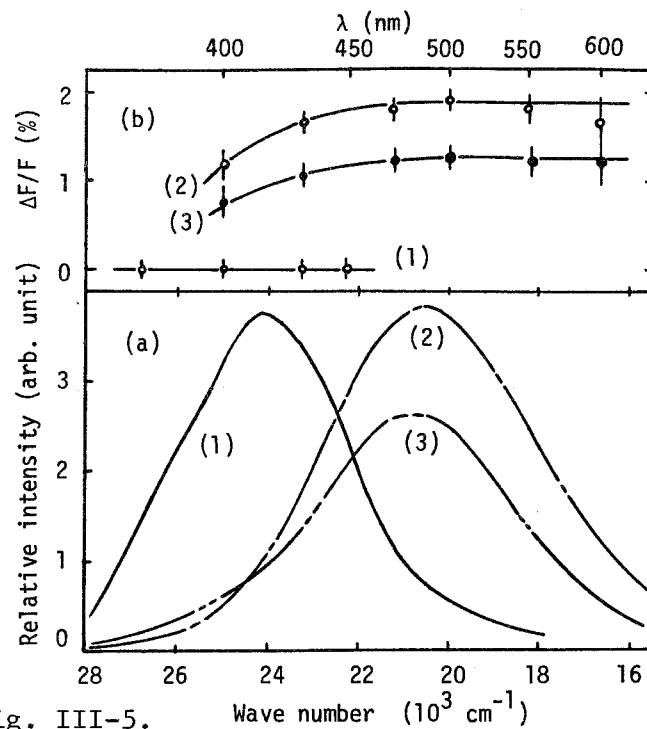
-101-

Fig. III-5. (a) Fluorescence spectra and

(b) emission-wavelength dependence of ΔF/F;

λ_ex = 330 nm, 2000 G, 25 °C.

(1) undoped PVCz film

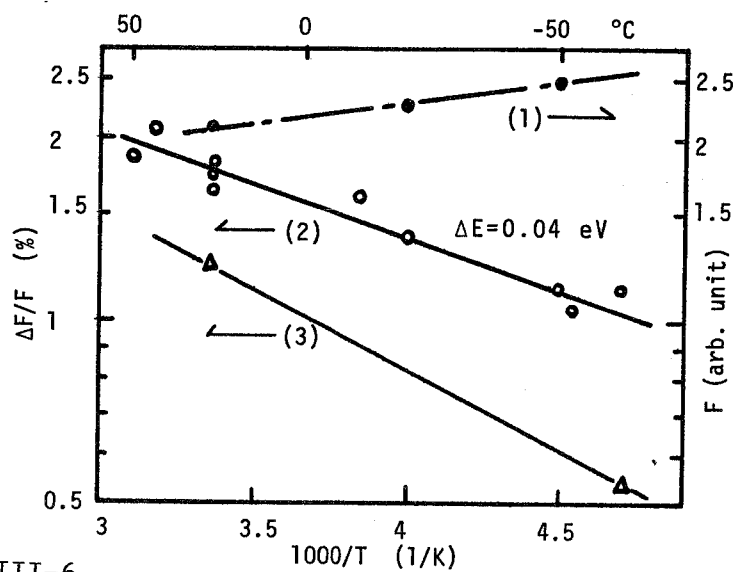(2) PVCz film doped with 3.3 mol% DMTP

(3) PVCz film doped with 4.3 mol% TMPD

Fig. III-6. Temperature dependence of F and ΔF/F in PVCz films doped with 3.3 mol% DMTP (1 and 2) and 4.3 mol% TMPD (3); λ_ex=330 nm, λ_em=500 nm, 2000G, 25 °C.

450-600 nm (1.9 %) within the experimental error. Therefore, the magnitude of the magnetic field effect on the exciplex fluorescence is safely considered to be independent of the emission-wavelength; it is about 2.0 % and 1.1 % at 25 °C for the DMTP and TMPD doped systems, respectively.

