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POLYMERIZATION OF *N*-VINYLCARBAZOLE IN THE PRESENCE OF ORGANIC SALTS WITH CHIRAL OR STEREODIFFERENTIATING LIGANDS

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ABSTRACT

Organic salts as initiators [$\mathrm{A^{*+}B^-}$: $\mathrm{Ph_3^*C^+ClO_4^-}$, $\mathrm{Ph_3^*C^+SbCl_6^-}$, $\mathrm{(-)Sp^{*+}ClO_4^-}$, and $(-)(Sp)^{*3+}_{2}(\mathrm{ClO_4})_3^-$] and catalysts [$\mathrm{A^+B^{*-}}$: (+)CSA*; $\mathrm{A^{*+}B^{*-}}$: $\mathrm{ph_3^*C^+(+)CSA^{*-}}$ and $\mathrm{(-)Sp^{*+}(+)CSA^{*-}}$] are prepared and characterized by the dissociation constant (K_d), fraction of free ions (α), and specific rotation. The asymmetrically stereoselective induction of the initiators and catalysts in the polymerization of *N*-vinylcarbazole is in the order $\mathrm{A^{*+}B^{*-} > A^+B^{*-} > A^{*+}B^-}$. The specific rotations of the poly(*N*-vinylcarbazole) (PVCZ)s obtained are generally in this order.

INTRODUCTION

Carbazole is a rather typical heteroaromatic molecule with established polarizability and electron donor properties. The combination of the electron donor properties of carbazole and the incorporation of carbazole into a polymer matrix offer special advantages for the design of charge generation and the transport layer required for electrophotography [1]. Several methods have been developed for the polymerization of *N*-vinylcarbazole (VCZ), e.g., free radical [2, 3], conventional cation (such as protonic acids, Lewis acid, carbocations) [4–6], Ziegler-Natta [7], *charge transfer* [8], electrochemical [9], solid state [10], etc. Some reports on model compounds have suggested that the low energy excimer arises mainly from isotactic sequences which are very important for the organic electroluminescent contained in the PVCZ layer [11]. Some optically active polymers containing carbazole groups have been synthesized in order to increase the content of isotactic sequences of PVCZ. Generally, four methods have been employed to obtain the polymers: 1) optically active vinyl monomers with an asymmetric carbon atom and containing carbazole moieties have been polymerized by common initiators [12], 2) the polymerization of carbazole-substituted *N*-carboxyanhydrides of optically active (L)-amino acids yields polyamino acids having pendant carbazole chromphores [13], 3) the copolymerization of prochiral VCZ with a readily available chiral monomer such as (–)-menthyl vinyl ether [14] and (–)-menthyl methacrylate [15], 4) cationic polymerization in the presence of D-(+)-camphor-10-sulfonic acid [(+)CSA*] as a catalyst having optical activity [16, 17].

For the present paper the asymmetrically stereoselective induction of organic salts with chiral or stereodifferentiating ligands as initiator or catalyst has been studied in the polymerization of VCZ, and optically active PVCZ has been obtained.

EXPERIMENTAL

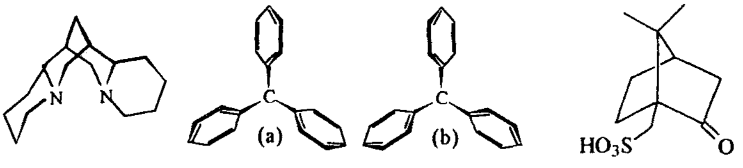
Measurements

Optical rotation measurements were performed at 25°C on a Perkin-Elmer model 141 spectropolarmeter with a sensitivity of ±0.003°. The equivalent conductivity of an organic salt solution having the cationic feature is determined by using a series of equivalent concentrations of organic salts (dilution method) at 25°C on a DDS-11A conductometer. The dissociation constants, K_d, and the fraction of free ions, α, can be calculated by the Fuoss equation [18]. The molecular weight of PVCZ is calculated by the viscosity method (solvent, THF; concentration, 0.5 g/dL at 25 ± 0.1°C) according to Sitaramaiah [19].

