

MORPHOLOGICAL CHARACTERIZATION OF POLY(N-VINYLCARBAZOLE) OBTAINED WITH ASYMMETRICALLY STEREOSELECTIVE POLYMERIZATION*

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Abstract The morphological characterizations of poly(N-vinylcarbazole)(PVCZ) obtained by asymmetrically stereoselective polymerization were studied using x-ray diffraction pattern, DSC and GPC. The results show that the PVCZs have lower crystallinities (11.0 ~ 18.6%) and lower melting heats (2.2 ~ 7.5 J/g), but the degree of crystallinities of the PVCZ samples obtained using the organic salts (acid) with chiral or stereodifferentiating ligands are higher than that using radical and general protonic initiator. It has shown that the crystallization is directly related to the packing density of the hexagonal array of the rodlike molecules formed from the helical chain.

Keywords Crystal, Optically active, Poly(N-vinylcarbazole)

INTRODUCTION

Asymmetrically stereoselective polymerization of N-vinylcarbazole(VCZ) has been carried out using organic salts (acid) with chiral or stereodifferentiating ligands as initiators (or catalysts) (Scheme 1). The organic salt $\text{Ph}_3\text{C}^+\text{ClO}_4^-$ is optically inactive but appears to have large stereodifferentiating ligands^[1]. Due to steric hindrance, the polymerization of VCZ with a bulky carbazole group gives rise to asymmetrically stereoselective induction, i.e. only one isomer of the triphenylmethyl salt (left or right handed) prefers to initiate the monomer and optically active PVCZ is formed. The asymmetrically stereoselective induction power of the organic salts (acid) during the polymerization of N-vinylcarbazole are in the order of $\text{A}^*\text{B}^* > \text{A}^+\text{B}^* > \text{A}^+\text{B}^-$ (an asterisk represents the chiral or stereodifferentiating ligand).

The specific rotations and isotactic mole fraction of PVCZs obtained generally correspond to this order^[2], but the mole extinction coefficients (ϵ_{max}) of PVCZs obtained from AIBN to $(-)\text{Sp}^*(+)\text{CSA}^*$ systems would gradually reduce with above order^[3]. A low mole extinction coefficient arises mainly from isotactic sequences which could have an efficient absorbency of light quantum resulting in low energy excitation, which is very important for the organic electroluminescent and photoconductor contained in the PVCZ layer^[4].

Recently, poly(N-vinylcarbazole) has been of considerable interest as organic electroluminescent and photoconductor systems^[5] for potential commercial use. An understanding

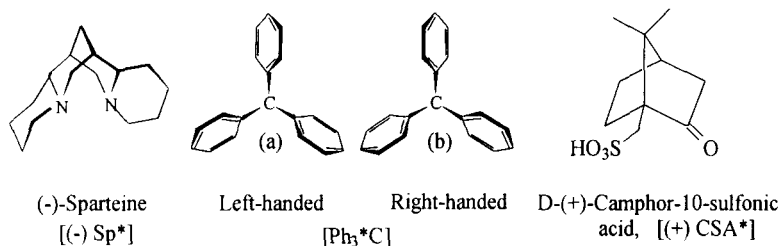
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of the photoconductive mechanism would depend upon interaction occurring between the electron systems of large pendant groups in their solid morphology. Therefore, studies of crystalline morphology of poly(N-vinylcarbazole) seem to be very important in the search for photoconductive systems. This paper reports on morphological characterization of the poly(N-vinylcarbazole) obtained from asymmetrically stereoselective polymerization.



Scheme 1 The structure of chiral or stereodifferentiating ligand

EXPERIMENTAL

Measurements

X-ray diffraction patterns were obtained on Rigaku D/max-3B diffractometer with 0.154 nm of wavelength of Cu K_{α} radiation. DSC was recorded on a METTLER DSC-25 with 6–10 mg sample and a temperature programming rate of 10°C/min. GPC (gel permeation chromatography) analysis was performed on a Water 201 with a μ -styragel column and THF as solvent and the molecular weight was calibrated with standard polystyrene.

Features of the Sample

The powder samples of PVCZ were prepared via precipitation from the polymerization solution as described in our previous paper^[2]. The results of sample characterization are shown in Table 1.

