

POLYMERIZATION MECHANISM OF N-VINYLCARBAZOLE WITH CHIRALLY ORGANIC SALT AS CATALYST*

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Abstract The polymerization mechanism is described by the conductance change with the time during the polymerization. The mechanism can be explained by the equilibrium feature (i.e. main ion-pairs) between the free ions and the ion-pairs dissociated by the organic salt $(-)\text{Sp}^{*+} (+)\text{CSA}^{*-}$ (An asterisk represents the chirality) and the scheme of the polymerization process is described mainly by the charge transfer complexes having chiral induction power.

Keywords Poly(N-vinylcarbazole); Ion-pairs; Chiral catalyst; Optical activity

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 catalyst^[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 performed in the presence of chiral $(+)\text{-camphor-10-sulfonic acid (CSA}^*)$ and optically active PVCZ was obtained^[9a,b]. In our previous paper stereo-selective induction polymerization of VCZ in the presence of 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 $(-)\text{Sp}^{*+} (+)\text{CSA}^{*-}$ $[(-)\text{sparteine-d-(+)camphor-10-}$

* Financial Support by the National Science Foundation of China, Grant No.: 29774039

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Received November 2, 1996

sulfonate] as catalyst have been investigated and the polymerization mechanism is explained by the conductance change with the time.

EXPERIMENTAL

Measurement

Optical rotation measurement was performed at 25°C on a Perkin Elmer model 141 spectropolarimeter with a sensitivity of $\pm 0.003^\circ$. The molecular weights of PVCZ were determined by viscosity method (solvent: THF, concentration: 0.5 g/dl, $T = 25 \pm 0.1^\circ\text{C}$) according to Situramaiah^[11]. 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 at 40°C on a DDB-11A conductometer.

Solvent treatment and polymerization

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 yields of polymer decrease with increasing of monomer concentration, but the specific rotations of the polymer increase. The results also showed that the yields increase with the molar ratios between monomer and catalyst and the specific rotations have an optimal value ($[\alpha]_D^{25}$: $10.8 \sim 15.1^\circ$) in the molar ratio of 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 fraction of free ions was very low and the ion-pairs were main parts for $(-)\text{Sp}^{*+}(+)\text{CSA}^{*-}$ in the solution^[10a]. In addition, N-vinylcarbazole is subjected to mesomeric polarization and partial transfer of a lone pair electron from the nitrogen to $=\text{CH}_2$ 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 have low yield. According to the same reason, the fraction of free ions dissociated by the ion-pairs would be decreased with increasing of the concentration of the $(-)\text{Sp}^{*+}(+)\text{CSA}^{*-}$. In these cases the ion-pairs having lower reactivity would

play the main role during initiating polymerization of VCZ and the stereoselective induction power is more than that of the corresponding free ions^[10a]. Hence, the yields of the polymer obtained by the ion-pairs are lower, but their specific rotations were generally higher. This is caused by the short-distance induction of the ion-pairs during the polymerization^[10a].

Influence of solvent polarity

The nature of the reaction media plays the most significant role in cationic polymerization. The influence of the polarity of solvent on the polymerization of VCZ are listed in Table 1.

Table 1 The influence of the solvent on the polymerization of VCZ in the presence of $(-)\text{Sp}^{*+} (+)\text{CSA}^{*-}$ as catalyst at 40°C in 48 h

Solvent ^{a)}	Dielectric constant (ϵ) ^{b)}	Yield (%)	$[\alpha]_D^{25\text{ c)}$
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 ($\epsilon = 7.58$), DCM: Dichloromethane ($\epsilon = 9.08$), DCE: Dichloroethane ($\epsilon = 10.60$).

b) Approximate value calculated from the expression $\epsilon (\text{mixture}) = (\text{vol}_1\% \epsilon_1 + \text{vol}_2\% \epsilon_2)$.

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

These results show that the polymerization of VCZ solution could be carried out only when the dielectric constants of the solvent was in the range of $\epsilon = 7.0 \sim 9.0$. Here, dielectric constant is generally used as an indication of the solvating power of a solvent and it is not necessarily a quantitative measure. It was reported^[12] that in polar solvent the proportion of free ions produced by the solvation of the ion-pairs was high. The free ions with the most reactive initiating species could initiate polymerization by direct attack on electrophilic monomers 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 $(-)\text{Sp}^{*+} (+)\text{CSA}^{*-}$ were roughly increased and decreased, respectively. These results were in agreement with that of the PVCZs obtained by $\text{CSA}^{*[9a]}$. But in the solvents with more higher dielectric constant, surrounding the cation with solvation shells the reactivity of the free ions is reduced because at least one solvent molecule of the solvent has to be removed from their solvation shell in order to allow the ions to contact with monomer. The polymerization of VCZ can not be performed in the case of $\epsilon > 9$. These findings demonstrate again the importance of solvation power in the polymerization process leading to the formation ability 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 of the power (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 $\text{A}^+ + \text{H}_2\text{C}=\text{CHR} \rightarrow \text{ACH}_2-\text{CHR}^+$ i.e. carbocationic polymerization of olefins is indicated by the involvement of direct addition of cation to olefin^[13]. More definite evidence for direct addition was provided by the trapping (by methanolysis) of the initial adduct between cycloheptatrinyl cation and VCZ^[14a], and by the triphenyl methyl cation addition in the polymerization of isobutyl vinyl ether^[14b].

