# Fluorescence from Poly(*N*-vinylcarbazole) in Uniaxially Stretched Polymer Films

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**ABSTRACT:** Steady-state and time-resolved fluorescence properties of poly(*N*-vinylcarbazole)(PVCz) dispersed in a polystyrene (PS) cast film were studied under tensile loadings at room temperature. The excited monomer emission of PVCz located around 350 nm decreased with increasing applied tensile strain from 0 to 0.8%. The strain enhanced the emission which was ascribed to the partial-overlap excimer of PVCz in a 360–430 nm region. The emission due to the full-overlap excimer of PVCz between 430 and 500 nm was unchanged by the action of the tensile loadings. The ratio of fluorescence intensities at 375 nm and 345 nm $I_{375}/I_{345}$ was proportional to the applied strain. The time-resolved fluorescence study indicated that the lifetimes of the excited monomer and of the partial-overlap excimer were not affected by the strain. The obtained results mean that the strain applied to the PS matrix increases the partial-overlap conformation of two adjacent carbazolyl chromophores in a PVCz chain and suggest that PVCz is a useful probe for detecting residual strains in polymer matrices. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 1569–1573, 1997

**Key words:** poly(*N*-vinylcarbazole); steady-state fluorescence; time-resolved fluorescence; excimer; detection of residual strain

## INTRODUCTION

Fluorescent molecules have been widely used as probes to study polymer physics and processing. The probes give information about the orientation[1] and relaxation of polymer chains,[2] compatibility of polymer blends,[3–5] the curing process,[6] and residual stresses and strains.[7] This article rates a new probe for monitoring residual strains in polymer materials.

Poly(*N*-vinylcarbazole)(PVCz) is a typical aromatic vinyl compound having many pendant chromophores. It is well known that PVCz shows a complicated fluorescence ascribed to an excited monomer and two types of excimers associated with adjacent chromophores as shown in Figure

1.[8–10] The fluorescence properties of PVCz may be sensitive to variations in the spatial distribution and alignment of molecules in the local environments,[10,11] and it is, therefore, to be expected that mechanical stretching[12] also strongly influences fluorescence from PVCz. In this article, we report that steady-state and time-resolved fluorescence from PVCz dispersed in a polymer film varies under tensile loadings. The obtained results suggest that PVCz is an effective molecular sensor for detecting residual strains in polymer matrices.

## EXPERIMENTAL

### Sample Preparation

The sample in this work was a polystyrene (PS) cast film containing a small amount of PVCz. PVCz (1 mg) and PS (2 g) were dissolved in chloroform (30 mL). PVCz (Aldrich Chemical. Co.,

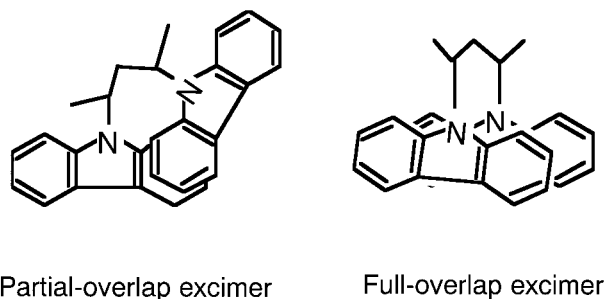Partial-overlap excimer        Full-overlap excimer

**Figure 1** Partial- and full-overlap excimers of two carbazolyl chromophores of PVCz.

$M_w$ 9.2 × 10$^5$), PS (Mitsui-Toatsu. Co., Torpolex 500), and a spectroscopic grade of chloroform (Dojindo Lab., Co., Luminazol) were used as received. The solution was then cast onto the Teflon plate. After evaporation of the solvent, the film was dried for more than 2 h at 80°C to release residual stresses. The sample thickness was 250 $\mu$m.

