

STRUCTURE AND PROPERTIES OF POLY(N-VINYLCARBAZOLE) OBTAINED VIA ASYMMETRICALLY STEREOSELECTIVE POLYMERIZATION*

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Abstract The structure and properties of poly(N-vinylcarbazole) (PVCZ) obtained via asymmetrically stereoselective polymerization have been studied by using ^1H NMR spectra, UV spectra, DSC analysis and GPC. The steric microstructure i.e. the content of isotactic sequences was found to be increased by using AIBN to $(-)\text{Sp}^{++}(+)\text{CSA}^{*-}$ as the initiators or catalysts and the mole extinction coefficient to be decreased. Bimodal molecular weight distribution (MWD)s of the obtained PVCZs were caused by two propagating species of the free ions and the ion-pairs associated with the organic salts during polymerization.

Keywords Poly(N-vinylcarbazole); Asymmetrical polymerization; Isotactic sequence.

INTRODUCTION

Asymmetrically stereoselective polymerization of achiral or racemic olefin monomers has been investigated by chirally ionic complex catalysts to obtain an optically active polymers or the polymers with a single screw direction along a growing polymer chain^[1-4]. Asymmetrically stereoselective polymerization of N-vinylcarbazole (VCZ) with bulky side group has been investigated by using the organic salts with chiral or stereo-differentiating ligands as initiators or catalysts in our previous paper^[5]. It was found that the optical rotations of the obtained polymers most depend on asymmetrically induced power of the initiators or catalysts during the polymerization, and the catalyst with chirally negative counterion would exert an important influence on the way of the monomer entering into the growing polymer

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chain^[5], i.e. the long-distance effect of the initiators and the short-distance effect of the catalysts. In the present paper the structure and properties of optically active PVCZs, i.e. the steric microstructure, the mole extinction coefficient and the molecular weight distribution have been investigated by ¹H NMR, UV, DSC and GPC.

EXPERIMENTAL

Measurements

Optical rotation measurement was performed at 25°C on a Perkin-Elmer Model 141 spectropolarimeter with a sensitivity of $\pm 0.003^\circ$. UV spectrum (THF) was recorded on HITACH-340 UV spectrograph. ¹H NMR spectrum (CDCl₃) were obtained on a Varian XL-200 (200 MHz) spectrometer at 45°C. TMS was used as internal standard. DSC was recorded on a Shimadzu apparatus DSC-41 with 3.4~3.9 mg sample and a temperature programming rate of 20°C/min. The glass transition temperature, T_g , could be measured from DSC spectrum. The molecular weight of PVCZ were measured by viscometry (solvent: THF, Conc.:0.5, Temp.:25 $\pm$ 0.1°C) according to Sitaramaiah^[6]. GPC (Gel Permeation Chromatography) analysis was accomplished on Water 201 with a μ -Styragel column and THF, DCE (dichloroethane) as solvent, and the molecular weight of PVCZ was calibrated with standard polystyrene.

Polymerization

The polymerization of VCZ was described in the previous paper^[5].

RESULTS AND DISCUSSION

Steric microstructure

The steric microstructure, i.e. the content of isotactic sequences of the PVCZs obtained by the organic salts with chiral or stereo-differentiating ligands (Scheme 1) is given in Table 1.

The content of isotactic mole fraction was determined by ¹H NMR spectrum. The methylene (1.20 ppm) and methine (2.60 ppm) signals in PVCZ chain structure are assigned to the isotactic sequences and methylene (1.60 ppm) and methine (3.44 ppm) signals to the syndiotactic sequences. Therefore, the higher field peaks of both methylene and methine protons may be tentatively assigned to the isotactic sequence and the correspondingly lower field peaks to the syndiotactic one. The isotacticity/syndiotacticity could be estimated by the ratio (I_H/I_L) of two peaks

intensities situated at the higher field (I_H) and lower field (I_L) for the methine signals. The isotactic mole fraction ($X_i > 0.5$) of the obtained polymer by the organic salts with chiral and stereo-differentiating ligands were higher than that by the free radical and common cation ($X_i = 0.28 - 0.48$) as shown in Table 1. Terrell et al. reported^[7] that the entropy difference between syndiotactic and isotactic propa-

