

## Fluorescence Spectra of the Poly (N-vinylcarbazole) Obtained with Asymmetric Polymerization\*

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**Abstract:** The fluorescence spectra of the poly (N-vinylcarbazole) in solution obtained with chirally organic salts or acid as catalyst or initiator [ (-)Sp: (-)-Sparteine, (+)CSA: D- (+)-Camphor-10-sulfonic acid)], respectively, have been investigated. It is found that the two emission peaks at the longer wavelength ( $\lambda_{\text{max}}$ , *ca.*, 415nm) and the shorter wavelength ( $\lambda_{\text{max}}$ , *ca.*, 370nm) are assigned to the sandwich excimer and second excimer (partial overlap) fluorescence, respectively. The sandwich excimer and partially overlapped excimer are attributed to a fully overlapped structure of neighbouring carbazole chromophores in a totally elipsed conformation of the isotactic sequence, and partially overlapped structure of the syndiotactic sequence. The estimated values of  $I_{415}/I_{370}$  and isotactic sequence content by using the fluorescence spectra are in the order: (-)Sp<sup>+</sup> (+)CSA<sup>-</sup> > (+)CSA<sup>-</sup> > (-)Sp<sup>+</sup>ClO<sub>4</sub><sup>-</sup> (no peak at 415nm for AIBN).

**Keyword:** Fluorescence Spectra; poly (N-vinylcarbazole); asymmetric polymerization.

### Introduction

Poly (N-vinylcarbazole) (PVCZ) has received much attention as a representative photoconductive polymer and extensive studies on mechanical, physical, chemical and electrical properties have been reported<sup>1-2</sup>. In general, the PVCZ obtained by radical and ordinary cation polymerization in solution shows two fluorescence peaks of the two components. The emission at longer wavelength (*ca.*, 418nm) was assigned to the sandwich excimer fluorescence and on the other hand, the assignment of the broad emission in the shorter wavelength region (*ca.*, 370nm) was the second excimer fluorescence. Both emissions would reflect the difference in the tacticity of PVCZ.

In previous papers we reported<sup>4ab</sup> that the optical activity and the stereo-microstructure of PVCZs could be controlled with chirally organic salts or acid as catalyst or initiator during the VCZ polymerization. The specific rotation and isotactic sequence content of the PVCZ obtained depended on the catalyst or initiator types *i.e.* A<sup>+</sup>B<sup>-</sup> > A<sup>+</sup>B<sup>-</sup> > A<sup>+</sup>B<sup>-</sup> (an asterisk represents chirality). The present paper deals with the relationship between the stereo-microstructure and the feature of the fluorescence spectra of optically active PVCZs obtained with chirally organic salts or acid.

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## Experimental

Optically active poly (N-vinylcarbazole)s were prepared as reported in a previous paper and the characterization of the PVCZ samples is shown in **Table 1**<sup>4ab</sup>.

The fluorescence spectra of PVCZs were measured on HITACHI-850 fluorescence spectrophotometer. All experiments were carried out in aerated THF solution at room temperature.

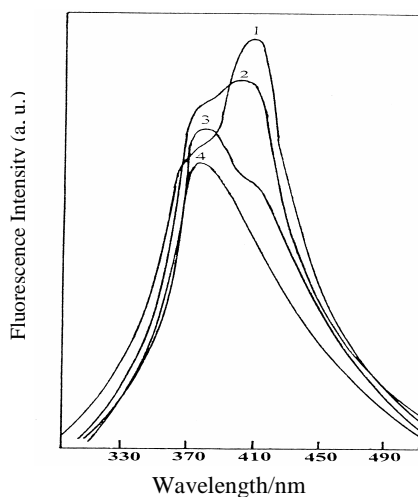
**Table 1.** Specific rotations and tacticities of PVCZ obtained with chirally organic salts (acid)

