

카바졸 치환체를 가지는 신디오택틱 폴리스티렌의 분자내/분자간 엑시머 발광

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Intra-/Intermolecular Excimer Emission of Syndiotactic Polystyrene Having Carbazole Substituents

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초록: (2-*N*-carbazolylmethyl)styrene을 디타노센 촉매와 라디칼 개시제를 사용하여 신디오택틱 및 아탁틱 poly(2-*N*-carbazolylmethyl)styrene을 합성하고 발광특성 중 엑시머 형성에 대하여 조사하였다. 아탁틱 고분자는 하나의 발광만을 나타낸 반면에 신디오택틱 고분자는 카바졸기가 부분적으로 오버랩되는 정렬에서 기인하는 단량체 발광과 엑시머 발광을 모두 나타내었다. 아탁틱 고분자의 발광은 용액농도와 온도 의존성이 나타나지 않았으나, 신디오택틱 고분자는 의존성의 크게 관찰되었다. 이러한 결과로 엑시머 발광은 치환기인 카바졸의 위치에 의존하는 것을 확인하였다.

Abstract: The syndiotactic and atactic poly(2-*N*-carbazolylmethyl)styrenes were obtained by a half-titanocene catalyst and a radical initiator for the investigation of photophysical properties, especially excimer formation. The atactic polymer exhibited only monomer emission, but the syndiotactic polymer showed both excimer emission and monomer emission resulting from the partial overlapping arrangement of carbazole pendants. The emission band of syndiotactic polymer was considerably dependent on solution concentration and temperature, however atactic polymer was independent because the excimer formation of syndiotactic helical conformation was more favorable than that of the random coil conformation of atactic polymer.

Keywords: carbazole, polystyrene, tacticity, excimer, emission.

Introduction

Carbazole and its derivatives have attracted extensive interest because of their useful photorefractive materials, photoconductors, light-emitting materials and hole-transporting materials.¹⁻⁵ Poly(*N*-vinylcarbazole) (PVK) has already played an important role in photocopiers and light emitting diodes(LEDs).⁶ The carbazole containing polymers have also proved successful as the hole(charge)-transporting component of photorefractive polymers.^{7,8} Since these polymers are easily modified and manufactured, they are widely used as a hole transporting materials. It is known that the hole-transporting capability of these polymers is dependent on several factors such as concentration, substituent and ionization potential of chromospheres. However, the effect of polymer structure on the hole-transporting capability

has hardly ever been studied. Uryu *et al.* observed that the hole mobility of isotactic poly(2-*N*-carbazoleethyl acrylate) was higher than that of atactic polymer.⁹

The vinyl polymer containing the carbazole molecules in the pendant groups, the flexible molecular spacer between the carbazole groups and the backbone will play an important role in the conductivities of these polymers. Most investigations have concentrated on functionalized carbazole at the (3,6), (2,7) and *N*-positions.

The photophysical and photochemical properties of PVK have been widely studied because of PVK had a unique photophysical property forming two distinct excimers. The emission bands of PVK consists of three maximum wavelengths at 350, 370 and 420 nm due to the excited monomer state and two distinct excimers, which were a high-energy excimer and a low-energy excimer, respectively, both in solution and solid state. The formation of these two excimers was determined by configuration of vinyl polymer containing

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carbazole group.¹⁰⁻¹³ The low-energy excimer is formed when two carbazole groups have achieved an eclipsed, sandwich like conformation and the formation of the high-energy excimer is induced by a partial overlap of two carbazole groups.¹⁴⁻¹⁷ The charge transport occurred by a hopping mechanism at a conjugated structures whereas PVK is not a conjugated polymer. Many researchers have devoted studies to the incorporation of carbazole and its derivatives into conjugated polymers as parts of the pendants for improvement the charge transport ability.¹⁸ However, few studies have dealt with the effect of stereoregular structures on photophysical properties of vinyl polymer containing the carbazole group. The excimer formation of syndiotactic polymers containing carbazole group has never been reported.