The $\Delta F/F$ depended slightly on temperature, as is shown in Fig. III-6. With an increase in temperature, the F value decreased slightly and $\Delta F/F$ increased, resulting in an activation energy of about 0.04 eV.

The electric field quenching of the exciplex fluorescence of PVCz films doped with DMTP, which has been reported by Yokoyama et al.,[4] also was observed in the present study. However, the ratio of $\Delta F/F$ due to the magnetic field was independent of applied electric fields up to $\pm$ 35000 V/cm, suggesting that magnetic and electric fields affect independently the exciplex fluorescence.

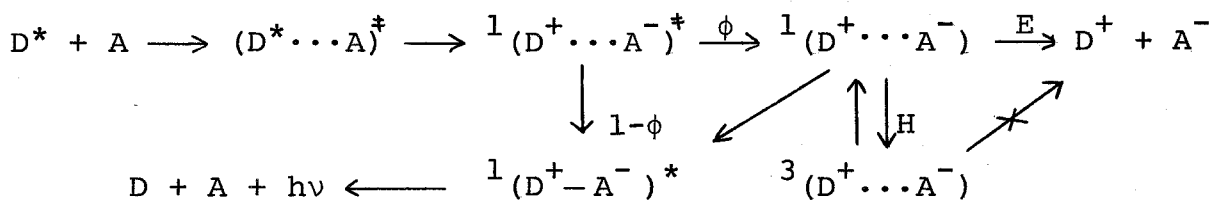The exciplex fluorescence in solution has not been affected by magnetic fields up to 4000 G at all.

Discussion

The positive magnetic field effect on the photoconductivity in the undoped and DMTP-doped PVCz films is observed only for the wavelength region shorter than 400 nm and is not observed for the dark current and for the photocurrent in the wavelength region longer than 400 nm. This effect is, therefore, attributable to a carrier generation process rather than to a carrier migration process.

Doping of DMTP enhances the magnitude of the photocurrent

by a factor of 1.5-3 in the π-π^* absorption region of PVCz, because of additional carrier generation process via the non-relaxed exciplex state.[2,17] The enhancement of $\Delta i/i$ with doped DMTP, therefore, clearly means that the efficiency of this carrier generation process is increased by a relatively weak magnetic field. This is also reasonable, judging from the fact that $\Delta i/i$ is very sensitive both to applied electric fields and to temperature as mentioned above.

The increase in both efficiency of the carrier generation and of the exciplex fluorescence is explained by means of a reduction of the rate of transformation between singlet and triplet states of the geminate ion pair $^1(D^+ \cdots A^-)$ by a weak magnetic field, which has been named magnetic hyperfine modulation,[12] provided that carriers are generated more efficiently via the singlet state than via the triplet state.

$$D^* + A \longrightarrow (D^* \cdots A)^{\ddagger} \longrightarrow {}^1(D^+ \cdots A^-)^{\ddagger} \xrightarrow{\phi} {}^1(D^+ \cdots A^-) \xrightarrow{E} D^+ + A^-$$

$$\downarrow {\scriptstyle 1-\phi} \qquad\qquad \uparrow\downarrow_H$$

$$D + A + h\nu \longleftarrow {}^1(D^+ - A^-)^* \qquad {}^3(D^+ \cdots A^-)$$

The ϕ has roughly been estimated to be 0.2 from the fact that the magnetic field effect on the prompt exciplex fluorescence (2 %) is smaller than that on the photoconductivity (10 %).

It is very interesting that a similar magnetic field effect on the photoconductivity is observed also for undoped PVCz films. This clearly suggests that a similar carrier generation process via an non-relaxed exciplex state plays an important role in photocarrier generation even in the undoped films.

