Ion-Pairs Feature of Polymerization Process of N-Vinylcarbazole with Chirally Organic Salt as Catalyst

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ION-PAIRS FEATURE OF POLYMERIZATION PROCESS OF N-VINYLCARBAZOLE WITH CHIRALLY ORGANIC SALT AS CATALYST

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ABSTRACT

The influence of the N-vinylcarbazole (VCZ) concentration and the ratios of VCZ to catalyst (-)Sp*+(+)CSA*- on the polymerization process has been investigated and the polymerization mechanism is described by the conductance change with the time during the polymerization. The mechanism would be explained by the equilibrium feature (i.e. main ion-pairs) between the free ions and the ion-pairs dissociated by the organic salt (-)Sp*+(+)CSA*- and the scheme of the polymerization process is described mainly by the charge transfer complexes having chiral induction power.

INTRODUCTION

Polymerization of N-vinylcarbazole(VCZ) and their characterizations have been investigated extensively by a variety of ways. For example, free radical [1], conventional cation [2-4] (such as protonic acids, Lewis acids, carbocation), Ziegler-Natta[5], charge transfer [6], electrochemical [7] and solid state polymerization [8] etc. Nozaki and Asakura *et al.* first reported that cationic polymerization of VCZ was

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performed in the presence of chiral (+)-camphor-10-sulfonic acid (CSA*) and optically active PVCZ was obtained [9a,b]. In our previous paper, stereoselective induction polymerization of VCZ, in the presence of the organic salts with chiral or stereodifferentiating ligands, has been studied [10a] and optically active PVCZs having high isotacticity were obtained [10b].

In this article, the influence of polymerization conditions, such as monomer concentration, catalyst ratios and solvent polarity (dielectric constant) upon the polymerization process of VCZ by (-)Sp*+ (+)CSA*-[(-)sparteine-d-(+)camphor-10-sulfonate] as catalyst (an asterisk represents chirality) is investigated and the polymerization mechanism is explained by the conductance change with the polymerization time.

EXPERIMENTAL

Measurement

Optical rotation measurement was performed at 25°C on a Perkin Elmer model 141 spectropolarmeter with sensitivity of (0.003(.The molecular weights of PVCZ were calculated by the viscosity method (solvent: THF, conc.: 0.5g/dL, temp: 25±0.1°C) according to Sitaramaiah [11]. The equivalent conductivity of an organic salt solution with the cationic feature was determinated by using a series of equivalent concentrations of organic salts (dilution method) at 25°C on a DDS-11A conductometer. The dissociation constant K_d and the fraction of free ions, α, can be calculated by the Fuoss equation [12]. The polymerization process of VCZ was studied by conductance change with the polymerization time.

Solvent Treatment and Polymerization

Solvents: THF (tetrahydrofuran), DCM (dichloromethane), DCE (dichloroethane) and $CHCl_3$, were dried and redistilled over CaH_2 or metal Na before use. The polymerization of VCZ was described in the previous paper [10a].

RESULTS AND DISCUSSION

Influence of Monomer Concentrations and Catalyst Ratios

The influence of monomer concentration on the polymerization of VCZ was shown in Table 1.

TABLE 1. Polymerization of VCZ in the Presence of (-)Sp*+(+)CSA*- as Catalyst at 40°C in THF

[VCZ] (mol/L)	[M]/[Cat.]	Time (hrs)	yield (%)	Mv(10^{-4} [a] (g/mol)	$[\alpha]^{25}_D$ [b]
0.22	77	144	8.0	1.2	+3.9°
0.33	77	140	7.5	1.6	+8.8°
0.66	77	140	3.2	1.0	+5.3°
0.33	10	140	traces	-	-
0.33	20	140	2.9	2.0	+15.1°
0.33	100	140	5.3	1.6	+10.8°
0.33	200	140	12.5	1.0	+5.5°

[a]Calculation by viscosity method according to Sitaraminiah *et al.* [11].

[b] $[\alpha]^{25}_D$: specific rotation.

The yields of polymer decreased with increasing of monomer concentration, but the specific rotations increased (Table 1). Table 1 also shows that the yields increased with the molar ratios between monomer and catalyst and the specific rotations possessed optimal values ($[\alpha]^{25}_D$: 10.88-15.1°) in the molar ratio from 20 to 100.