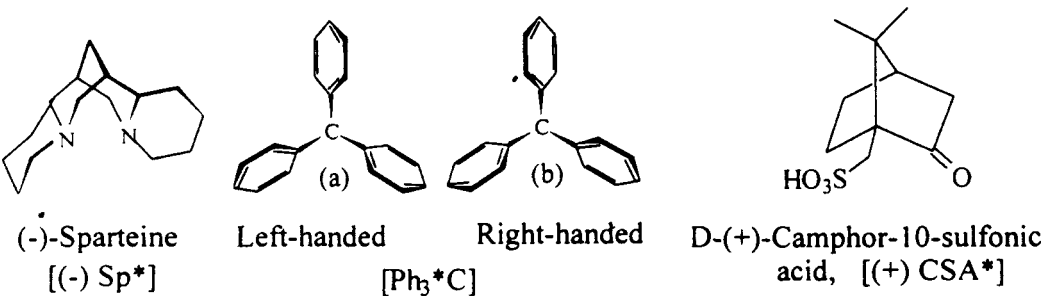
Table 1 UV absorption and tacticity of PVCZ obtained with organic salts as initiators and catalysts

Types	UV spectra ^{a)}						$[\alpha]_D^{25b)}$	X_i ^{c)} in mole % by ¹ H-NMR by T_g
	¹ B _b		¹ L _a		¹ L _b			
	$\lambda_{\max}$ in nm	$\epsilon_{\max}$ in M^{-1} (cm^{-1})	$\lambda_{\max}$ in nm	$\epsilon_{\max}$ in M^{-1} (cm^{-1})	$\lambda_{\max}$ in nm	$\epsilon_{\max}$ in M^{-1} (cm^{-1})		
AIBN	294	2316	328	2650	340	2229	0	28.0(−)
H ⁺ ClO ₄ [−]	285	2107	330	2525	342	2573	0	39.0(−)
Ph ₃ C ⁺ ClO ₄ [−]	285	2072	328	2498	342	2529	+2.2°	47.0(29.3)
Ph ₃ C ⁺ SbCl ₆ [−]	285	2114	328	2559	342	2620	−2.6°	48.3(34.9)
(−)Sp ⁺⁺ ClO ₄ [−]	284	1615	329	1841	342	1957	+2.4°	48.0(65.3)
(+)CSA [−]	—	—	—	—	—	—	+4.2°	50.6(75.0)
Ph ₃ C ⁺ (+)CSA [−]	284	1726	329	1803	342	1932	+4.4°	51.5(74.2)
(−)Sp ⁺⁺ (+)CSA [−]	284	1783	329	1734	342	1902	+8.3°	51.4(76.1)

^{a)} Conc.: $0.9 - 1.0 \times 10^{-3} M$ (THF), ¹B_b, ¹L_a and ¹L_b are Platt's representations for the electronic transitions of the carbazoyl residue

^{b)} Specific rotation $[\alpha]_D^{25}$ unit: deg·cm²/g (c, 0.5, THF)

^{c)} Isotactic diad mole fraction, $X_i = I_{HF}/I_{LF}(CH)/I + I_{HF}/I_{LF}(CH)$, where I_{HF} and I_{LF} represent two peaks strength placed in high and low frequency of chemical shift, respectively, for CH on the PVCZ chain



Scheme 1 The structures of chiral or stereo-differentiating ligands

gation strongly favoured syndiotactic one using free radical and common cationic polymerization of VCZ and the variation in the steric microstructure, i.e. isotactic mole fraction, was between 0.25 and 0.47, respectively. It was found that in the previous paper^[5], the stereoselective induction power of the organic salts were in the order of $A^{++}B^{--} > A^+B^{--} > A^{++}B^-$, which generally is in correspondence with the order of the specific rotation and the isotactic sequences of the obtained PVCZs.

It is caused by the monomer entering into the growing chain and controlled by the negative counterion chirality. Therefore, the chirally negative counterion could play an important role in asymmetrically stereoselective polymerization^[1]. Okamoto et al. reported^[8] that the optically active polymers are found to have the largest amount of isotactic sequences.

The content of isotactic sequence of obtained PVCZ was determined also from the glass transition temperature (T_g) measurement and the syndiotactic mole fraction (X_s) was determined from the T_g value by using the following expression, $(T_g - 399)(1 - X_s) + (T_g - 549) = 0$ ^[9]. It is reported that PVCZ chain would have stereoblock arrangement of isotactic 3_1 and syndiotactic 2_1 helices^[10]. Hence, the isotactic mole fraction (X_i) may be calculated by $X_i = 1 - X_s$.