It should be noted, however, that despite the very high reactivity of VCZ, it does not react efficiently with triphenyl methyl salts possibly because of steric hindrance 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. carbazole) by primary electron transfers. The polymerization of VCZ in the presence of $(-)\text{Sp}^{*+} (+)\text{CSA}^{*-}$ as catalyst could be carried out in fact through electrostatic interaction way. Such propagation cannot be expected to continue giving rise to polymers of high molecular weight. The termination might occur through several possible ways, such as termination between two growing chains by hydrogen transfer or termination by impurities such as adventitious water. However, the growing chain may be terminated by proton transfer with the formation of vinyl end groups. The IR spectra of the obtained PVCZ revealed an absorption at ca. 900cm^{-1} ($11.11\ \mu$) characteristic of the above group. The PVCZ having end double bond could possess further reaction ability to increase its viscosity. Biswas et al.^[15] and Kennedy et al.^[16] found that

the PVCZ with vinyl end group possessed an absorption at ca. 11.20μ and 11.25μ , respectively. The initiation is thus regarded as involving a number of steps as shown in Fig. 1.

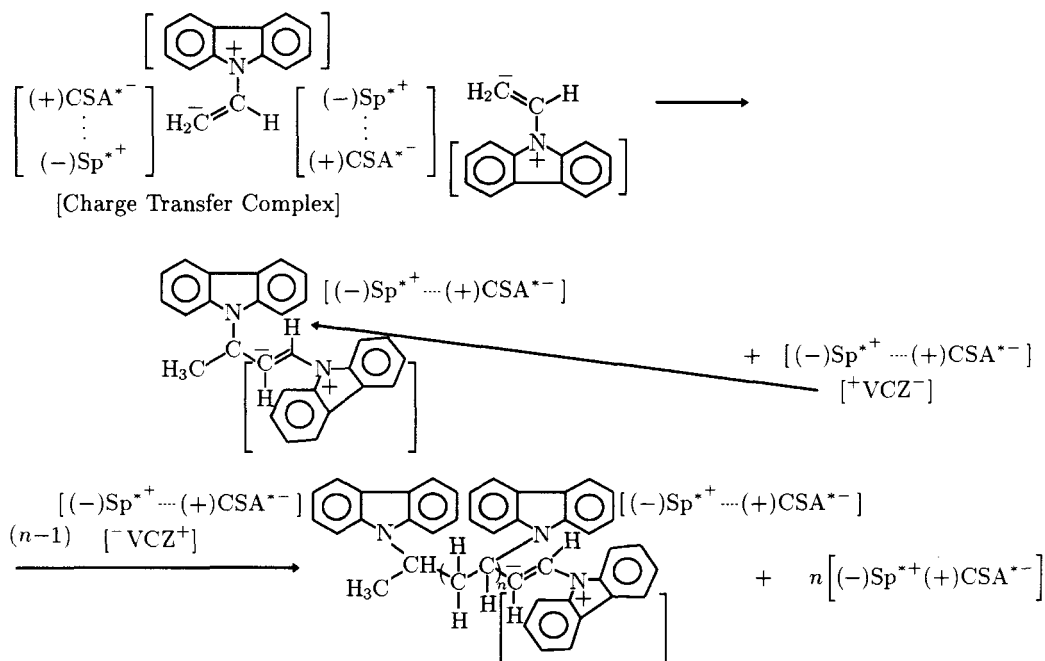


Fig. 1 Polymerization of VCZ in the presence of $(-)\text{Sp}^{*+} (+)\text{CSA}^{*-}$ (All charges shown are partial charges)

The interaction between the polarizing VCZ, $=\text{N}^+-\text{CH}=\text{CH}_2^-$, and $(-)\text{Sp}^{*+} (+)\text{CSA}^{*-}$ is insufficient to yield readily recognized complexes checked up by U.V. spectra. In Fig.1 it is indicated also 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 too. It was shown that with the loss of one double bond in the initiation step, one of the two acceptor molecules, $[(-)\text{Sp}^{*+} (+)\text{CSA}^{*-}]$, involved in the initiation step was eliminated. The existence of double bond placed at the end of PVCZ would be caused by the depolarization of $=\text{N}^+-\text{CH}=\text{CH}^-$ group after termination using CH_3OH . Hence, the growing end of the polymer chain is regarded as carrying the terminal double bond. The PVCZ obtained was not contaminated with a catalyst, $(-)\text{Sp}^{*+} (+)\text{CSA}^{*-}$, residue according to ^1H NMR, IR spectral analyses and elemental analysis. Therefore, the polymerization mechanism suggested in Fig.1 is quite reasonable. This mechanism could also be explained by

conductance change with the reaction time as shown in Fig. 2.