For the organic salt it is generally accepted that an equilibrium exists between the free ions and the ion-pairs species in a non-aqueous solvent. The fractions of free ions of (-)Sp*+(+)CSA*- in DCM and DCE possessed 5.6 and 27% at 25(C, respec-tively [10a]. The fraction of free ions was very low and the ion-pairs became main parts in the solution. In addition, N-vinylcarbazole is subjected to mesomeric polarization and partial transfer of a lone pair electron from the nitrogen to =CH$_2$ increases the positive charge on the nitrogen. Therefore, the dipolar interaction of polarizing VCZ having high concentration with the ion-pairs could restrain the dissociation of the ion-pairs and decrease the fraction of free ions. Hence, the obtained PVCZs would get low yields and high specific rotations. For the same reason, the fraction of free ions dissociated by the ion-pairs would be decreased with increasing of the concentration of the (-)Sp*+(+)CSA*-. In these cases, the ion-pairs having lower reactivity would play a main role during initiating polymerization of VCZ and the stereoselective induction power is more than the corresponding free ions [10a]. Hence, the yields of the polymer obtained by the ion-pairs were lower, but their specific rotations were generally high (Table 1.). This is caused by the stereoselective induction of the ion-pairs during the polymerization.

TABLE 2. The Influence of the Solvent on the Polymerization of VCZ in the Presence of (-)SP*+ (+)CSA*- as Catalyst at 40°C in 48 hours.

solvent[a]	dielectric constant (ε)[b]	yield (%)	$[(\alpha]^{25}_D$ [c]
THF+CHCl$_3$	6.00	no polymerization	
	7.00	yellow traces	
THF	7.58	11.5	+8.5°
THF+DCE	8.00	8.5	+5.2°
	8.50	9.1	+5.1°
THF+DCM	8.50	17.4	+4.6°
THF+DCE	9.00	13.8	+2.2°
DCM	9.08	no polymerization	
DCM+DCE	9.50	no polymerization	

[a]THF: Tetrahydrofuran(ε=7.58), DCM: Dichloromethane(ε=9.08), DCE: Dichloroethane(ε=10.60).

[b] Approximate value calculated from the expression, ((mixture)=(vol$_1$%($_1$ + vol$_2$%($_2$).

[c] $[\alpha]^{25}_D$: specific rotation.

Influence of Solvent Polarity

The stereoregularity of PVCZ obtained by cationic polymerization was hardly changed by the polymerization temperature, it changed with the solvent polarity from an isotactic-rich configuration in toluene or CH_2Cl_2 to a syndiotactic-rich configuration in nitrobenzene. The PVCZs with isotactic-rich obtained in toluene or CH_2Cl_2 are produced by initiation of the ion-pairs (toluene and CH_2Cl_2 is non-polar solvent) [13]. Therefore, the nature of the reaction media plays a most significant role in cationic polymerization. The influence of the polarity of the solvent on the polymerization of VCZ has been listed in Table 2.

Table 2 shows that the polymerization of VCZ solution could be carried out only when the dielectric constants of the solvent was in the range of (=7.0-9.0. Here, dielectric constant is generally needed as an indication of the solvating power of a solvent and it is not necessarily a quantitative measure. It was reported [14] that in polar solvent the proportion of free ions produced by the solvation of the ion-pairs was high. The free ions are often the most reactive initiating species, and initiates polymerization by direct attack on electrophilic monomer in cationic polymerization. The solvent with higher dielectric constant favors the ionization and dissociation of

ion-pairs into free ions. Hence, they speed the rate of cationic polymerization. With increasing of dielectric constants (ε, 7.0 to 9.0) the yields and the specific rotations (isotactic content) of PVCZ obtained by (-)Sp*+(+)CSA*- were roughly increased and decreased, respectively (see Table 2). These were in agreement with the results of PVCZs obtained by CSA* [9a]. But in higher dielectric constant, surrounding the cation with solvation shells the reactivity of the free ions is reduced because at least one molecule of the solvent has to be removed from their solvation shell to allow for contacting with monomer. The polymerization of VCZ is not performed in the case of ($\varepsilon > 9$. Pepper *et al.* reported [15] that the polymerization of styrene catalyzed by the perchloric acid ($HClO_4$) carried out in solvent having solvating power and showned that the propagation rate constant increased by five orders of magnitude going from the low dielectric constant ($\varepsilon = 2.3(CCl_4)$) to the high dielectric constant ($\varepsilon = 9.7(ClCH_2CH_2Cl)$). Szwarc *et al.* found [16] that sodium reaction with naphthalene(Nph) dissolved in an aprotic ether yielded a solution of Nph⁻Na⁺ ion-pairs, and an equilibrium is eventually established when the ratio [Nph⁻Na⁺]/[Nph] reaches its equilibrium value, namely (≈ 0.9 for the cation performed in THF($\varepsilon = 7.58$) at ambient temperature,but only (≈ 0.02 when the reduction takes place in diethyl ether ($\varepsilon = 4.4$). These findings again demonstrate the importance of solvation power in polymerization process leading to the formation of free ions with higher reactivity, and ion-pairs with lower reactivity in higher dielectric constant (solvating power). The corresponding polymerization rates would be in agreement with the order (ε,7.0 to 9.0)