This study conducted polymerization of 2-*N*-carbazoyl methyl styrene by using a radical initiator and half titanocene catalysts, producing the atactic and stereoregular poly(2-*N*-carbazoylmethyl)styrene for investigation of excimer formation. Their emission properties, which are related to the nature of the excimer formation, were investigated in solution and film states. This work describes for the first time how the highly controlled a syndiospecific polymer backbone gives rise to pendant carbazoyl polymers. The synthesis and characterization of the different stereoregular poly(2-*N*-carbazoylmethyl)styrene were detailed, and the conformation of carbazoyl pendants were simulated the optimized geometry of molecular mechanics for the verification of overlapping carbazoyl groups.

Experimental

Synthesis of 2-*N*-Carbazoylmethyl Styrene. 5 g of carbazole was dissolved in 50 mL of dry dimethylformamide (DMF) at room temperature and vigorously stirred. In the solution state, 0.87 g (36 mmol) of sodium hydride (60% dispersion in mineral oil) added slowly and stirred for 3 hrs. 4-Chloro methyl styrene (5.5 g, 36 mmol) was added to completely dissolved solution and stirred at 60 °C for 10 hrs. The resulting solution was poured into 200 mL NH₄Cl aqueous solution, and aqueous mixture was extracted with chloroform (150 mL × 3). After evaporation, the residue was recrystallized from tetrahydrofuran (THF) to give colorless needles.

Yield : 42%, ¹H NMR (in CDCl₃) : 5.2, 6.6 (3H, Ar-CHCH₂), 5.7 (2H, -N-CH₂-Ar), 7.2, 7.6 (4H, Ar-H), 7.4, 7.5, 8.1 (8H, Carbazole-H)

Polymerization. Atactic Polymer (Polymer 1): Atactic poly(2-*N*-carbazoylmethyl)styrene was obtained by common radical polymerization with AIBN (0.01 mol%) as an initiator. The polymerization was carried out in a 250 mL glass reactor

equipped with a magnetic bar. The reactor was back-filled three times with nitrogen and charged with the required amount of DMF. At the stipulated temperature of 70 °C, the reaction solution was vigorously stirred after the monomer and initiator were added. After 2 hrs, the polymerization was terminated by the addition of methanol. The product was washed with methanol several times to remove residual monomer and was further extracted by water vapor with Soxhlet extractor for 24 hrs. The final product was dried at 60 °C in vacuum oven.

Yield : 36%, ¹³C NMR (in CDCl₃) : 144.4, 134.0, 127.1, 124.8 (four main peaks of phenyl), 140.5, 122.9, 120.3, 119.1, 108.9 (five main peaks of carbazole), 46.4 (C1-main chain α-carbon), 41.0 (C1-main chain β-carbon).

Syndiotactic Polymer (Polymer 2): Syndiotactic poly(2-*N*-carbazoylmethyl styrene) was obtained by using half titanocene catalyst (Cp*TiCl₃) and MMAO cocatalyst. The polymerization was carried out in a 300 mL glass reactor. The reactor was back-filled three times with nitrogen and charged with the required amount of toluene. Monomer and the proper amount of MMAO ([Al]/[Ti]=1000) were added in this order. Finally pre-diluted half-titanocene catalyst (Cp*TiCl₃, 0.4 μmol) in toluene was syringed. The reaction was kept at 70 °C for 24 hrs and terminated by adding 10% acidified methanol. The polymer was worked up by filtration, washed three times with fresh methanol and extracted by water vapor with Soxhlet extractor for 24 hrs. It was dried at 60 °C in a vacuum oven.

Yield : 38%, ¹³C NMR (in CDCl₃) : 144.0, 134.3, 127.7, 125.9 (four main peaks of phenyl), 140.5, 122.2, 120.3, 119.3, 108.7 (five main peaks of carbazole), 45.7 (C1-main chain α-carbon), 40.0 (C1-main chain β-carbon).