Types	Name	$[\alpha]_D^{25}$ a degree	Xi <sup>b</sup> in mole% by <sup>1</sup> H NMR (by Tg <sup>c</sup> )
	AIBN	0	28.0 (--)
	H <sup>+</sup> ClO <sub>4</sub> <sup>-</sup>	0	39.0 (--)
A <sup>+</sup> B <sup>-</sup>	(-)Sp <sup>+</sup> ClO <sub>4</sub> <sup>-</sup>	+2.4	48.0 (65.3)
A <sup>-</sup> B <sup>+</sup>	(+)CSA <sup>-</sup>	+4.2	50.6 (75.0)
A <sup>+</sup> B <sup>-</sup>	(-)Sp <sup>+</sup> (+)CSA <sup>-</sup>	+8.3	51.4 (76.1)

- a. Specific rotation  $[\alpha]_D^{25}$  unit: deg.cm<sup>2</sup>/g (c, 0.5, THF);  
 b. Isotactic diad mole fraction  $\text{Xi} = I_{\text{HF}}/I_{\text{HF}} + I_{\text{LF}}$ , where  $I_{\text{HF}}$  and  $I_{\text{LF}}$  represent two peak strengths located at the high and low frequency chemical shift, respectively, of CH on the PVCZ chain<sup>5</sup>  
 c. According to ref. 6.

## Results and discussion

**Figure 1** shows the fluorescence spectra of PVCZ obtained with chirally organic salts (acid) and free radical polymerization. Both of the emission peaks at shorter wavelength ( $\lambda_{\text{max}}$ , ca. 370nm) and longer wavelength ( $\lambda_{\text{max}}$ , ca. 415nm) existed in the fluorescence spectra.

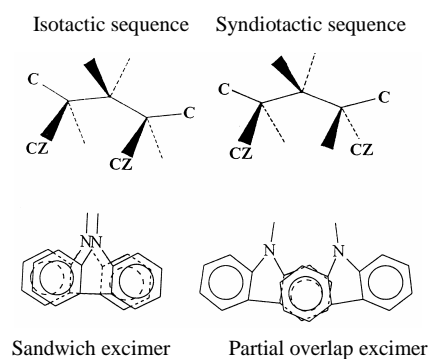


**Figure 1.** Fluorescence spectra of PVCZ obtained with various catalysts (initiator): 1. (-) Sp<sup>+</sup> (+) CSA<sup>-</sup> 2. (+) CSA<sup>-</sup> 3. (-) Sp<sup>+</sup>ClO<sub>4</sub><sup>-</sup> 4. AIBN in aerated THF at room temperature.

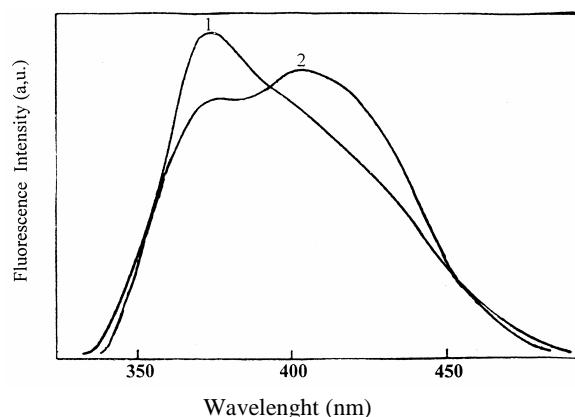
Itaya *et al.*<sup>3</sup> have studied the fluorescence spectra of the various PVCZ samples obtained by radical and general cation polymerization and have observed the broad emission at the

longer wave length ( $\nu_{\max}$  ca.  $23900\text{cm}^{-1}$ ) and at the shorter wavelength ( $\nu_{\max}$  ca.  $27000\text{cm}^{-1}$ ), respectively. Terrell *et al.*<sup>7</sup> explained that longer wavelength emission was attributed to a “sandwich-type” excimer formed between neighbouring carbazole group on the polymer chain. However, the short wavelength emission peak was less well characterized. Sakai *et al.* reported that the photophysical processes of PVCZ was of great interest because of two specially distinct excimer fluorescences and a clear relation between photophysical properties and chain tacticity<sup>8</sup>. Examining the relation between stereoregularity and the fluorescence spectra of PVCZ, we can attribute the one excimer fluorescence maximum at 420nm to a fully overlapped structure of neighbouring carbazolyl chromophores in a totally elipsed conformation of the isotactic sequence (sandwich excimer), while the other excimer maximum at 370nm to a structure with only one elipsed aromatic ring from two carbazolyl chromophores in the tt conformation of the syndiotactic sequence (second excimer or partial overlap excimer). This is schematically shown in **Figure 2**.