UV absorption spectrum

UV absorption spectrum of PVCZ is caused by the specific interaction between the carbazole pendant chromophores in the polymer chain. The mole extinction coefficients ($\epsilon_{\max}$) of the PVCZs obtained from AIBN to $(-)\text{Sp}^{*+}(+)\text{CSA}^{*-}$ different systems have been shown in Table 1. The absorption maxima ($\lambda_{\max}$) appear at 284—294 (^1B_b), 328—330 (^1L_a) and 340—342 nm (^1L_b), respectively. Here, ^1B_b , ^1L_a and ^1L_b are Platt's representations for the electronic transitions of the carbazolyl residue^[11]. The mole extinction coefficients ($\epsilon_{\max}$) of absorption maxima ($\lambda_{\max}$) in our condition decrease from AIBN to $(-)\text{Sp}^{*+}(+)\text{CSA}^{*-}$ systems (see Table 1). Okamoto et al. reported^[12] that the spectral properties of the PVCZ, such as hypochromism arise from some electronic interactions between neighboring chromophores in the polymer chain and are irrespective of the method of polymerization. In fact, the decrease in the absorption intensity (extinction coefficient) or the hypochromism are attributed to excitation interaction and dispersion force interaction in the polymer with an ordered structure^[13], i.e. high isotactic sequences. The diminution of extinction coefficient could not be explained by the hypochromism and could only be related to some regular orientation of the carbazole rings of the polymer with high isotactic sequence. It was reported that the extinction coefficient of the charge transfer complex formed from PVCZ with TCNQ (tetracyanoquinodimethane) having $1310 \text{ M}^{-1} \text{ cm}^{-1}$ will have good photoconductivity^[14]. The optical density of the biological macromolecules such as nucleic acids and proteins decreases as the molecules transform from a random coiled conformation to a helical one^[15,16]. In addition, the hypochromism of polystyrene with a much smaller pendant π -electron system is observed in the isotactic polymer and is regarded as being due to the coulombic dipole-dipole interaction in neighboring chromophores because of the

retention of the local ordered helix structure in solution^[17].

Molecular weight distribution (MWD)

It is generally accepted that an equilibrium existed between the free ions and ion-pairs species dissociated from the organic salts in non-aqueous solvent. The dissociation constant and degree of dissociation (fraction of free ions) were listed in Table 1 of our previous paper^[5]. The MWDs of PVCZs obtained from the organic salts are shown in Fig.1.

The obtained polymers show a bimodal MWD which are attributed to the free ions and ion-pairs propagation for $\text{Ph}_3\text{C}^+(\text{+})\text{CSA}^{*-}$ and $(-)\text{Sp}^{*+}(\text{+})\text{CSA}^{*-}$ catalytic systems and an unimodal MWD to mainly the free ions for $(\text{+})\text{CSA}^{*-}$ and $(-)\text{Sp}^{*+}\text{ClO}_4^-$ initiator systems. The equal reactivity of free ions and corresponding ion-pairs in cationic polymerization involving large counterions were ever studied by Penczek et al.^[18]. But as well known that the reactivity of the ion-pairs which generally shows no specific solvation would be lower than

the free ions. Bimodal MWD indicates the presence of two different propagating species, i.e. free ions and ion-pairs, which by virtue of their different rates of propagation and termination could produce a polymer with different MWD^[19]. The bimodal MWDs of the obtained PVCZs in the cases would concern the initiating and growing mechanism of both the free ions and the ion-pairs which will be studied in the following papers.

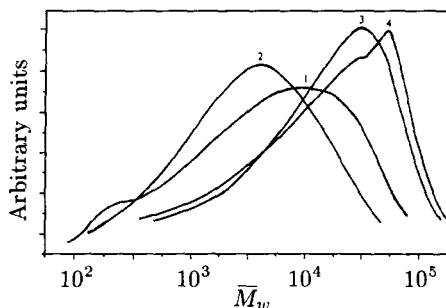


Fig.1 Molecular weight distributions of the PVCZs obtained

- 1) at 40°C in THF by $(-)\text{Sp}^{*+}(\text{+})\text{CSA}^{*-}$;
- 2) at 25°C in DCE by $(-)\text{Sp}^{*+}\text{ClO}_4^-$;
- 3) at 40°C in THF by $(\text{+})\text{CSA}^{*-}$;
- 4) at 25°C in DCE by $\text{Ph}_3\text{C}^+(\text{+})\text{CSA}^{*-}$

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