Characterizations. The UV-vis absorption and photoluminescence (PL) spectra were measured on JASCO 620V spectrophotometer and JASCO FP-6500 spectrofluorometer, respectively. The ¹H NMR and ¹³C NMR spectra were measured in CDCl₃-*d*₁ containing tetramethylsilane as the internal standard using an Advance Digital 400 NMR spectrometer (Bruker). The weight average molecular weight (*M*_w) and number average molecular weight (*M*_n) of the polymer were evaluated using gel permeation chromatography (Waters, Alliance 2000, THF, polystyrene universal calibration) at room temperature.

Molecular Simulation. The bent angle of 2-*N*-carbazoylmethyl styrene monomer and main chain conformation of syndiotactic and atactic poly(2-*N*-carbazoylmethyl styrene) were calculated by using SpartanModel simulation kit. The optimized geometry of **Polymer 1** and **2** were simulated by using 10 repeating units.

Results and Discussion

Synthesis and Characterization. Syndiospecific and aspecific poly(2-*N*-carbazoylmethyl styrene) were synthesized for the investigation of the effect of main chain stereoregularity on fluorescent properties of carbazole containing polymers. **Polymer 1** and **2** were synthesized by a radical initiator (AIBN) and half-titanocene catalysts (Cp^*TiCl_3), respectively, and the results are summarized in Table 1.

Syndiotacticity of polymers was calculated from the phenyl C-1 carbon ($\delta=144.0$) according to the literature.¹⁹

Polymer 1 was readily polymerized under a typical radical initiator. **Polymer 2** was obtained by using a half-titanocene catalyst, had a fairly high yield. The weight average molecular weight (M_w) of **Polymer 1** and **2** were 1.4×10^4 and 11.6×10^4 , respectively. The syndiotacticity of **Polymer 2** was much higher than that of **Polymer 1**.

Fluorescence Emission. Figure 1 showed UV-vis. spectra **Polymer 1** and **2** in film state. **Polymer 1** and **2** exhibited two major absorptions at 30211 and 30120 cm^{-1} (331 and 332 nm), as well as at 28985 and 28901 cm^{-1} (344 and 345 nm) originated in $\pi \rightarrow \pi^*$ transitions of partially conjugated double bonds due to nitrogen atom, respectively. The shifts of the phonon side bands ($30211 \sim 30120 \text{ cm}^{-1}$) of **Polymer 1** and **2** are considered to be caused by the locally excited emissive photons, with C-N band stretching vibration, res-

Table 1. Properties of Polymers

Samples	Catalyst	Yield	$10^{-4} \times M_n$	$10^{-4} \times M_w$	M_w/M_n	Syndiotacticity
Polymer 1	AIBN	36%	0.9	1.4	1.6	23.5
Polymer 2	Cp^*TiCl_3	38%	6.4	11.6	1.8	55.3

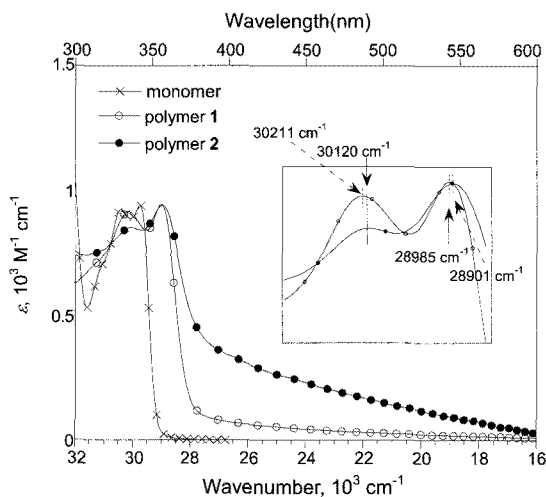


Figure 1. UV-vis spectra of 2-*N*-carbazoylmethyl styrene and poly(2-*N*-carbazoylmethyl styrene); **Polymer 1** and **2** (in film states).

pectively.

