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CHARACTERIZATION OF POLY(*N*-VINYLCARBAZOLE) OBTAINED VIA ASYMMETRICAL POLYMERIZATION

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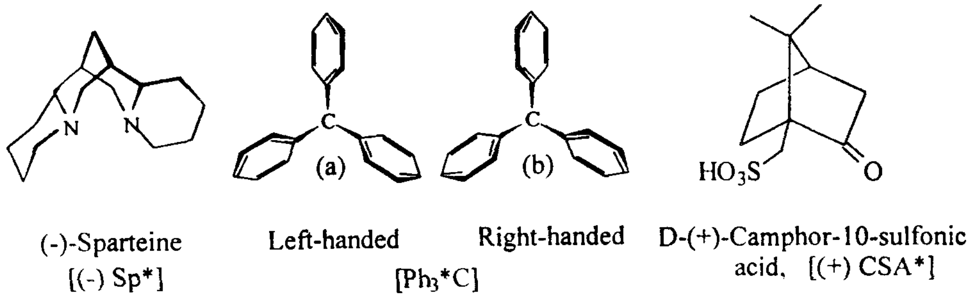
ABSTRACT

The characterizations of poly(*N*-vinylcarbazole) (PVCZ) obtained via asymmetrical polymerization have been studied by using ^{1}H-NMR spectrum, UV spectrum, DSC, and GPC analysis. The tacticities, i.e., the isotactic diad mole fractions, were found to increase when using the initiator AIBN to the catalyst $(-)\mathrm{Sp}^{*+}(+)\mathrm{CSA}^{*-}$, and the extinction coefficients to decrease. Bimodal molecular weight distribution (MWD)s were caused by two propagating species of the free ions and the ion-pairs during the polymerization process.

INTRODUCTION

Asymmetrical polymerization of achiral or racemic olefin monomers has been investigated by chirally ionic complex catalysts to obtain optically active polymers or polymers with a single screw direction along a growing polymer chain [1-4]. The possibilities have been realized with a few synthetic polymers, for example, optically active helix polyisocyanides (*tert*-butyl isocyanide) obtained with complexes of nickel(II) and optically active amines [5, 6], poly(trichloroacetaldehyde) obtained with the lithium alkoxide of methyl mandelate having optical activity [7, 8], and poly(triphenylmethyl methacrylate) (PTrMA) obtained with chiral anionic complex initiators [9, 10]. The structure of these polymers was ascribed to the bulky side groups which force the isotactic polymer chain to assume a one-handed helix conformation.



SCHEME 1. The structures of chiral or stereodifferentiating ligands.

The asymmetrical polymerization of VCZ with a bulky carbazole side group has been investigated by using the organic salts with chiral or stereodifferentiating ligands as initiators or catalysts in a previous paper [11] (Scheme 1).

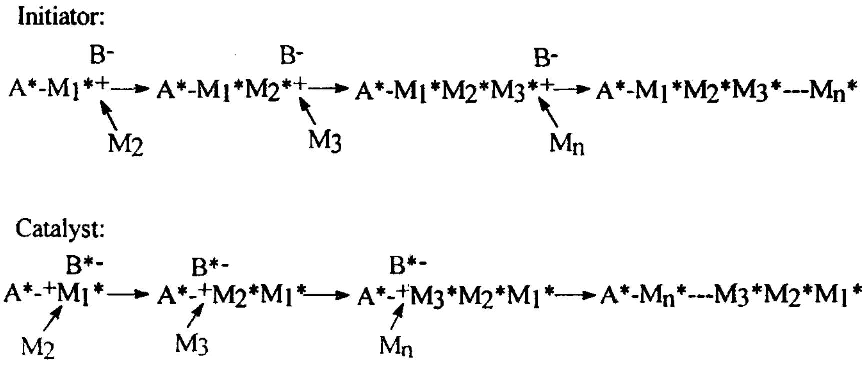
It was found that the optical rotations of the polymers obtained depended on the asymmetrically induced power of the initiators and the catalysts during the polymerization. Chirally negative counterion especially exert an important influence on the placement of the incoming monomer into the growing polymer chain [11], i.e., the long-distance effect of the initiators and the short-distance effect of the catalysts (Scheme 2).

In the present paper the characterizations of optically active poly(*N*-vinylcarbazole) obtained with organic salts, i.e., the tacticities, the extinction coefficients, and the molecular weight distributions, have been studied by ^{1}H NMR, UV, DSC, and GPC.

EXPERIMENTAL

Measurements

Optical rotation measurement was performed at 25°C on a Perkin-Elmer model 141 spectropolarmeter with a sensitivity of ±0.003°. The UV spectrum were recorded on a Hitachi-340 UV spectrograph. ^{1}H-NMR spectrum were carried out on



SCHEME 2. The induced power of initiator and catalyst during polymerization.

a Varian XL-200 (200 MHz) spectrometer ($CDCl_3$) at 45°C with TMS used as the internal standard. DSC was recorded on a Shimadzu Co. DSC-41 model. The glass transition temperature, T_g, was measured by using the DSC spectrum. The molecular weights of PVCZ were calculated by the viscosity method (solvent, THF; concentration, 0.5%; temperature, 25°C) according to Sitaramaiah [12]. GPC (gel permeation chromatography) analysis was accomplished on a Water 201 with a μ-Styragel column and THF as solvent, and the molecular weight was calibrated with standard polystyrene.