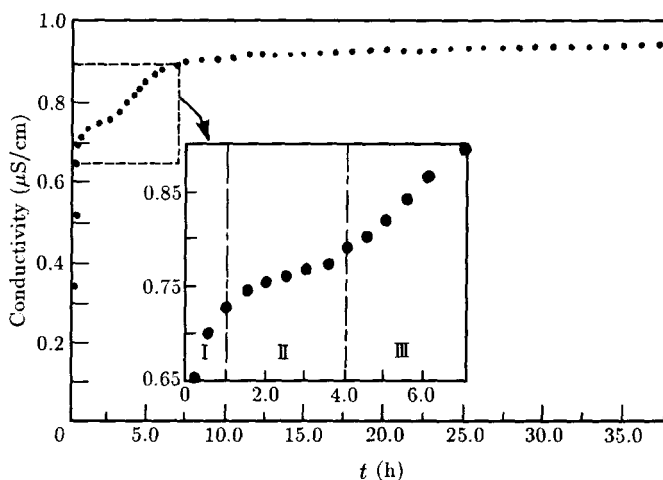


Fig. 2 The relationship between conductivities and the time during polymerization of VCZ in the presence of $(-)\text{Sp}^{*+}(+)\text{CSA}^{*-}$ at 40°C in THF

It is known that in non-aqueous solution of partially dissociated salts, the free ions produced are in equilibrium with nonconducting ion-pairs e.g. $\text{A}^+\text{B}^- = \text{A}^+ + \text{B}^-$. 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. Fig. 2 could be divided into three regions: I, when $(-)\text{Sp}^{*+}(+)\text{CSA}^{*-}$ was added to the VCZ solution the free ions dissociated from the organic salt would increase the conductivity quickly. II, during the formation of the complexes produced with electrostatic interaction the conductance values would keep from change or have little increase. 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 electrostatic interaction obtained from the ion-pairs and the monomer. The asymmetrically stereoselective induction of the catalyst, $(-)\text{Sp}^{*+}(+)\text{CSA}^{*-}$, during the polymerization of VCZ in previous paper^[10a] was also explained through the mechanism. Therefore, in this case, the PVCZs with high isotacticity and optical activity were obtained naturally.

REFERENCES

- [1] Ellinger, L.P., *J. Appl. Polym. Sci.*, **1965**, 9, 3939
- [2] Tazuke, S., *Chem. Commun.*, **1970**, 1277

- [3] Bilbao, E., Rodriguez, M., Leon, L.M., *Polym. Bull.*, **1984**, *12*, 359
- [4] Tsubokawa, N., Inagaki, M., Kubota, H., Endo, T., *J. Polym. Sci., Polym. Chem.*, **1993**, *31*, 3193
- [5] Soloman, O.F., Dimmonie, D., Ambroz, K., Tomesku, M., *J. Polym. Sci.*, **1961**, *52*, 205
- [6] Shirota, Y., Mikawa, H., *J. Macromol. Sci-Rev. Macromol. Chem.*, **1977~1988**, *C 16(2)*, 129
- [7] Phillips, D.C., Davies, D.H., Smith, J.D.B., *Makromol. Chem.*, **1973**, *169*, 177
- [8] Ayscough, P.B., Roy, A.K., Croce, R.G., Munari, S., *J. Polym. Sci., Polym. Chem., Part A*, **1968**, *6*, 1307
- [9] a) Nozaki, K., Asakura, J., Yoshihara, M., Maeshima, T., *J. Macromol. Sci. Chem.*, **1984**, *A21*, (11 & 12), 1405
b) Asakura, J., Yoshihara, M., Maeshima, T., *Makromol. Chem. Rapid Commun.*, **1983**, *4*, 103
- [10] a) Chen, C.F., Su, Q., Liu, W.H., Chen, Y.M., Xi, F., *J. Macromol. Sci-Pure & Appl. Chem.*, **1996**, *A33* (8), 1017
b) Chen, C.F., Su, Q., Liu, W.H., Chen, Y.M., Xi, F., *J. Macromol. Sci-Pure & Appl. Chem.*, **1997**, *A34* (4), 655
- [11] Situramaiah, G., Jacobs, D., *Polymer*, **1970**, *11*, 165
- [12] Kennedy, J.P., "Cationic Polymerization of Olefins, a Critical Inventory", Wiley, New York, **1975**, p.279
- [13] Ledwith, A., *Makromol. Chem.*, **1974**, *175*, 1117
- [14] a) Bowyer, P.M., Ledwith, A., Sherrington, D.C., *Polymer*, **1971**, *12*, 509
b) Kunitake, T., Matsuguma, Y., Aso, C., *Polymer J. (Tokyo)*, **1971**, *2*, 345
- [15] Biswas, M., Maity, M.M., Ganguly, N.G., *Makromol. Chem.*, **1969**, *124*, 263
- [16] Kennedy, J.P., Minckler, Jr. L.S., Wanless, G.G., *J. Polym. Sci., Part A*, **1964**, *2*, 1441