Monomer and Synthesis of the Organic Salts

N-Vinylcarbazole(Fluka AG) was purified by recrystallization from *n*-hexane, mp 65°C. (–)-Sparteine monoperchlorate [$(-)\mathrm{Sp}^{*\,+}\mathrm{ClO}_4^-$] and disparteine triperchlorate [$(-)(\mathrm{Sp})^{*\,3+}_{2}(\mathrm{ClO}_4)^-_3$] were synthesized from (–)-sparteine (Aldrich Chemical Co) and perchloric acid according to Krueger [20]. Triphenylmethyl hexachloroantimorate [$\mathrm{Ph}^*_3\mathrm{C}^+\mathrm{SbCl}_6^-$] and triphenylmethyl perchlorate [$\mathrm{Ph}^*_3\mathrm{C}^+\mathrm{ClO}_4^-$] were obtained from triphenylmethane chloride (Aldrich Chemical Co), triphenylmethanol, and perchloric acid according to Sharp [21] and Hofman [22], respectively. The chiral or stereodifferentiating ligands of these organic salts are shown in Scheme 1.

Triphenylmethyl(+)-camphor-10-sulfonate [$\mathrm{Ph}^*_3\mathrm{C}^+(+)\mathrm{CSA}^{*\,-}$] was prepared from triphenylmethanol and D-(+)-camphor-10-sulfonic acid [(+)CSA*] (Tokyo Kase Co.) in the presence of acetic anhydride and acetic acid. $(-)\mathrm{Sp}^{*\,+}(+)$-$\mathrm{CSA}^{*\,-}$ was obtained from (–)Sp and (+)CSA according to Leonard [23].



(-)-Sparteine [(-) Sp*]
Left-handed (a) Right-handed (b) [Ph$_3$*C]
D-(+)-Camphor-10-sulfonic acid, [(+) CSA*]

SCHEME 1. The structures of chiral or stereodifferentiating ligands.

Polymerization

The polymerization of VCZ is carried out in a glass ampule under a dry nitrogen atmosphere. The VCZ are placed in a glass ampule which is then evacuated on a vacuum line and flushed with dry nitrogen. After this procedure is repeated three times, DCE (1,2-dichloroethane) or THF is added with a hypodermic syringe in the described amount to dissolve the solid monomers. The monomer solution is placed in a thermostated oil-bath. The prescribed amount of an organic salt as initiator or a catalyst solution aged for a definite time under nitrogen is added to the ampules by syringe. After a certain time the reaction is terminated by the addition of a small amount of methanol. The product is poured into a large amount of methanol, precipitated, and then collected by centrifugation. The polymer is dried under vacuum at 50°C for 24 hours.

RESULTS AND DISCUSSION

Characterization of the Organic Salts as Initiator or Catalyst

Characterization results of the organic salts with chiral or stereodifferentiating moieties are shown in Table 1. (An asterisk represents the chiral or stereodifferentiating ligand.)

TABLE 1. Characterization of the Organic Salts with Chiral or Stereodifferentiating Ligands

Organic salts	$[\alpha]_D^{25}$	$K_d \times 10^4 M^{-1}$[a]	α[b]
$Ph_3^*C^+ClO_4^-$	0°	–	–
$Ph_3^*C^+SbCl_6^-$	0°	2.6	0.87
$(-)Sp^{*+}ClO_4^-$	−13.2°	1.1	0.37
$(-)(Sp)_2^{*3+}(ClO_4)_3^-$	−17.1°	0.9	0.35
(+)CSA*	+20.1°	–	–
$Ph_3^{*+}(+)CSA^{*-}$	+45.5°	–	–
$(-)Sp^{*+}(+)$-CSA^{*-}	+23.4°	1.0	0.27

[a] K_d = Dissociation constant in 1,2-dichloroethane.
[b] α = Fraction of free ions.