Summary

Magnetic fields were found to increase the photocurrent in PVCz films by 5—6 % at 1000 G. This positive magnetic field effect was sensitive both to applied voltage and to temperature, and was enhanced with DMTP doping by a factor of two. Magnetic fields were also found to increase the prompt exciplex fluorescence of PVCz films doped with DMTP and TMPD by 2 % at 500 G. This positive magnetic field effect was explained by means of a reduction of the rate of transformation between the singlet and triplet states of the geminate ion pair by a weak magnetic field, provided that carriers are generated more effectively via the singlet state than the triplet state. These results confirm that a carrier generation process with the participation of an non-relaxed exciplex state has an important role in photo-carrier-generation even in undoped PVCz films.

Chapter 3

Photo-oxidation Effect on the Electronic Spectra and

the Photoconductivity of Poly(N-vinylcarbazole)

Introduction

In the carrier generation mechanism described in the previous

chapter, the energy required to prepare an electron-hole ion pair

at a separation r_0 is expressed by $(I_c - E_{ac} - e^2/\varepsilon r_0)$, where I_c, E_{ac},

and ε are the ionization potential(5.9—6.1 eV), the electron

affinity(1.5 eV), and the dielectric constant(3.0) of PVCz in film,

respectively. The value for $r_0 = 25\text{Å}$ is estimated to be 4.2—4.4 eV,

which is higher than the energy of the lowest excited singlet

state(3.6 eV). Therefore, a compound having the electron affinity

of 0.6—0.8 eV or above can act as an electron acceptor (A).

Some unknown materials contaminated in course of synthesis

of monomers and/or polymers, dissolved oxygen, or photo-oxidation

products of the polymer can be considered as the electron-

accepting impurities in PVCz films. Judging from the migration

efficiency of the singlet exciton, the concentration of electron-

accepting impurities of about 10^{-3} mol/mol monomer unit seems to

be necessary to interpret a high yield of photo-carrier-generation

(ca. 0.1). Contamination by such a concentration of impurities

is improbable in the course of the synthesis. In the case of

contamination of triplet oxygen in the ground state, whose

electron affinity is ca. 0.42 eV,[18] considerable thermal

activation should be necessary to give an electron-hole ion pair.

Therefore, it is impossible to explain the high yield of the photo-carrier-generation in PVCz films by considering only unknown contaminating impurities and oxygen. Any photo-oxidation products of PVCz should be considered as electron-accepting impurities which may be effective for the photo-carrier-generation. Therefore, detailed information on the photo-oxidation of PVCz films is very important in understanding the origin of the high photoconductive properties of polymers. It has briefly been reported that photo-oxidation products were obtained by irradiation of light on PVCz suspended in a sulfuric acid - ethanol mixture under a stream of air[19] and of PVCz films in air.[3] However, no detailed study has been reported on the photo-oxidation of PVCz films.

In this chapter, the author described the photo-oxidation of PVCz films and DCzP(a) films, by measuring the change in the absorption and fluorescence spectra caused by UV-irradiation. It has also been investigated how the photo-oxidation affects the photoconductivity in PVCz films.

Experimental

For photo-oxidation, films were irradiated in air under atmospheric pressure through a water filter (21 cm) with the full spectrum of a 500 W high pressure mercury lamp. The radiation density ($\lambda < 350$ nm) was about 1×10^{17} photons/cm^{2}s.

Results and Discussion

(1) Electronic Spectra.