Polymerization

The polymerization of VCZ was described in a previous paper [11].

RESULTS AND DISCUSSION

Tacticities

The tacticities, i.e., the isotactic diad mole fractions of the PVCZs obtained by organic salts with chiral or stereodifferentiating ligands, are given in Table 1.

Apparently the isotactic diad mole fractions of the PVCZs are affected by the type of organic salt used as initiator or catalyst. The optical rotations and the isotactic diad mole fractions of the PVCZs obtained from free radical (AIBN), common cation ($H^+ClO_4^-$), and chiral catalyst $[(-)Sp^{*+}(+)CSA^{*-}]$ increased gradually. It was shown that the chirality of the initiator or catalyst, especially the chirality of the counterion contained in the organic salts, played an important role in stereoselective induction during polymerization (Scheme 2). It is now generally accepted that the polymerization of VCZ using different initiator (catalyst) systems produces a variety of polymers possessing different tacticities [13]. Terrell et al. reported [14] that the entropy difference between syndiotactic and isotactic propagation strongly favored syndiotactic propagation using free radical and common cationic polymerization of VCZ. The variation in the isotactic diad mole fraction was between 0.25 and 0.47. The isotactic diad mole fraction was determined by the ^{1}H-NMR spectrum (Fig. 1).

Many authors have reported that the PVCZ chain has isotactic 3_1 and syndiotactic 2_1 helix parts in a stereoblock manner [15]. According to Terrell [14] and Okamoto et al. [15a], there are mainly isotactic and syndiotactic sequences in the PVCZ chain and the heterotactic sequence is very small. The peak of the methine (2.60 ppm) signals (higher field) in the PVCZ chain are assigned to the isotactic sequence and the peak of the methine (3.44 ppm) signals (lower field) to the syndiotactic sequence [14] (Fig. 1). Therefore, the isotacticity/syndiotacticity could be roughly estimated by the ratio of two peaks intensities (I_H/I_L) placed in the higher field (I_H) and lower field (I_L) for the methine signals. The isotactic diad mole fractions (X_i) of the PVCZ chain obtained by the organic salts with chiral and stereodifferentiating ligands were higher than that by the free radical and common cation as shown in Table 1. This is due to the difference of the stereoselective induction power of the initiators and the catalysts [11]. Because of the incomplete relaxation of isotactic configuration in the methine proton in our ^{1}H-NMR spectrum ($CDCl_3$, at 45°C), the isotactic diad mole fractions generally possess low values. The syndiotac-

TABLE 1. UV Absorption and Tacticity of PVCZ Obtained with the Organic Salts as Initiators and Catalysts

	UV spectra[a]							
	^1B_b		^1L_a		^1L_b			
Types	λ_{max} in nm	ε_{max} in $M^{-1}\cdot cm^{-1}$	λ_{max} in nm	ε_{max} in $M^{-1}\cdot cm^{-1}$	λ_{max} in nm	ε_{max} in $M^{-1}\cdot cm^{-1}$	$[\alpha]_D^{25}$ [b] degrees	X_i[c] in mole % by ^1H NMR (by T_g[d])
AIBN	294	2316	328	2650	340	2229	0	28.0 (−)
$H^+ClO_4^-$	285	2107	330	2525	342	2573	0	39.0 (−)
$Ph_3C^+ClO_4^-$	285	2072	328	2498	342	2529	+2.2	47.0 (29.3)
$Ph_3C^{*+}SbCl_6^-$	285	2114	328	2559	342	2620	−2.6	48.3 (34.9)
$(-)Sp^{*+}ClO_4^-$	284	1615	329	1841	342	1957	+2.4	48.0 (65.3)
$(+)CSA^{*-}$	—	—	—	—	—	—	+4.2	50.6 (75.0)
$Ph^*_3C^+(+)CSA^{*-}$	284	1726	329	1803	342	1932	+4.4	51.5 (74.2)
$(-)Sp^{*+}(+)CSA^{*-}$	284	1783	329	1734	342	1901	+8.3	51.4 (76.1)

[a] Concentration: 0.9–1.0 × 10^{-3} M (THF); ^1B_b, ^1L_a, and ^1L_b are Platt's representations for the electronic transitions of the carbazolyl residue [22].

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

[c] Isotactic diad mole fraction, $X_i = I_{HF}/I_{LF}(CH)/1 + I_{HF}/I_{LF}(CH)$, 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 [25].

[d] According to Ref. 16.