**Figure 2.** Schematic model of the carbazolyl group eclipse with the partial overlap excimer and the sandwich excimer fluorescence.



**Figure 3.** Fluorescence spectra of PVCZ samples in deaerated solution of 2-methyltetrahydrofuran with different syndiotactic dyad mole fractions: 1.Xs=0.63-0.70, 2.Xs=0.5<sup>[7]</sup>



Ledwith *et al.*<sup>9</sup> have shown that the optically active polymers containing carbazole units with chiral carbon atom or copolymers of N-vinylcarbazole and optically active (-) menthyl vinyl ether exhibit in solution either strong circular dichroism (CD) or enhanced optical rotation resulting from their predominantly helical conformations. Helical

conformations for stereoregular polymers of carbazole derivatives are also indicated by previous fluorescence studies in solution<sup>10</sup> and x-ray crystallographic studies in the solid state<sup>11</sup>. Kimura et al proposed also on the basis of x-ray diffraction data that PVCZ consists of the stereoblock arrangement of isotactic  $3_1$  and syndiotactic  $2_1$  helices<sup>12</sup>. Therefore, PVCZ possesses generally two diad sequences, *i.e.* isotactic and syndiotactic sequences<sup>13</sup>. The fluorescence spectra peaks at 415nm and 370nm as shown in **Figure 1** have reflected the sandwich excimer fluorescence originating from isotactic sequence and the partial overlap excimer originating from syndiotactic sequence, respectively. They could be directly correlated with the mole fraction of isotactic and syndiotactic diad in the PVCZ.

The fluorescence spectra in **Figure 3** were obtained with PVCZ samples with different mole fractions of syndiotactic diads ( $X_s$ =syndiotactic diad mole fraction)<sup>7</sup>, and the mole fraction of isotactic diads was  $X_i$  ( $X_i=1-X_s$ )<sup>4b</sup>. Remarkably, when  $X_s=0.5$ , *i.e.*  $X_i=0.5$ , the peak intensity of the sandwich excimer with the long-wavelength peak (*ca.* 420nm) and that of the second excimer with the short wavelength peak (*ca.* 375nm) were almost equal<sup>7</sup>. Okamoto et al<sup>14</sup> reported that cationically polymerized samples have increased isotactic content compared with free radically prepared polymer. The PVCZs obtained by chirally organic salts (acid) possessed higher content of isotactic diads (see **Table 1**). In **Figure 1** the higher peak intensity at 415nm compared with the peak intensity at 370nm, the estimated values of  $I_{415}/I_{370}$  ( $X_i$ , content of isotactic diads) by the fluorescence spectra are 1.36 (58%), 1.07 (52%) and 0.47 (32%), respectively, for (-)Sp<sup>+</sup>(+)CSA<sup>-</sup>, (+)CSA<sup>-</sup> and Sp<sup>+</sup>ClO<sub>4</sub><sup>-</sup> and are corresponding with the order: (-)Sp<sup>+</sup>(+)CSA<sup>-</sup> > (+)CSA<sup>-</sup> > (-)Sp<sup>+</sup>ClO<sub>4</sub><sup>-</sup> (no peak at 415nm for AIBN), *i.e.* A<sup>+</sup>B > A<sup>+</sup>B > A<sup>+</sup>B<sup>-</sup><sup>4a</sup>. The results showed that the PVCZ with higher optical activities gives larger contents of sandwich (larger values of  $I_{415}/I_{370}$  and higher content of isotactic diads). Some reports on model compounds have suggested that the low energy excimer arises mainly from isotactic sequences which are very important for the organic electroluminescent devices containing PVCZ as a hole-transport layer<sup>15</sup>. It is further studied by the photophysics feature of PVCZ obtained by asymmetrical polymerization.

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