Figure III-7 shows the change in the absorption spectra of PVCz films caused by UV-irradiation. With irradiation time, the absorption intensity of Cz chromophores decreases and new absorption (300-340 nm and 350-420 nm) appears and increases. Three isosbestic points are observed at 248, 341, and 303 nm. These new bands are attributed to photo-oxidation products, because no change in the absorption was observed for a PVCz film irradiated under a vacuum of 10^{-1} Torr. Further irradiation causes a deviation from these isosbestic points and also a decrease of the absorption intensities of the photo-oxidation product, as is shown in Fig. III-8. Similar phenomena were observed also for DCzP(a) films. The dependence of the absorption intensity (370 nm) due to the photo-oxidation product on irradiation time is shown in Fig. III-8. Assuming that there is no
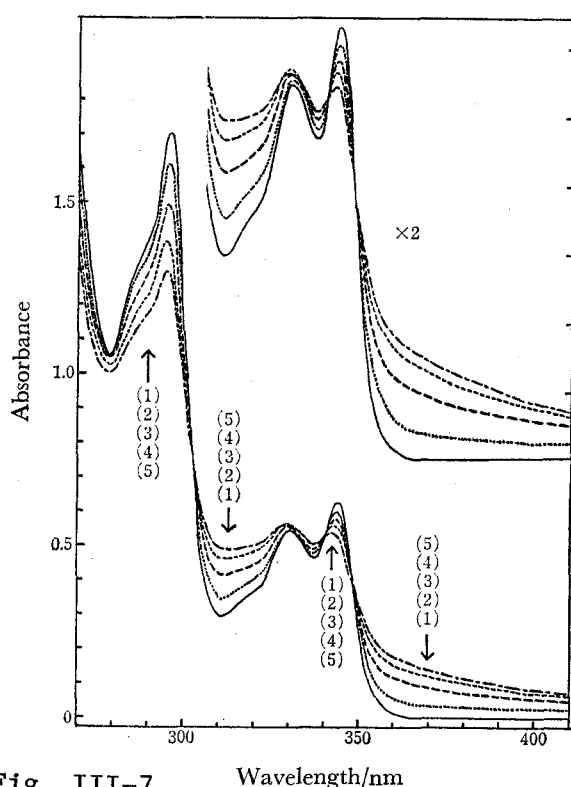
Fig. III-7. Wavelength/nm

Change in the absorption spectra of a PVCz film caused by photoirradiation. Irradiation time; (1) 0, (2) 6, (3) 12, (4) 18, and (5) 25 min.
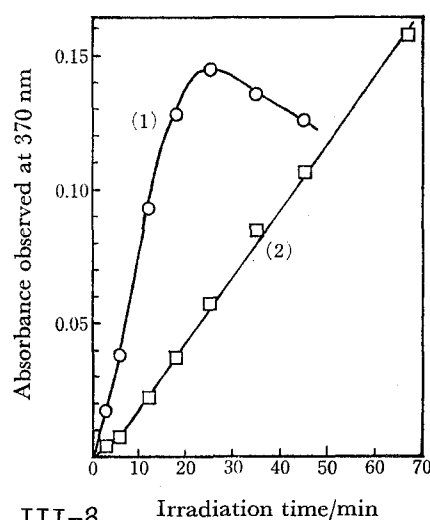
Fig. III-8. Irradiation time/min

Dependence of the absorption intensity at 370 nm on photoirradiation time for (1) PVCz and (2) DCzP(a) films.

remarkable difference in the molar extinction coefficient of the photo-oxidation product between PVCz and DCzP(a), Fig. III-8 shows that the formation rate of the photo-oxidation product observed for PVCz films is larger than that for DCzP(a) films by a factor of ca.4. This may be attributed to the presence of the sites which are susceptible to photo-oxidation in PVCz films. Judging from the fact that the concentration of the sandwich-like excimer-forming site in PVCz films is higher than that in DCzP(a) films, the sandwich-like excimer-forming site seems to be susceptible. This is supported by the fact that the decrease of the sandwich-like excimer fluorescence (ca, 23900 cm^{-1}) caused by photo-oxidation is larger than that of the second excimer fluorescence (ca. 26500 cm^{-1}), as is clearly seen in Fig. III-10.