Mechanism of Polymerization Process

In general, the initiation reaction for a vinyl polymerization involving any cation (A^+) way represented by the equilibrium $A^+ + H_2C=CHR -- ACH_2\text{-}CHR^+$ i.e. carbocationic polymerization of olefins is indicated to involve direct addition of cation to olefin [17]. More definite evidence for direct addition was provided by the trapping (by methanolysis) of the initial adduct between tropylium ion and VCZ [18a], and by the triphenyl methyl addition in the polymerization of isobutyl vinyl ether [18b].

It must be noted, however, that despite the very high reactivity of VCZ, it does not react efficiently with triphenyl methyl salts possibly because of steric interaction between the phenyl group and the carbazole ring. The reaction mechanism implies propagation through a VCZ dication and regeneration of Ph_3C^+ at the end of the polymerization [3]. For cationic polymerization, the carbocation readily forms in most charge transfer complexes with electron donor molecules (e.g.
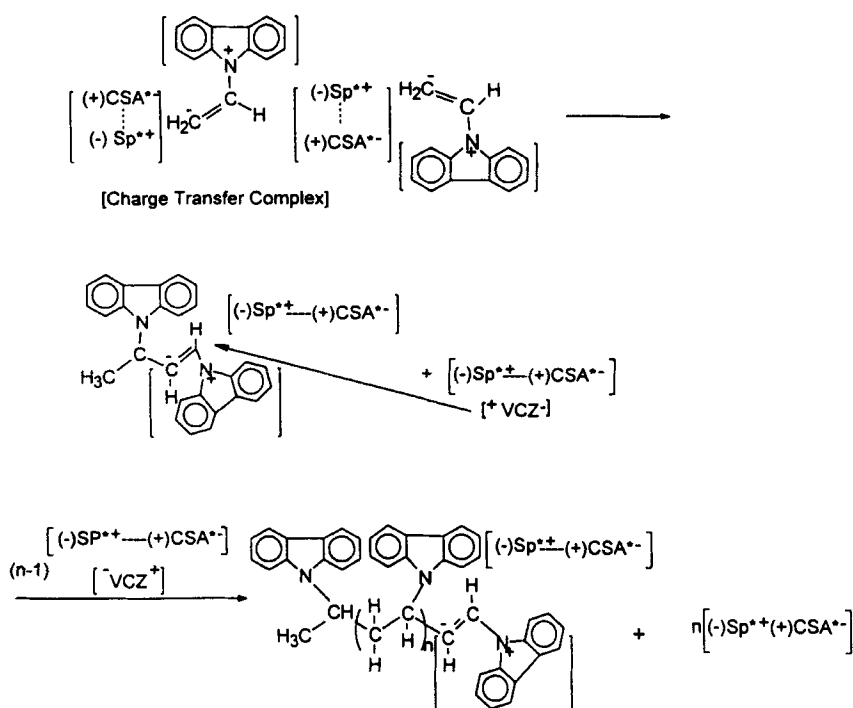
Figure 1.   Polymerization of VCZ in the presence of (-)Sp*+(+)CSA*-. All charges shown are partial charges.

carbazole) by primary electron transfers. The polymerization of VCZ in the presence of (-)Sp*+(+)CSA*- as catalyst could be carried out in fact through a polarizing complexes way. Such propagation cannot be expected to continue giving rise to polymers with high molecular weight. The termination might result in several possibilities, such as termination between two growing chains or termination by impurities such as adventitious water. However, the growing chain might be terminated by proton transfer leading to the formation of vinyl end groups. The IR spectra of the polymer revealed an absorption at ca. $900 cm^{-1}$ (11.11μ) characteristic of the above group. The PVCZ having end double bond could possessed reaction ability to increase its viscosity. Biswas $et\ al.$ [19] and Kennedy $et\ al.$ [20] have found that the PVCZ with vinyl end group possessed an absorption at ca. 11.20μ and 11.25μ, respectively. The initiation is thus regard as involving a number of steps shown in Figure 1.