**Spectroscopic Measurements**

A schematic illustration of the fluorescence measurement under tensile loadings is displayed in Figure 2. A handmade jig was used for the uniaxial elongation of the sample. The given strain was reduced to a tensile stress using a tensile stress–strain curve obtained on an Instron tensile tester (Fig. 3). The stress–strain curve was measured at an elongation speed of 5 mm/min. All measurements were carried out at room temperature.
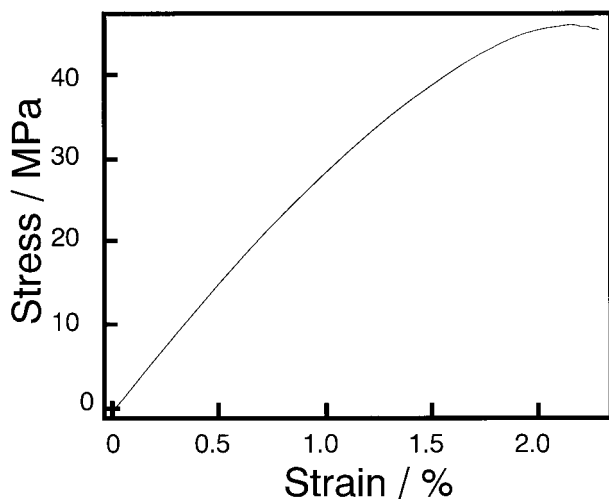
Steady-state fluorescence spectra were ob-



**Figure 2** A schematic illustration of a test apparatus for the fluorescence measurement under tensile loadings.
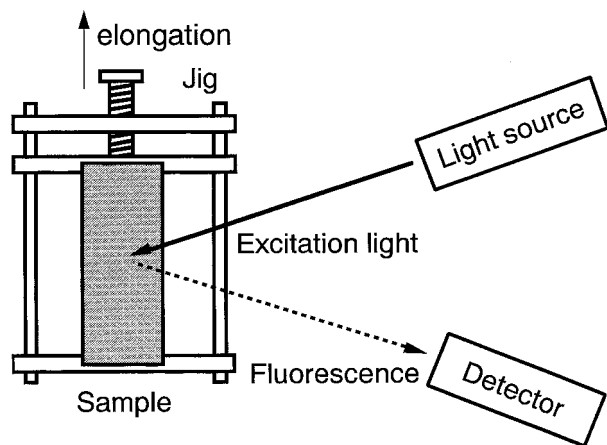


**Figure 3** A stress–strain curve of the sample measured at room temperature.

tained on a JASCO FP-777 spectrofluorophotometer. The excitation wavelength was 300 nm. Time-resolved fluorescence measurements were performed using a fluorescence lifetime measuring system with a streak camera (Hamamatsu Photonics, C4780). The nitrogen laser with a pulse duration of ca. 500 ps (Laser Photonics, LN120C, 337 nm) was used as an excitation light source. The decay data were analyzed using eq. (1):

$$I(t) = \sum A_n \exp(-t/\tau_n) \qquad (1)$$

where $I(t)$ is the fluorescence intensity; $A_n$, the constant, and $\tau_n$, the decay time. The deconvolution and curve fitting were performed by least-squares calculations. The emission originated from PS was proved to be negligible in our experimental conditions.

## RESULTS AND DISCUSSION

### Steady-state Fluorescence Spectra of PVCz Under Tensile Elongation

Figure 4 shows the steady-state fluorescence spectrum of the sample (solid line) and the fluorescence spectra of three model compounds obtained from refs. 8 and 9 (dotted lines a, b, and c). Spectrum a is a datum of *N*-ethylcarbazole and indicates a model of the excited monomer in PVCz. In spectrum b, the partial-overlap excimer emission is given by *rac*-2,4-di(*N*-carbazolyl)pentanes. Spectrum c represents the full-overlap excimer emission from *meso*-2,4-di(*N*-carbazolyl)pentanes.
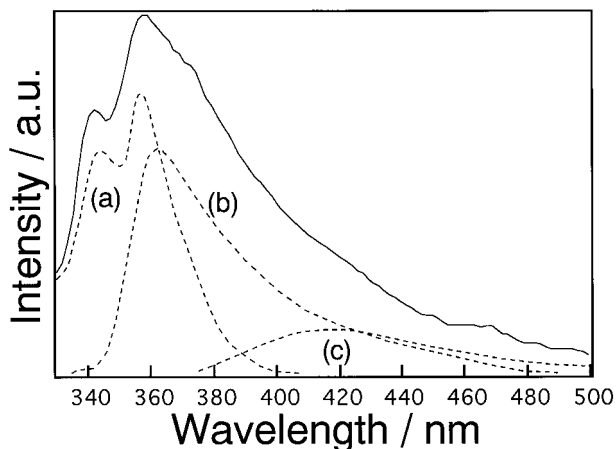
**Figure 4** Steady-state fluorescence spectrum of PVCz in PS (solid line) and fluorescence spectra of three model compounds for PVCz (dotted lines a, b, and c). Spectrum a is a datum of *N*-ethylcarbazole and indicates emission of the excited monomer in PVCz. In spectrum b, the partial-overlap excimer emission is given by *rac*-2,4-di(*N*-carbazolyl)pentanes. Spectrum c represents the full-overlap excimer emission of *meso*-2,4-di(*N*-carbazolyl)pentanes. The data of the three model compounds were obtained from refs. 8 and 9.