IR spectra of photo-oxidized PVCz films are shown in Fig. III-9. The increasing absorption observed at around 1700 cm^{-1} is attributable to carbonyl groups. A similar phenomenon was observed also for DCzP(a) films. These results show that the photo-oxidation product formed in both PVCz and DCzP(a) films has carbonyl group, which is an electron-accepting substituent. The formation of the carbonyl group has been reported also in photo-oxidized polystyrene films.[20]

The change in the fluorescence spectra of PVCz films caused by photoirradiation in air is shown in Fig. III-10. Little change was observed in the fluorescence spectra of PVCz films by
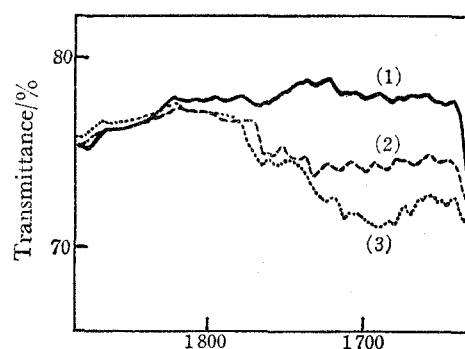

Fig. III-9. Wave number/cm⁻¹

Change in the infrared absorption spectra of a PVCz film caused by photoirradiation. Irradiation time; (1) 0, (2) 20, and (3) 100 min.

photoirradiation under a vacuum of 10^{-1} Torr. Remarkable change

in the fluorescence spectra is observed for very slightly

photo-oxidized PVCz films, compared with the case of the

absorption spectra. With irradiation time, the excimer

fluorescence of PVCz films decreases and a new fluorescence band

in the longer-wavelength region ($\nu < 20000$ cm^{-1}) appears.

Further irradiation causes a decrease of both the excimer and

the new fluorescence intensities. A quite similar phenomenon

was observed for DCzP(a) films, as is shown in Fig. III-11.

The broad and structureless emission band with a peak (or should-

er) at 19000-20000 cm^{-1} of the slightly photo-oxidized PVCz and

DCzP(a) films may be assigned to the exciplex fluorescence,

which is formed between an excited Cz chromophore and the photo-

oxidation product with carbonyl group. This assignment is

supported by the following observation. The fluorescence

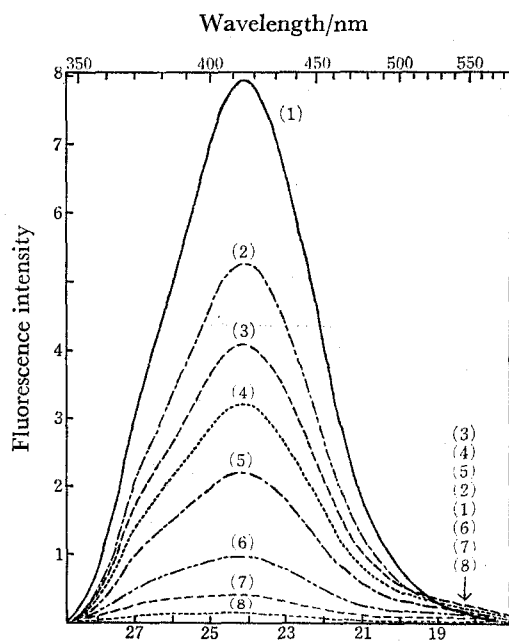observed at 515 nm for a slightly photo-oxidized PVCz film

Fig. III-10. Wave number/10^3 cm^{-1}

Change in the fluorescence spectra of PVCz films caused by photoirradiation. Irradiation time; (1) 0, (2) 0.5, (3) 1, (4) 1.5, (5) 2.5, (6) 4.5, (7) 9, and (8) 15 min.
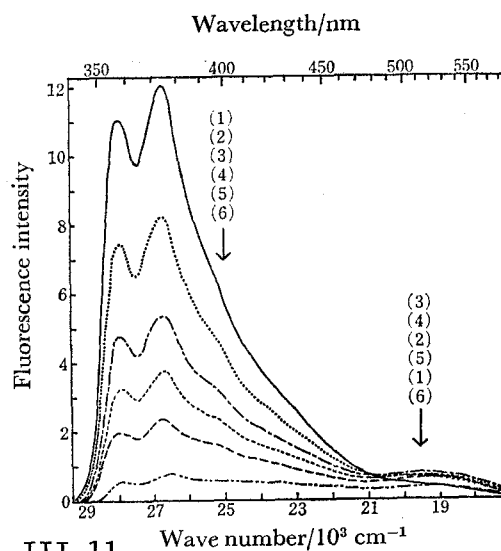
Fig. III-11. Wave number/10^3 cm^{-1}

