

SYNTHESIS OF OPTICALLY ACTIVE POLY(N-VINYLCARBAZOLE)S

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ABSTRACT

The organic salts as initiators [$A^{*+}B^{-} \cdot Ph_3C^{+}ClO_4^{-}$, $Ph_3C^{+}SbCl_6^{-}$, $(-)\text{Sp}^{*+}ClO_4^{-}$ and $(-)(\text{Sp})_2^{*+3}(ClO_4^{-})_3$] and catalysts [$A^{+}B^{*-} \cdot (+)\text{CSA}^{*}$, $A^{*+}B^{*-} \cdot Ph_3C^{+}(+)\text{CSA}^{*-}$ and $(-)\text{Sp}^{*+}(+)\text{CSA}^{*}$] are prepared and characterized by specific rotation. The asymmetrically stereoselective induction of the initiators and catalysts in the polymerization of N-vinylcarbazole is in an order of $A^{*+}B^{*-} > A^{+}B^{*-} > A^{*+}B^{-}$. The specific rotations of obtained poly(N-vinylcarbazole) (PVCZ) generally are in accordance with mentioned order.

INTRODUCTION

Some reports on model compounds of poly(N-vinylcarbazole) suggested that the low energy excimer arises mainly from its isotactic sequences which is very important for organic electro-luminescent contained PVCZ layer^[1]. Over a period of one decade some optically active polymers containing carbazole group were synthesized in order to increase the content of the isotactic sequences of PVCZ. Generally there are four ways for the preparation of polymers: 1) optically active vinyl monomers with asymmetric carbon atom containing carbazole moieties have been polymerized by common initiators^[2], 2) the polymerization of carbazole-substituted N-carboxyanhydrides of optically active (L)-aminoacids yields polyamino-acids having pendant carbazole chromophores^[3], 3) the most convenient method used to synthesize optically active polymers containing carbazole group implies the copolymerization of prochiral VCZ with readily available chiral monomer such as $(-)$ -menthyl vinyl ether^[4] and $(-)$ -menthyl methacrylate^[5], 4) optically active PVCZ is obtained by cationic polymerization in the presence of D-(+)-camphor-10-sulfonic acid[(+) CSA] as catalyst having optical activity^[6,7]. In the present paper the asymmetrically stereoselective induction of the organic salts with chiral or stereo-differentiating ligands as initiator or catalyst were studied in the polymerization of VCZ and the optically active PVCZ were obtained.

EXPERIMENTAL

Organic salts

The organic salts were used either as initiators or as catalysts:

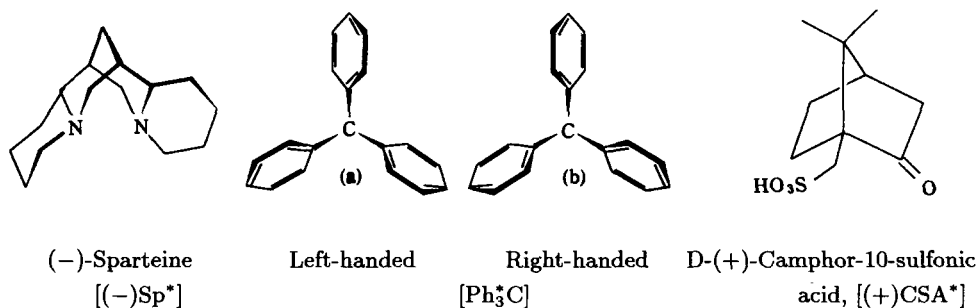
Initiators: $A^{+}B^{-}$: Triphenylmethyl perchlorate $[Ph_3C^{+}ClO_4^{-}]$, Triphenylmethyl hexachloroantimoniate $[Ph_3C^{+}SbCl_6^{-}]$, $(-)$ -Sparteine monoperchlorate $[(-)Sp^{*+}ClO_4^{-}]$, $[\alpha]_D^{25} - 13.2^{\circ}$, and Disparteine triperchlorate $[(-)(Sp)_2^{*+3}(ClO_4^{-})_3]$, $[\alpha]_D^{25} - 17.1^{\circ}$.

Catalysts: $A^{+}B^{-}$: $(+)$ -Camphor-10-sulfonic acid $[(+)(CSA)^{-}]$, $[\alpha]_D^{25} + 20.1^{\circ}$

$A^{*+}B^{*-}$: Triphenylmethyl $(+)$ -camphor-10-sulfonate $[Ph_3C^{+}(+)CSA^{*-}]$, $[\alpha]_D^{25} + 45.5^{\circ}$

$(-)$ -Sparteine $(+)$ -camphor-10-sulfonate $[(-)Sp^{*+}(+)CSA^{*-}]$, $[\alpha]_D^{25} + 23.4^{\circ}$

The chiral or stereo-differentiating ligands of these organic salts are shown in the Scheme 1.



Scheme 1 The structures of chiral or stereo-differentiating ligands

Polymerization

The polymerization of VCZ is carried out in a glass ampule under dry nitrogen atmosphere. The VCZ are placed in glass ampule which is 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 through a hypodermic syringe in described amount to dissolve the solid monomer. The ampule then is placed in a thermostated oil-bath. The prescribed amount of the organic salt as initiator or catalyst solution aged for a definite time under nitrogen is added into the ampules by a syringe. After a certain interval the reaction is terminated by the addition of a small amount of methanol. Then the product is poured into a large amount of methanol, precipitated and collected by centrifugalization. The polymer is dried under vacuum at $50^{\circ}C$ for 24h.