It is considered that excimer has been crucial to aspects of photophysical and photochemical properties. Therefore vinyl polymers containing excimer-forming molecules such as polystyrene (PS), poly(*N*-vinylcarbazole) (PVK) and poly(vinylnaphthalene) (PVN), have been widely examined.²⁰⁻²² The intramolecular excimers were first observed in PS the most common polymer of this type.^{21,23,24}

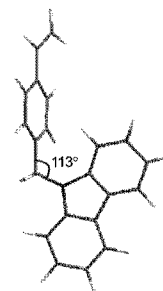
Longworth *et al.*^{25,26} have studied the effects of orientation and tacticity on excimer formation of PS and PVK. They reported that fluorescence yield increased with increasing tacticity due to the excimer formation, namely sandwich-like excimer and partial overlapped excimer. The isotactic conformation is more favorable for excimer formation than the atactic conformation.

Polymer 1 and **2** have a relatively extended side chain, in comparison with molecular structures of PVK and PS, they have the flexible molecular spacer between the carbazole groups and main chain. The bent angle between styrene and carbazole is approximately 113° at the lowest energy as shown in Scheme 1. The intramolecular interaction between localized π and delocalized electrons is feasible due to the flexible, bent molecular spacer between the carbazole groups and random coil conformation of main chain.²⁷

The syndiotactic polystyrene (sPS) has the trans-planar conformation and the 2-1 helical conformation. The chain periodicities of sPS were 5.5 and 7.7 Å.²⁸

Polymer 2 is very much alike in configuration to that of syndiotactic polystyrene (sPS) and has more excimer forming sites than atactic polymer in concentrated solution and film state.

The fluorescence emission spectra of **Polymer 1** and **2** films are shown in Figure 2. The spectra of both polymers mainly consist of monomeric emission ($\lambda_{\text{max}}=373$ and 372 nm for **Polymer 1** and **2**) and excimer emission ($\lambda_{\text{max}}=394$ and 393 nm for **Polymer 1** and **2**). The excimer emission is considered to result from partial overlapped conformation of carbazole groups.



Scheme 1. Molecular model of 2-*N*-carbazoylmethyl styrene at the lowest energy.

Remarkably, the intensity of excimer emission band for **Polymer 2** is much higher than that of monomer emission band. In the spectrum of **Polymer 2**, the intensity ratio of excimer emission (I_{ex}) to intensity of monomeric emission (I_m) was higher than that of **Polymer 1**, as $I_{ex}/I_m = 0.99$ and 0.80, respectively. These results indicated that excimer formation of the syndiotactic conformation got ahead of the random atactic conformation. The efficiency of the singlet-

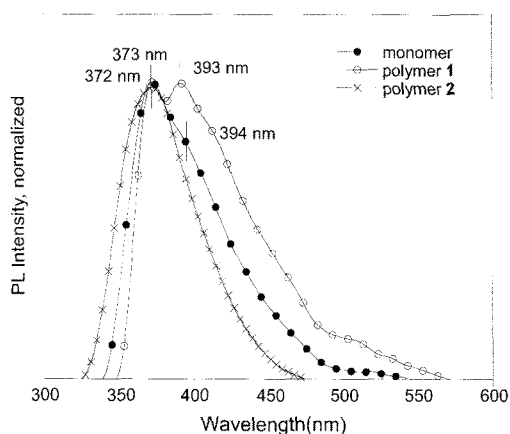
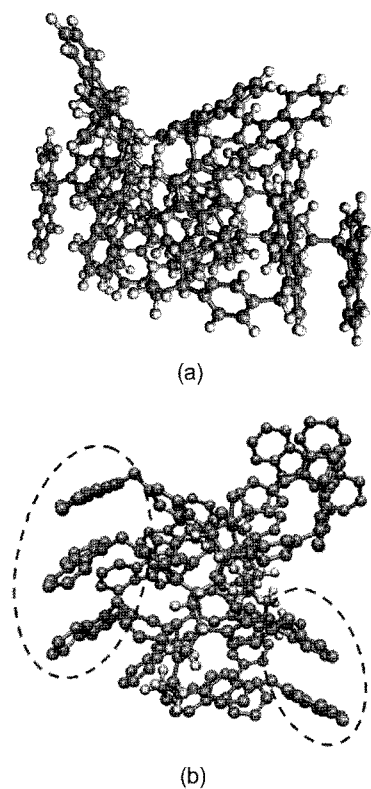