As shown in Figure 4, the steady-state fluorescence was found to be composed of the monomer emission, the partial-overlap excimer emission, and the full-overlap excimer emission. The latter is relatively weak compared with the first two. Sakai et al. reported that the full-overlap excimer is governed in its fluorescence behavior by a PVCz solution.[10] According to their report, the full-overlap conformation of two adjacent chromophores is thermodynamically stable in the excited state, while a PVCz chain avoids an interaction between the two adjacent chromophores in the ground state. When the excitation light is irradiated, the solution allows a conformational change in a PVCz chain. On the other hand, the obtained result in this study contrasts with the behavior in the solution. Figure 4 indicates that a rigid polymer matrix restricts the molecular motion of PVCz chains.

Figure 5 shows the steady-state fluorescence spectra of the sample under tensile loadings. Emission around 340–360 nm decreases as the strain is increased, while emission in the 360–430 nm region increases. However, emission around 430–500 nm is unchanged by the action of an external strain. These results mean that the relative intensity of the excited monomer emission decreases under tensile loadings while that of the
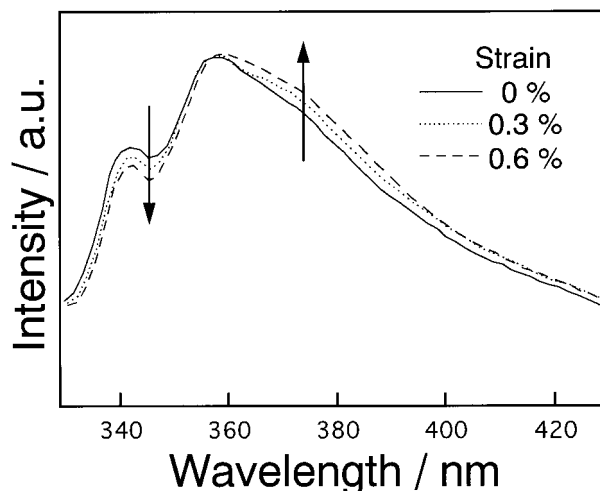


**Figure 5** Steady-state fluorescence spectra of PVCz dispersed in PS under tensile elongation.

partial-overlap excimer emission increases. They also indicate that the full-overlap excimer emission is not affected by the strain. Figure 6 shows the relationship between the ratio of fluorescence intensities at 375 and 345 nm $I_{375}/I_{345}$ and the applied tensile strain. The ratio is proportional to the applied strain of 0–0.8%. Interesting behavior is observed in the elastic deformation of PS. Figure 6 suggests that we can estimate tensile strain or stress on the matrix nondestructively from the fluorescence intensity ratio $I_{375}/I_{345}$.