Change in the fluorescence spectra of DCzP(a) films caused by photoirradiation. Irradiation time; (1) 0, (2) 0.17, (3) 0.5, (4) 1, (5) 1.5, and (6) 10 min.

is partly quenched by applying an electric field and the decrease in the fluorescence shows a quadratic dependence on the field strength, as is shown in Fig. III-12. A similar phenomenon has been observed for the exciplex fluorescence of PVCz films doped with DMTP.[4]

A quenching factor, Q, is defined for convenience by the following equation;

$$Q_t = (I_o - I_t)/I_t$$

where I_o and I_t are fluorescence peak intensities before and after photo-irradiation, respectively. The dependence of the quenching factor of photo-oxidized PVCz and DCzP(a) films on the irradiation time is shown in Fig. III-13. The value of Q obtained for the thin films is larger than that obtained for the thick films. This result suggests that the process of the photo-oxidation proceeds near the surface of films. Therefore, the photo-oxidation product is not formed in the bulk of film uniformly. However, an approximately linear relationship exists
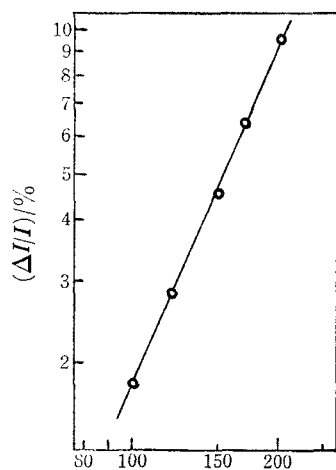

Fig. III-12. Applied voltage/V

Electric field-strength dependence of the fluorescence decrease observed at 510 nm for the weakly photo-oxidized PVCz film ($\approx$0.5 μm thick). Irradiation time; 25 s. Excitation wavelength; 335 nm.

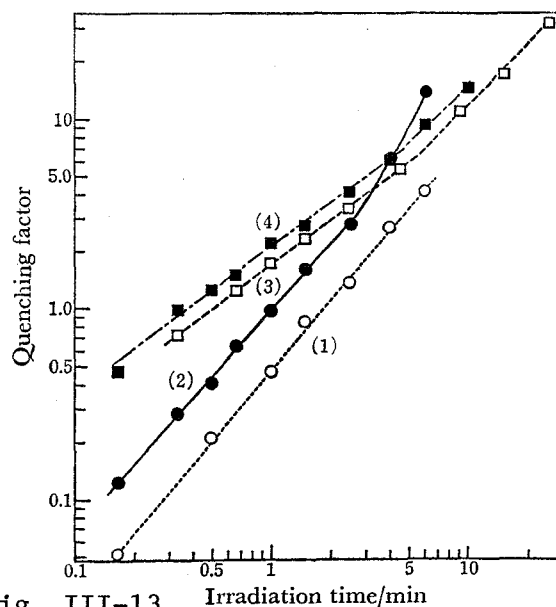Fig. III-13. Irradiation time/min

Quenching factor vs. irradiation time. (1) PVCz film ($\approx$0.7 μm thick), (2) PVCz film ($\approx$0.2 μm thick), (3) DCzP(a) film ($\approx$0.3 μm thick), and (4) DCzP(a) film ($\approx$0.2 μm thick). Excitation wavelength; 330 nm.

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between Q and the irradiation time, t, in an early stage of photo-irradiation, suggesting that the photo-oxidation product acts as an exciton trap in competition with the excimer-forming sites. The value of Q obtained for DCzP(a) films is larger than that obtained for PVCz films. Considering that the concentration of the photo-oxidation product formed in PVCz films is higher than that formed in DCzP(a) films, this fact suggests that the number of Cz chromophores covered by a singlet exciton during its lifetime in a DCzP(a) film is larger than that in a PVCz film. This fact is consistent with the result obtained by the investigation of the excitation energy migration in chapter 1 of Part II.