Table 1. Characterization of poly(N-vinylcarbazole) obtained by organic salts (acids) as initiators or catalysts

Type	Name	$M_n \times 10^{-5}$	$[\alpha]_D^{25a}$ degree	X_I in mole% by $^1\text{H-NMR}^b$ (by T_g) ^c
Radical	AIBN	3.15	0°	28.0(-)
Protonic	H^+ClO_4^-	0.80	0°	39.0(-)
A^+B^-	$\text{Ph}_3\text{C}^+\text{ClO}_4^-$	2.56	+2.2°	47.0(29.3)
	(-) $\text{Sp}^{++}\text{ClO}_4^-$	5.60	+2.4°	48.0(65.3)
A^+B^-	(+) CSA^+	0.16	+4.2°	50.6(75.0)
A^+B^-	(-) $\text{Sp}^{++}(+)\text{CSA}^+$	0.12	+8.3°	51.4(76.1)

a) Specific rotation $[\alpha]_D^{25}$ unit: $\text{deg} \cdot \text{cm}^2/\text{g}$ (c, 0.5, THF),

b) Isotactic diad mole fraction, $X_I = I_{\text{HF}}/I_{\text{LF}}(\text{CH})/1 + I_{\text{HF}}/I_{\text{LF}}(\text{CH})$, where I_{HF} and I_{LF} represent two peaks strength placed in the high and low frequency of the chemical shift, respectively, for CH on the PVCZ chain. (According to Ref.[6]),

c) According to reference^[7]

The heat treatment of the sample was carried out at 230°C(A) and 270°C(B) in a nitrogen atmosphere.

RESULTS AND DISCUSSION

Degree of Crystallinity

X-ray diffraction curves of poly(N-vinylcarbazole) powder precipitated from the polymerization solution obtained by a varieties of initiators (catalysts), i.e. from AIBN to (-) $\text{Sp}^{++}(+)\text{CSA}^+$, are shown in Fig. 1.

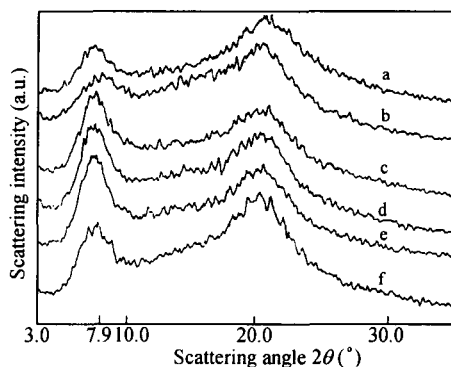


Fig. 1 X-ray diffraction curves of poly(N-vinylcarbazole) precipitated as a powder from the solution obtained by a) AIBN, b) H^+ClO_4^- , c) $\text{Ph}_3^+\text{C}^+\text{ClO}_4^-$, d) $(-)\text{Sp}^+\text{ClO}_4^-$, e) $(+)\text{CSA}^+$, f. $(-)\text{Sp}^+(+)\text{CSA}^+$.

The crystalline peak at $2\theta = 7.9^\circ$ represents a terplaner spacing of 1.038 nm. The amorphous field is characterized by an amorphous region at $2\theta = 20.8^\circ$ and a weaker reflection in the vicinity of crystalline peak. These results are in general agreement with Denwell's results for PVCZ, i.e. 8.2° (1.078 nm) and $20\sim 25^\circ$, respectively^[8].

Solomon et al.^[9] reported that polymerization of VCZ with butyllithium and titanium tetrachloride catalyst was carried out and the PVCZ with a degree of stereoregularity greater than 80% as well as clear crystalline structure established by X-ray analysis was obtained, but they indicated that influence of the steric hindrance on spherical structure showed by an optical study in polarized light was small. Heller et al.^[10] also showed that the X-ray diffraction pattern of the PVCZ obtained with TiCl_4 -*n*-BuLi has only amorphous halos. The lack of a crystalline diffraction pattern could mean that the stereoregular polymer has not crystallized under the polymerization conditions. Attempts to induce crystallization by various annealment treatments have so far failed. These findings are in discrepancy with the work of Solomon et al.^[9]. In our work the degree of crystallinity of PVCZ obtained using x-ray diffraction is shown in Table 2.

Table 2. Influence of heat treatment on the crystallinity of PVCZ obtained from a varieties initiators and catalysts as shown by X-ray diffraction analysis

Initiator or catalyst	Crystallinity (%) by X-ray before heat treatment	Heat treatment temp.(time, h)	Crystallinity (%) by X-ray after heat treatment	Change of crystallinity (%)
AIBN	12.40	B(0.5)	12.80	+0.40
H^+ClO_4^-	11.10	B(0.5)	4.70	-6.40
$\text{Ph}_3^+\text{C}^+\text{ClO}_4^-$	18.60	B(4.0)	11.70	-6.90
$(-)\text{Sp}^+\text{ClO}_4^-$	17.10	B(0.5)	10.10	-7.00
$(-)\text{Sp}^+\text{ClO}_4^-$	17.10	A(4.0)	9.95	-7.15
$(+)\text{CSA}^+$	17.70	A(4.0)	9.52	-8.18
$(-)\text{Sp}^+(+)\text{CSA}^+$	16.80	A(4.0)	6.35	-10.45
$(-)\text{Sp}^+(+)\text{CSA}^+$	16.80	B(0.5)	7.46	-9.34