## Time-Resolved Fluorescence Under Tensile Elongation

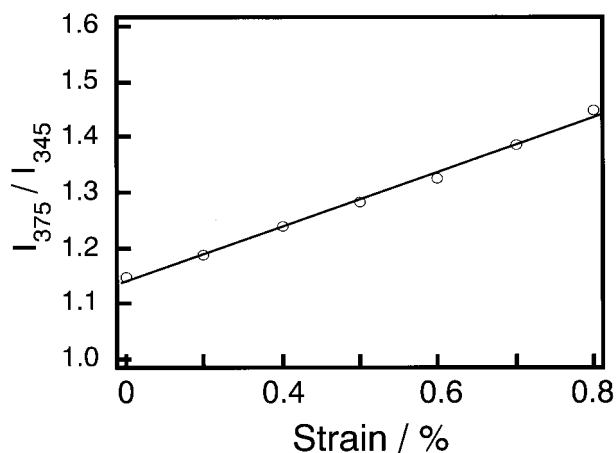Figure 7 shows the normalized time-resolved fluorescence spectra of the sample in the absence of



**Figure 6** Relationship between the ratio of fluorescence intensities at 375 and 345 nm ($I_{375}/I_{345}$) and applied tensile strain.
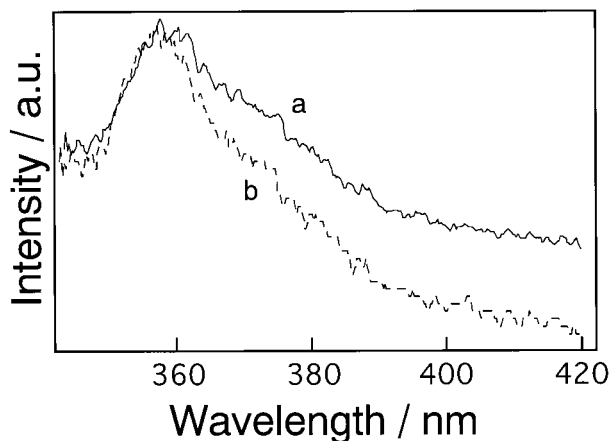
**Figure 7** Normalized time-resolved fluorescence spectra of PVCz in PS. Spectra a and b represent fluorescence with time windows between −1 and +1 ns and between 4 and 7 ns, respectively. The time window at $t = 0$ is set at the time when the excitation laser pulse reaches a maximum.



**Figure 8** A typical fluorescence decay curve of PVCz in PS measured in a 350–400 nm region.

a tensile loading. The time window at $t = 0$ is set at the time when the intensity of the excitation laser pulse is maximal. In the early gated spectra between −1 and +1 ns, the fluorescence maximum is observed at 360 nm and a shoulder appears around 380 nm. In the time range of 4–7 ns, the peak of the fluorescence band is still located at 360 nm but the shoulder has disappeared. Figure 7 indicates that both the excited monomer and the partial-overlap excimer form immediately after an excitation and that the partial-overlap excimer emission decays more rapidly than does the monomer emission in the rigid PS matrix. The former results suggest that, even in the ground state, the partial-overlap excimer conformation of two chromophores has already existed in a PVCz chain before excitation. The latter means that the lifetime of the partial-overlap excimer is shorter than that of the excited monomer.

Figure 8 shows a decay curve of fluorescence in the 350–400 nm region. The decay curve could not be fitted by a single exponential decay function. As indicated in Figure 4, the intensity of the full-overlap excimer emission is relatively weak in this wavelength region. In addition, Figure 7 indicates that the partial-overlap excimer decays more rapidly than does the monomer emission. Therefore, the decay curve has been tentatively analyzed by two exponentially decaying functions which are ascribed to the monomer and the partial-overlap excimer. Table I shows the decay fitting parameters analyzed by a sum of two expo-
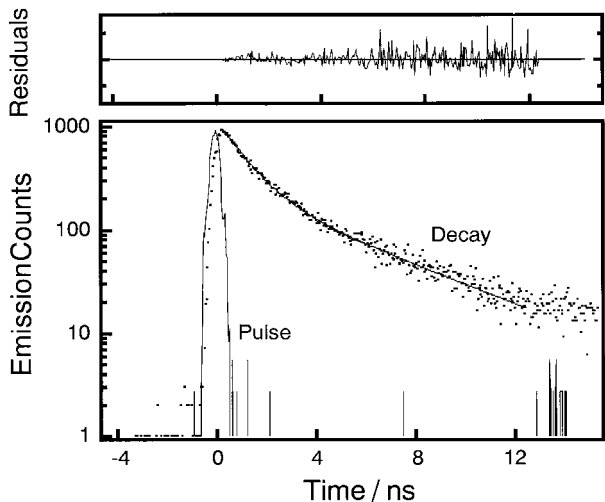
nential functions for the sample under tensile loadings. The fits were reasonable ($\chi^2 = 1.2$). The shorter decay time is about 0.9 ns and the longer is about 5.6 ns. We have concluded that the lifetimes of the partial-overlap excimer and of the excited monomer are 0.9 and 5.6 ns, respectively. These lifetimes have been kept constant with increasing tensile strain. The results suggest that the molecular structures of the excited monomer and of the partial-overlap excimer are not influenced by the tensile stress or strain applied to the matrix. On the other hand, the ratio of the constants $A_1/A_2$ increases under the tensile loadings. This is qualitatively in good agreement with the result obtained by the steady-state fluorescence in Figures 5 and 6. The time-resolved fluorescence measurements indicate that the strain applied to the matrix increases the partial-overlap conformation of two neighboring chromophores in a PVCz chain.