It is generally accepted that an equilibrium exists between the free ions and the ion-pairs species in a nonaqueous solvent and that the latter is less reactive (Scheme 2). Therefore, the following approximating method is utilized. The general expression adopted to relate the dissociation constant by free ions (K_d^+) and ion-pairs ($K_d^{\pm}$) with the experimentally observed dissociation constant (K_d) is

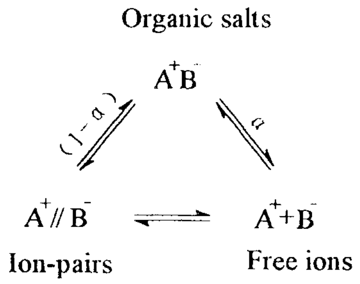
$$K_d = K_d^+\alpha + K_d^{\pm}(1 - \alpha)$$

where α is the fraction of free ions. The ion-pair dissociation equilibria for triphenylmethyl (Ph_3C^+) salts have been widely studied in CH_2Cl_2 [24] and give $K_d = 2.1 \times 10^{-4}$ M at 25°C for $Ph_3C^+AsF_6^-$ [26], which is closed to our result of 2.6×10^{-4} M at 25°C for $Ph_3^*C^+SbCl_6^-$. The fraction of free ions of $Ph_3^*C^+SbCl_6^-$, $\alpha = 0.86$, is larger than that of $(-)Sp^{*+}ClO_4^-$ (0.37), $(-)(Sp)_2^{*3+}(ClO_4)_3^-$ (0.35), and $(-)Sp^{*+}(+)CSA^{*-}$ (0.27). Therefore, by comparison, it is believed that the propagating species can exist predominantly as free ions for $Ph_3^*C^+SbCl_6^-$ and as ion-pairs for other organic salts. Ion-pairs, which are generally without specific solvation effects, are less reactive than free ions. The greater capability of free ions to polarize monomer molecules, such as *N*-vinylcarbazole, is due to their greater effective charge density.

Initiation and Catalysis Process

The polymerization results of VCZ with the organic salts mentioned above with chiral or stereodifferentiating ligands are displayed in Table 2.

Poly(triphenylmethyl methacrylate) (PTrMA) [26] and polychloral [27] with a bulky side group, triphenylmethyl and trichloral, respectively, as obtained from atropogenic polymerization only by chirally ionic complex initiators, were one-handed helical polymers having optical activity. PVCZs obtained by using free radical, AIBN, and protonic acid ($H^+ClO_4^-$, etc.) as initiators are optically inactive but have a helical chain comformation [28]. Organic salts with chiral or stereodifferentiating ligands as initiators or catalysts have shown an asymmetrically stereoselective induction during the atropogenic polymerization of VCZ, leading to the formation of optically active PVCZ. The triphenylmethyl group has left (a) and right-handed (b) isomers with a three propeller blade structure, and both of them have structural asymmetry [29] (Scheme 1). The organic salts $Ph_3^*C^+ClO_4^-$ and



SCHEME 2. The dissociation equilibrium of organic salts in nonaqueous solvent. α: The fraction of free ions.

TABLE 2. Polymerization of *N*-Vinylcarbazole in the Presence of Organic Salts as Initiators (I*) or Catalysts (C*)

I* or C*		Polymerization conditions				Polymeric products		
Type	Name	M.R.[a]	Solvent[b]	Temp, °C	Time, h	Yield, %	$M_v \times 10^{-5}$	$[\alpha]_D^{25}$
Radical	AIBN	100	TOL	80	–	94.9	–	0°
Protonic	$H^+ClO_4^-$	50	THF	25	–	90.0	–	0°
$A^{*+}B^-$	$Ph_3^*C^+ClO_4^-$	50	DCE	25	0.5	100.0	2.56	+2.2°
	$Ph_3^*C^+SbCl_6^-$	50	DCE	25	0.3	95.9	5.60	−2.6°
	$(-)Sp^{*+}ClO_4^-$	50	DCE	40	43.0	77.7	0.93	+2.4°
	$(-)Sp_2^{*3+}(ClO_4)^-$	50	DCE	40	45.5	95.9	1.30	+0.9°
A^+B^{*-}	(+)CSA*	10	THF	40	43.0	41.8	0.16	+4.2°
$A^{*+}B^{*-}$	$Ph_3^*C(+)CSA^*$	50	DCE	25	28.0	64.8	0.17	+4.4°
	$(-)Sp^{*+}(-)CSA^{*-}$	25	THF	40	118.5	7.8	0.12	+8.3°