It is noted from Table 2 that the degree of crystallinity of PVCZ is very low (11.1%~18.6%) which is quite difference from the result obtained by Solomon et al.^[9] but also from Heller et al.^[10]. But the degree of crystallinities of the PVCZ samples obtained using the organic salts (acid) with chiral or stereodifferentiating ligands is higher than that using radical and general protonic initiator (see Table 2.). In addition, the melting heats (ΔH_m) of PVCZ crystals measured by DSC as shown in Table 3 are small (2.2~7.5 J/g). It is found that these ΔH_m values of PVCZ obtained using the

organic salts (acid) with chiral or stereodifferentiating ligands as catalyst are also higher than that using radical and general protonic initiator. Graffiths et al. have explained that crystallizability would be a function of molecular weight^[11]. Under our conditions, although the PVCZ obtained with organic salts (acids) as catalyst has lower molecular weight (see Table 1), it exhibits a higher degree of crystallinity which is due to their higher tacticity comparing to the PVCZ obtained with AIBN etc.(see Table 2). The tacticity of PVCZ should play a role during crystallization and its isotactic configuration could be favorable for crystallization^[12].

Table 3. A comparison of T_g , t_m and ΔH_m of pvcz obtained from a variety of initiators and catalysts before and after heat treatment as shown by DSC results

Initiator or catalyst	Before heat treatment			After heat treatment(A or B)			$\Delta H_m'-\Delta H_m$ (J/g)
	$T_g(^{\circ}\text{C})$	$T_m(^{\circ}\text{C})$	$\Delta H_m(\text{J/g})$	$T_g'(^{\circ}\text{C})$	$T_m'(^{\circ}\text{C})$	$\Delta H_m'(\text{J/g})$	
AIBN	241.1	375.8	2.3	225.2(B)	370.7(B)	2.6(B)	+0.3
H^+ClO_4^-	210.8	262.8	2.6	205.3(B)	320.3(B)	3.1(B)	+0.5
$\text{Ph}_3\text{C}^+\text{ClO}_4^-$	232.1	300.0	2.2	210.5(A)	304.1(A)	2.6(A)	+0.4
$(-)\text{Sp}^{*+}\text{ClO}_4^-$	178.7	282.8	3.4	180.0(A)	231.2(A)	3.0(A)	-0.4
$(+)\text{CSA}^*$	163.5	261.8	4.5	120.0(A)	228.7(A)	3.7(A)	-0.8
$(-)\text{Sp}^{*+}(+)\text{CSA}^{*-}$	161.9	276.4	7.5	142.0(A)	234.6(A)	4.1(A)	-3.4
				154.2(B)	213.2(B)	4.6(B)	-2.9

a. Rate: 10°C/min, Sample weight: 6~10mg

Influence of Heat Treatment on the Degree of Crystallinity

It is well known that the influence of heat or annealing treatment on the crystallization of crystallizable polymers is very important. However, under our conditions, the degree of crystallinity of PVCZ is not increased, but on the contrary, decreased through heat treatment at 230°C (A) and 270°C (B) in nitrogen atmosphere as shown in Tables 2 and 3. Thus, the decrease in the degree of crystallinity of PVCZ obtained using the organic salts (acid) with chiral or stereodifferentiating ligands as initiator (or catalyst) is generally larger than that using radical and protonic initiator. The decrease of the melting heat of PVCZ obtained by DSC analysis shows the same tendency as the above results using X-ray diffraction analysis (see Table 3) and the melting heat is little increased for AIBN ($M_n=3.15\times10^5$) and $\text{Ph}_3\text{C}^+\text{ClO}_4^-$ ($M_n=2.56\times10^5$). The crystals of PVCZ consisted of a hexagonal array of parallel rodlike chains^[13]. The crystallization of PVCZ, in fact, is a process in which increase of packing density of the rodlike molecules formed from the helical chain in some conditions, for example, heat treatment. Therefore, though heat treatment near their melting point, the rodlike molecules formed from the helical chain with high isotactic diad mole fraction could be destroyed, resulting in a decrease in packing density, especially the helical chain structure with low molecular weight (see Table 1). These results would be also explained by the decrease in the molecular weight with GPC analysis after heat treatment. This is

Table 4. Change of the molecular weight of the poly(N-vinylcarbazole) obtained by a varieties of initiator (or catalyst) after heat treatment determined by GPC

I or C	Heat treatment	M_n	M_w	M_w/M_n	$[\alpha]_D^{25}$ ^a
AIBN	no treatment	17192	174566	10.1	0°
	B(270°C)	14689	172940	11.7	0°
$(-)\text{Sp}^{*+}\text{ClO}_4^-$	no treatment	3421	14548	4.2	+2.4°
	A(230°C)	1369	5422	3.9	0°
$(+)\text{CSA}^*$	no treatment	1220	5352	4.4	+4.2°
	A(230°C)	998	4245	4.2	0°
$(-)\text{Sp}^{*+}(+)\text{CSA}^{*-}$	no treatment	1379	4174	2.9	+8.3°
	B(270°C)	318	714	2.2	0°

a: See Table 1. footnote a

due to the degradation of the main chain of PVCZ near melting point, and resulted in the derotation, which was shown in Table 4.

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