**Table I  Decay Fitting Parameters of PVCz Fluorescence Measured in a 350–400 nm Region**

| Strain (%) | $\tau_1$ (ns)[a] | $\tau_2$ (ns)[b] | $A_1/A_2$ | $\chi^{2 c}$ |
|---|---|---|---|---|
| 0 | 0.86 | 5.61 | 2.0 | 1.2 |
| 0.4 | 0.83 | 5.56 | 2.2 | 1.2 |
| 0.6 | 0.90 | 5.61 | 2.3 | 1.2 |

[a] Decay time of the partial-overlap excimer.
[b] Decay time of the excited-monomer.
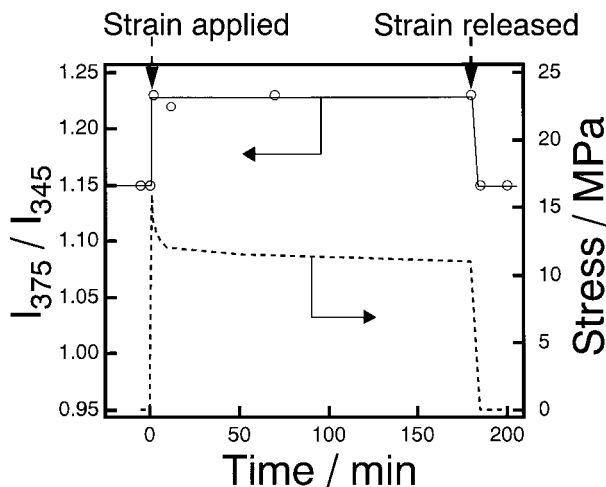[c] Chi-square of the weighted residuals.

**Figure 9** The ratio of fluorescence intensities at 375 and 345 nm $I_{375}/I_{345}$ on the stress-relaxation process (solid line). The dotted line represents a stress-relaxation curve. The applied strain was 0.4%.

## Fluorescence Intensity Ratio on Stress Relaxation

Figure 8 shows the ratio of fluorescence intensities $I_{375}/I_{345}$ on the stress-relaxation process. As a strain of 0.4% was applied to the sample, the ratio increased immediately from 1.15 to 1.23. Although the stress relaxes from 15 to 10 MPa within 175 min, the ratio scarcely changed. When the strain was removed, the ratio recovered the initial value of 1.15 before application of the tensile strain. From these results, we maintain that the change in the fluorescence intensity ratio $I_{375}/I_{345}$ is governed by the strain rather than by the stress. So, it seems to us that PVCz is a useful probe to detect strain in the matrix.

## CONCLUSION

This article described the possibility of a new door to the nondestructive method for detecting internal strain in a polymer matrix. The polymer products made by injection, extrusion, and blow molding have more or less residual strains.[13] The strains cause microcracks,[13,14] deformation,[13] and flow marks.[15] Therefore, the measurement of residual strains in polymer products is important in understanding the reliability of the products. Although it is known as one of the techniques for detecting internal stress or strain, the photoelastic method can be applied only to transparent resins.[16] On the contrary, the photoluminescent probe method in this study can be applied to opaque materials, such as crystalline polymer and polymer composites and so on. The obtained results suggest that PVCz is a useful photoluminescent probe to detect tensile strains acting on polymer matrices.

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