[a] M.R. = [M]/[I*] or [C*]; [M], [I*], and [C*] represent the molar concentrations of *N*-vinylcarbazole, initiator, and catalyst, respectively.

[b] Amount of solvent, 40 mL/g monomer; DCE = 1,2-dichloroethane; TOL = toluene.

$Ph_3^*C^+SbCl_6^-$ possess optical inactivity but appear to have large stereodifferentiating [30]. 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 salts (left or right) prefers to initiate the monomers, and optically active PVCZ is formed. This is called the stereodifferentiating effect of a conformational enantiomer [31]. According to above-mentioned feature of the organic salts, it is suggested that $Ph_3^*C^+ClO_4^-$, $Ph_3^*C^+SbCl_6^-$, $(-)Sp^{*+}ClO_4^-$, and $(-)(Sp)_2^{*3+}(ClO_4)_3^-$ be abbreviated by using $A^{*+}B^-$ and initiator (I*), and that (+)CSA*, $Ph_3^*C^+(+)CSA^{*-}$, and $(-Sp^{*+}(+)CSA^{*-}$ be abbreviated by using A^+B^{*-}, $A^{*+}B^{*-}$, and catalyst (C*), respectively. The asymmetrically stereoselec-

$$I^* \xrightarrow{M_1} I^*\text{---}M_1^* \xrightarrow{M_2} I^*\text{---}M_1^*M_2^* \xrightarrow{\qquad} \text{---} \xrightarrow{Mn} I^*\text{---}M_1^*M_2^*\text{---}Mn^* \qquad (\lambda^n)$$

$$C^* \xrightarrow{M_1} C^*\text{---}M_1^* \xrightarrow{M_2} C^*\text{---}M_2^*M_1^* \xrightarrow{\qquad} \text{---} \xrightarrow{Mn} C^*\text{---}Mn^*\text{---}M_2^*M_1^*$$

SCHEME 3. The induced power of initiator (I*) or catalyst (C*) in the polymerization.

tive induction of the initiators or the catalysts with chiral or stereodifferentiating ligands makes a considerable difference during polymerization of the VCZ substituted bulky side group as shown in Scheme 3, where M = monomer and λ = induced power factor ($\lambda < 1$) [31]. The induced power decreases with the propagation of the polymer chain by the index number (λ^n) for initiators (long-distance effect) and increases by the addition of the induced power of every monomer entering into the growing chain for the catalysts (short-distance effect). The $A^{*+}B^{*-}$ among the catalysts, especially $(-)Sp^{*+}(+)CSA^{*-}$ and $Ph_3^*C^+(+)$-CSA^{*-}, provide both initiation and catalysis induction during the polymerization process. Therefore, the induced powers are in the order $A^{*+}B^{*-} > A^+B^{*-} > A^{*+}B^-$. The specific rotations obtained for PVCZs generally correspond with this order.

CONCLUSIONS

The polymerization of *N*-vinylcarbazole by organic salts with chiral or stereodifferentiating ligands as initiators or catalysts is characteristically distinct from its polymerization by conventional cationic initiators. The stereoselectivity induced powers of the organic salts are in the order $A^{*+}B^{*-} > A^+B^{*-} > A^{*+}B^-$, which generally corresponds with the specific rotations obtained for poly(*N*-vinylcarbazole)s.

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