Figure 2. Fluorescence emission spectra (excited at 330 nm) of 2-*N*-carbazolymethyl styrene monomer, **Polymer 1** (atactic) and **Polymer 2** (syndiotactic) of film states.



Scheme 2. Simulation results by molecular mechanics showing the optimized geometry with minimized energy in (a) **Polymer 1**; (b) **Polymer 2**.

exciton migration along the polymer chain is also different with tacticity.¹¹ The syndiotactic conformation was favorable to form excimer which may be more effective exciton migration than atactic conformation. In the same vein, the neighboring carbazole groups in **Polymer 2** have a high tendency to form partial overlap conformation in ground states, whereas **Polymer 1** was hardly observed excimers, as shown by the simulation results in Scheme 2(a). Because the main chain and carbazole group are bent, they may not form a sandwich-like arrangement but a slightly overlapping arrangement of the carbazole groups. It is considered that electron delocalization may be extended to several carbazole groups in comparison with **Polymer 1**.

Fluorescent emission spectra of **Polymer 1** and **2** at various concentration of methylene chloride solution are shown in Figure 3. The emission spectra were shifted to long wavelength with increasing concentration. In dilute solution (low-density), the spectra of **Polymer 1** and **2** showed similar behavior because excited molecules were brought down the ground

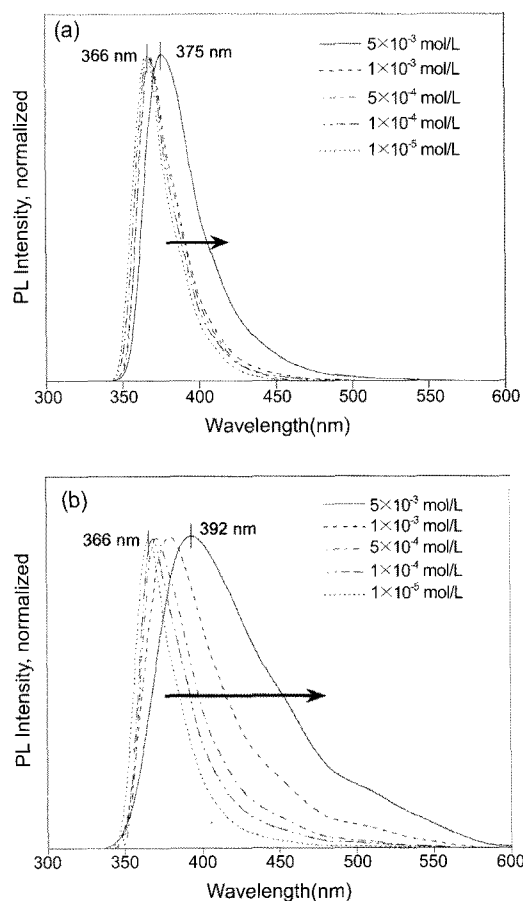


Figure 3. Fluorescence emission spectra (excited at 330 nm) of **Polymer 1** (atactic) (a); **Polymer 2** (syndiotactic) (b) with various concentrations of methylene chloride solution at room temperature.