RESULTS AND DISCUSSION

Initiation and catalysis process

The organic salts with chiral or stereo-differentiating ligands as initiator or catalyst have shown an asymmetrically stereoselective induction during the atrotogenic polymerization of VCZ to lead the formation of optically active PVCZ. Triphenylmethyl group has left(a) and right(b)-handed isomers with propeller structure of three propeller blades and both of them has structural asymmetry^[8] (Scheme 1). The organic salts, $\text{Ph}_3\text{C}^+\text{ClO}_4^-$ and $\text{Ph}_3\text{C}^+\text{SbCl}_6^-$ themselves possess optical inactivity but appear obviously stereo-differentiating^[9]. Due to steric hinderance the bulk carbazole group during polymerization of VCZ gives rise to an asymmetrically stereoselective induction, i.e. only one isomer of triphenylmethyl salts (left or right) prefers to initiate the monomer and the optically active PVCZ is formed. This is called as stereo-differentiating effect of conformational enantiomer^[10].

The polymerization results of VCZ by the mentioned organic salts with chiral or stereo-differentiating ligands are displayed in Table 1.

Table 1 Polymerization of N-vinylcarbazole in the presence of organic salts as initiators (I^*) or catalysts (C^*)

Type	I^* or C^* Compounds	Polymerization conditions				Polymeric products		
		$M.R.$ ^{a)}	Solvent ^{b)}	Temp. (°C)	Time (h)	Yield (%)	$\overline{M}_v$ $\times 10^{-5}$	$[\alpha]_D^{25c)}$
Radical	AIBN	100	TOL	80	—	94.9	—	0°
Protonic	H^+ClO_4^-	50	THF	25	—	90.0	—	0°
A^{++}B^-	$\text{Ph}_3\text{C}^+\text{ClO}_4^-$	50	DCE	25	0.5	100.0	2.56	+2.2°
	$\text{Ph}_3\text{C}^+\text{SbCl}_6^-$	50	DCE	25	0.3	95.9	5.60	-2.6°
	$(-)\text{Sp}^{++}\text{ClO}_4^-$	50	DCE	40	43.0	77.7	0.93	+2.4°
	$(-)(\text{Sp})_2^{++3}(\text{ClO}_4^-)_3$	50	DCE	40	45.5	95.9	1.30	+0.9°
	$(+)\text{CSA}^*$	10	THF	40	43.0	41.8	0.16	+4.2°
$\text{A}^{++}\text{B}^{*-}$	$\text{Ph}_3\text{C}(+)\text{CSA}^*$	50	DCE	25	28.0	64.8	0.17	+4.4°
	$(-)\text{Sp}^{++}(-)\text{CSA}^{*-}$	25	THF	40	118.5	7.8	0.12	+8.3°

^{a)} $M.R. = [\text{M}]/[\text{I}^*]$ or $[\text{C}^*]$; $[\text{M}]$, $[\text{I}^*]$ and $[\text{C}^*]$ represent the molar concentration of N-vinylcarbazole, initiator and catalyst, respectively.

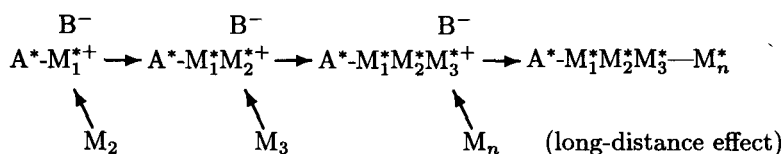
^{b)} Amount of solvent, 20ml/g monomer; DCE: 1,2-Dichloroethane, TOL: Toluene.

^{c)} Specific rotation unit: $\text{deg}\cdot\text{cm}^2/\text{g}$, $[\text{c}: 0.5, \text{THF at } 25^\circ\text{C}]$.

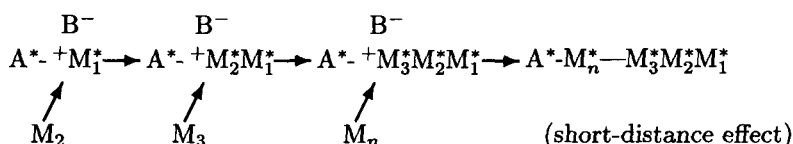
Induced power

The asymmetrically stereoselective induction of the initiator or catalyst with chiral or stereo-differentiating ligands has considerable difference during the polymerization of VCZ substituted bulk side group as shown in Scheme 2.

Initiator:



Catalyst:



Scheme 2 The induced power of initiator (I^*) or catalyst (C^*) during the polymerization of VCZ

It should be noted that the differentiating effects of optically active initiators are different from those of optically active catalysts in that the differentiating effect of the initiator decreases as the reactive end of the polymer chain becomes more distant from it (due to the addition of further monomer unit), whereas that of a catalyst is constant at each step of monomer addition. In the former case, if the initial differentiating ability is λ ($\lambda < 1$) then when the degree of polymerization is n , the apparent differentiating ability at that step will be λ^n [10]. All induced power could decrease with the propagation of the polymer chain by index number for initiator and could be smaller than it for catalyst. The $A^{*+}B^{*+}$ among the catalysts, especially $(-)\text{Sp}^{*+}(+)\text{CSA}^{*-}$, has not only initiation but also catalysis induction during the polymerization process. Therefore, a conclusion could be drawn that all induced powers are in an order of $A^{*+}B^{*-} > A^+B^{*-} > A^{*+}B^-$. The specific rotations of the obtained PVCZs generally are in agreement with the mentioned order.

Keywords:

N-vinylcarbazole; Optical activity; Stereo-differentiating; Chiral

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