The host fluorescence was depressed to half its original intensity at a guest concentration equal to the concentration of the excimer-forming sites, in the case of PVCz films. This concentration in a PVCz(r) film was ca. 3×10^{-3} mol/mol basic unit. This concentration level of the photo-oxidation product is reached by irradiating a thin PVCz film for one minute, as is seen in Fig. III-13. Considering the number of absorbed photons, the yield of the formation of the photo-oxidation product is estimated to be ca. 10^{-4}.

(2) Photoconductivity.

Dependence of the photocurrent in the photo-oxidized PVCz films on irradiation time is shown in Fig. III-14. The photocurrent observed in the $\pi-\pi^*$ absorption region increases steeply, by a factor of about 15, with photo-oxidation. It decreases when the film was exposed to radiation until a change in the absorption spectra by photo-oxidation could be observed.

Voltage, spectral, light-intensity, and temperature dependences of the photocurrent in the photo-oxidized PVCz film were almost the same as those in the unirradiated PVCz film.[17]

Figure III-15 shows the dependence of the positive magnetic field effect in the photo-oxidized PVCz films on irradiation time. The effect is enhanced by a factor of about 3 by slight photo-oxidation, as observed for the DMTP-doped system.

It is clear from these results that the yield of photo-carrier-generation in the slightly photo-oxidized PVCz films is much higher than the yield in the unirradiated films. That is, even if the concentration of the photo-oxidation product is too low to be detected in the absorption spectra, the product acts effectively as an electron-accepting impurity (A) in the photo-carrier-generation mechanism described in the previous chapter, to enhance effectively the yield of the photo-carrier-generation process in a PVCz film.
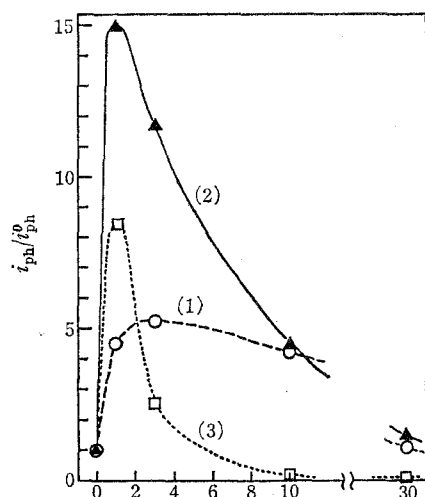

Fig. III-14. Irradiation time/min
Irradiation time dependence of the relative photocurrent(i_{ph}^+) in a photo-oxidized PVCz film under 35000 V/cm.
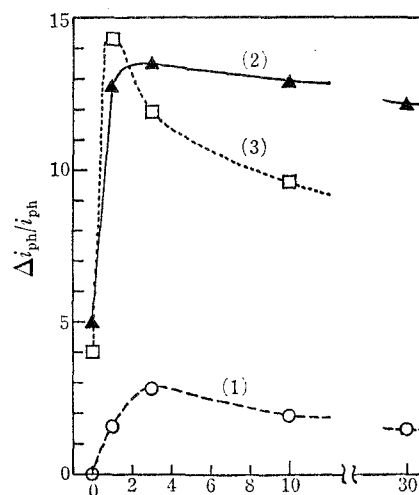(1) 400, (2) 360, and (3) 330 nm.

Fig. III-15. Irradiation time/min
Dependence of the positive magnetic field effect in a photo-oxidized PVCz film on irradiation time. Magnetic field; 1000 G. Applied voltage; 35000 V/cm.
(1) 400, (2) 360, and (3) 330 nm.