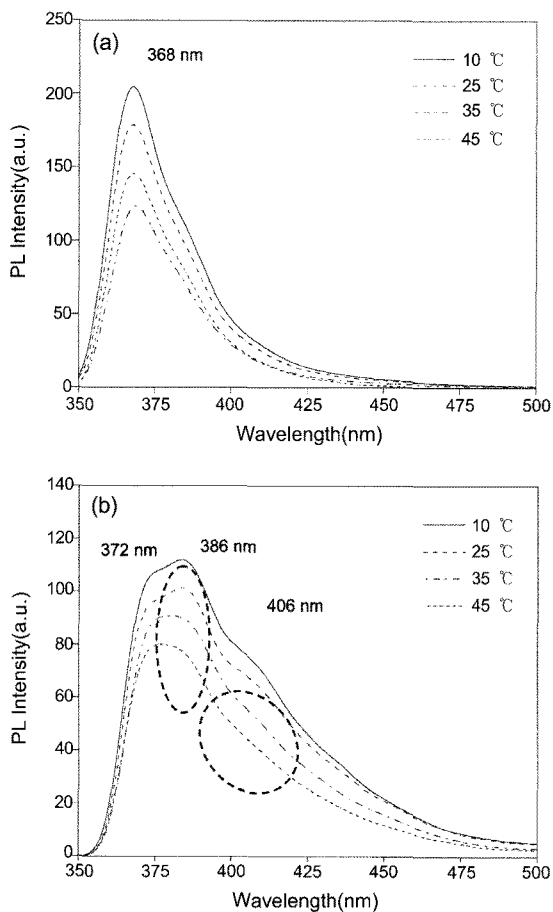


Figure 4. Fluorescence emission spectra(excited at 330 nm) with changes of temperature in methylene dichloride($c=5 \times 10^{-3}$ M) of (a) **Polymer 1**(atactic); (b) **Polymer 2**(syndiotactic).

state before they interact with an unexcited molecule to form an excimer.

On the other hand, spectrum of **Polymer 2** was considerably shifted to the long wavelength and emissions occurred in a broad spectrum in contrast with **Polymer 1** at high concentration. The excimer formation was dependent on interaction of the neighboring carbazole groups in an excited states, it was promoted by high monomer density. Namely, intra-/intermolecular interaction were very active in film states and concentrated solution. The excimers are only formed in the excited states as well as intermolecular interactions are possible in even ground states. The delocalization of electron could occur for lots of polymer chain in both ground and excited states and their emission exhibited in a wide range and shifted to long wavelength.

Figure 4 shows the dependence of the emission spectra in methylene chloride solution of **Polymer 1** and **2** at elevated temperature. The emission bands of **Polymer 1** and **2** showed remarkably different at experimental temperature from 10 to 45 °C. In both polymers, emission intensity of 368 nm

(I_{368}) and 372 nm (I_{372}) decreased with increasing temperature, which is monomeric emission. In case of **Polymer 2**, the emission intensity around 386 nm (I_{386}) increased at relatively low temperature though emission intensity of whole spectra decreased. These phenomena could lead to a partial overlap excimer which occurred intersystem crossing and energy transfer by intermolecular collisions at high temperature.⁸ It is considered that the different emission of **Polymer 1** and **2** may occur the different conformation of main chain. The main chain conformation of **Polymer 1** was random coil though it had a little syndiotactic property. **Polymer 2** had 2-1 helical conformation so easily formed excimer by intra-/intermolecular overlap of carbazole substituent.

Conclusions

Vinyl polymers containing carbazole group were synthesized for investigation of photophysical properties, especially excimer formation. The syndiotactic and atactic poly(2-*N*-carbazolymethyl styrene)s were obtained by half-titanocene catalyst and radical initiator, respectively. Fluorescent emission was dependant on their conformation of main chain. Atactic polymer exhibited only monomeric emission, whereas syndiotactic polymer showed excimer emission because syndiotactic polymer had 2-1 helical conformation so easily formed excimer by intra-/intermolecular overlapping of carbazole substituent. The emission band of syndiotactic polymer was considerably dependant on solution concentration and temperature. It is considered that syndiotactic polymer containing carbazole group uses as hole-transporting material. The study of their mobility will be conducted henceforth.

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