The interaction between the polarizing VCZ, $=N^+-CH=CH_2^-$, and (-)Sp*+(+)CSA*- was insufficient to yield readily recognized complexes checked by
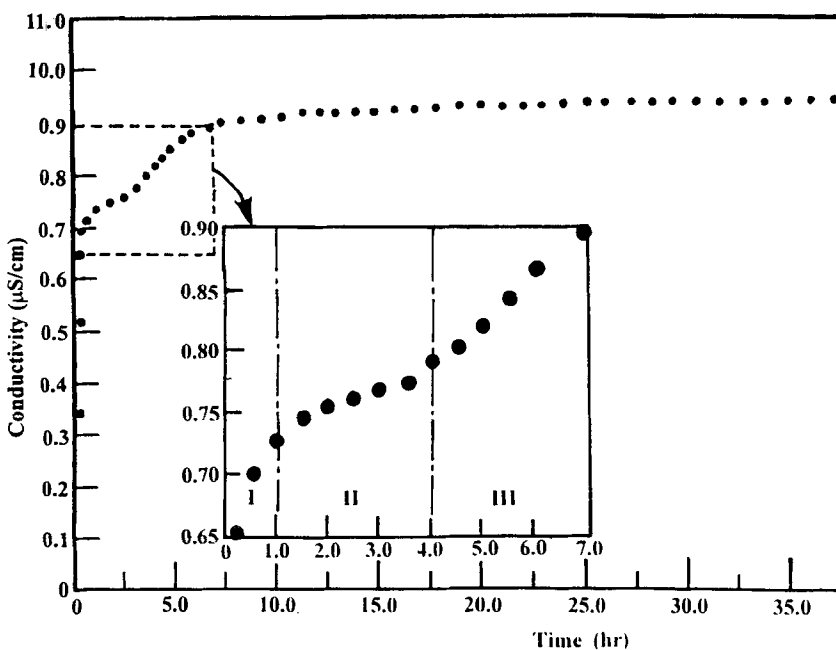
Figure 2. The relationship between the conductivites and the polymerization time of VCZ in the presence of (-)Sp*+(+)CSA*- at 40°C in THF.

U.V. spectra. But according to Figure 1, it also indicates that the formation of a bond between the two VCZ molecules involves not only the loss of a double bond but also necessitates a 1,3 hydrogen shift. The occurrence of hydrogen shift under these conditions was a characteristic feature, not only of the initiation step, but of the subsequent propagation stages also. It was shown that with the loss of one double bond in the initiation step, one of the two acceptor molecules, [(-)Sp* +(+)CSA*-], involved in the initiation step was eliminated. The existence of the terminal double bond of PVCZ would be caused by the depolarization of $=N^+-CH=CH^-$ group after termination using CH_3OH. The polymerization mechanism is almost the same with the polymerization process of VCZ by $CH_2=CHCN$ as charge transfer donor [21]. The PVCZ obtained was not contaminated with a catalyst,(-)Sp*+(+)CSA*-, residue according to ^{1}H NMR, IR spectral analyses and elemental analysis. Therefore, it could be suggested that the polymerization mechanism showed in Figure 1 is almost reasonable. This mechanism could also be explained by conductance change with the reaction time to be shown in Figure 2.

It is known that in non-aqueous solution of partially dissociated salts, the producing free ions are in equilibrium with nonconducting ion-pairs e.g. $A^+B^- = A^+$

+ B-. The relation between the conductance and concentration of dilute ionogens solutions is given by the mass law. The electric neutrality of ion-pairs prevents them from conducting electric current. Hence, the changes of conductance value would reflect the changes of concentration of free ions. Figure 2 could be divided into three regions: I, when (-)Sp*$^+$(+)CSA*$^-$ was added to the VCZ solution the free ions dissociated by the organic salt would make the conductivity increase quickly. II, during the formation of the charge transfer complexes the conductance values would keep from change. III, the conductance values would increase gradually with the time in which the free ions are produced by dissociation of the eliminated ion-pairs. The polymerization of VCZ would be mainly performed by the charge transfer complexes obtained from the ion-pairs and the monomer.The asymmetrically stereoselective induction of the catalyst, (-)Sp*$^+$(+)CSA*$^-$, during the polymerization of VCZ in the previous paper [10a] was also explained by the mechanism. Therefore, in this case, the PVCZs with high isotacticity and optical activity were obtained.

CONCLUSION

The better yield and specific rotation of the PVCZ could be obtained by using suitable monomer concentrations and catalyst ratios in the presence of (-)Sp*$^+$(+)-CSA*$^-$. The ion-pairs in the dissociation equilibrium would play an important role in the characterization of the polymerization mechanism through charge transfer complexes. It was in agreement with the stereoselectivity induced power with short-distance effect [10a].

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