Summary

When PVCz and DCzP(a) films were irradiated by UV light in air, a photo-oxidation product with carbonyl group was formed near the surface of the films with a yield of 10^{-4}. This photo-oxidation product acted as a singlet exciton trap and formed an exciplex with an excited Cz chromophore. A very slight amount of the photo-oxidation product, whose concentration is too low to be detected in the absorption spectra, enhanced the photo-conductivity in PVCz films by a factor of ca. 15 and the positive magnetic field effect by a factor of ca. 3. These results suggest that the product acts as an electron-accepting impurity in the photo-carrier-generation mechanism in the lowest π-π^* absorption region of PVCz.

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CONCLUSION

The purpose of this thesis is to present information with regard to the photophysical process of aromatic vinyl polymers and to clarify the mechanism of photoconductivity of the polymers on the basis of this information. The following conclusions were obtained in this thesis.

1) It was revealed by the NMR spectroscopy and others that the tacticity of PVCz, P5VBCz, and P7VBCz varies depending on the polymerization method. The cationic polymers were rich in isotacticity and the radical polymers were rich in syndiotacticity.

2) The polymers composed of both the isotactic and the syndiotactic sequences (PVCz, P7VBCz, and P5VBCz(r)) showed one broad emission band composed of the second and the sandwich-like excimer fluorescences. The intensity of the second excimer fluorescence increased with an increase in the content of the syndiotactic sequence. The intensity of the sandwich-like excimer fluorescence was independent of the tacticity.
The polymer composed of only the isotactic sequence (P5VBCz(c)) showed the monomeric and the sandwich-like excimer fluorescences. The second excimer fluorescence was emitted from only the syndiotactic sequence. The structure of the second excimer was suggested that only one benzene ring in each neighboring Cz chromophores overlaps with the other one.

3) The parameters of the photophysical process for PVCz(r) were evaluated by the quenching experiments. The parameters indicate that the sandwich-like excimer is formed easily from

the second excimer.

4) PVPh, PPhEVE, and PPhMA showed the structured monomeric fluorescence and no excimer one. The fluorescence properties of these polymers indicate the formation of a non-fluorescent excimer in PVPh. The excimer was easily formed in the vinyl polymers having aromatic chromophores connected directly to the skeletal chain, even if the aromatic chromophores did not form any excimer between those.

5) PCzEVE showed an anomalous and structureless fluorescence composed of two components. One of the emitting species may be the second excimer.

6) The efficiency of the singlet exciton migration in polymer films was determined by the concentration of the intrinsic trap sites such as the excimer-forming sites. It decreases in the following order: DCzP(a) > PCzEVE > PVCz(r) ~ PVCz(c) > PACz ~ BPVCz.

7) The concentration of the second excimer-forming site, c_s, was higher in the syndiotactic rich polymer than in the iso-tactic rich polymer. As the concentration of the sandwich-like excimer-forming site, c_E, was much higher than c_s, there was little difference in $c_E + c_s$ between PVCz(r) and PVCz(c).

8) The efficiency of the triplet exciton migration also was determined by the concentration of the intrinsic trap sites. The decreasing order is; PVCz(r) > PVCz(c) > PCzEVE in film, and PVCz(r) > PVCz(c) in rigid solution.

9) The delayed fluorescence increased with an increase in the concentration of triplet quenchers such as naphthalene and fluorene, suggesting the presence of a heterogeneous T-T annihilation.

10) The singlet quenchers significantly reduced the photo-current of PVCz and BPVCz, but the triplet ones did not, indicating that charge carriers are generated via the singlet exciton rather than the triplet one.

11) The study of magnetic field effect on the photo-conductivity and the exciplex fluorescence of PVCz revealed that the photo-carriers are generated by field assisted dissociation of the singlet non-relaxed exciplex.

12) UV-irradiation on PVCz films yielded the photo-oxidation product with carbonyl group near the surface of the film with a yield of 10^{-4}. This product acts as an effective electron-acceptor and enhances the photo-carrier-generation.

As mentioned above, many information were obtained on the photophysical process of PVCz and its related compounds.
The author believes that this thesis would contribute to advanced understanding of the optical and electrical properties of organic materials.

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