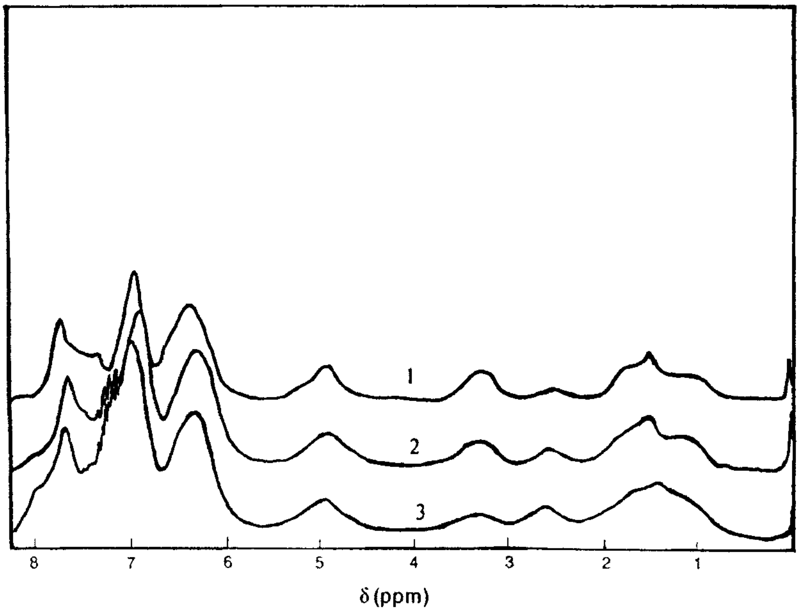


FIG. 1. ^{1}H-NMR spectra of the PVCZs obtained with different initiator (catalyst) systems. (1) AIBN, (2)$H^+ClO_4^-$, (3)(−)Sp^{*+}(+)CSA^{*-}.

tic diad mole fractions (X_s) was determined from the T_g value by using the following expression, $(T_g - 399)(1 - X_s) + (T_g - 549) = 0$ [16], hence, the isotactic diad mole fraction (X_i) may be calculated by $X_i = 1 - X_s$. In general, the X_s values which could be compared to each other are determined by using the PVCZs with high molecular weights [13]. In our conditions the X_i values obtained via T_g measurement appear to be slightly high values which are due to the low molecular weight fragment, but the change of these values corresponds with the stereoselective induction power. Therefore, the isotactic diad mole fractions determined either from the methine proton in the ^{1}H-NMR spectra or from the T_g analysis could be compared in our experiments. As shown in the previous paper [11], during VCZ polymerization the stereoselectively induced powers of the organic salts as initiator or catalyst are in the order $A^{*+}B^{*-} > A^+B^{*-} > A^{*+}B^-$, which generally corresponds with the order of the specific rotations and the isotactic diad mole fractions obtained from poly(*N*-vinylcarbazole)s (see Table 2 in Ref. 11). This is caused by monomer entry into the growing chain end controlled by the negative counterion chirality.

UV Absorption Spectrum

The UV absorption spectrum is caused by specific interaction between the carbazole pendant chromophores in the polymer. The UV absorption spectrum and the corresponding data of the PVCZs obtained from AIBN to (−)Sp^{*+}(+)CSA^{*-} systems are shown in Fig. 2 and Table 1 respectively.

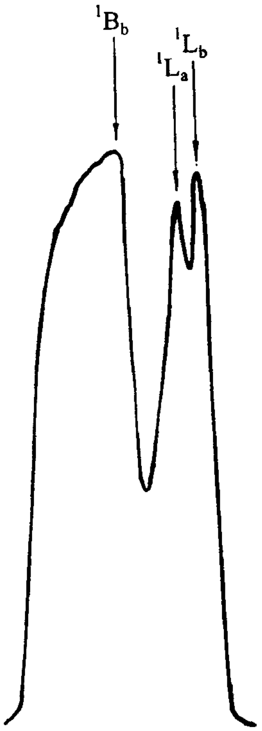


FIG. 2. UV spectrum of PVCZ.

The absorption maxima (λ_{max}) are at 284-294 (^1B_b), 328-330 (^1L_a), and 340-342 (^1L_b) nm. Here, ^1B_b, ^1L_a, and ^1L_b are Platt's representations for the electronic transitions of the carbazolyl residue [17]. By comparing these spectra, one finds a small shift for each absorption band and an appreciable change in the absorption intensity. The mole extinction coefficients (ϵ_{max}) of the absorption maxima (λ_{max}) in our conditions decrease from AIBN to $(-)Sp^{*+}(+)CSA^{*-}$ systems (Table 1). Okamoto et al. reported [18] that the spectral properties of the PVCZ, such as hypochromism and the change in the structure of the ^1B_b band, arise from some electronic interactions between neighboring chromophores in the polymer chain irrespective of the method of polymerization. In fact, the decrease in the absorption intensity (i.e., extinction coefficient) and the hypochromism are attributed to excition interaction and dispersion force interaction in the polymer with an ordered structure [19], i.e., highly isotactic sequences. It was reported that the hypochromism, i.e., diminution of absorption intensities (extinction coefficient) of the carbazolyl group in PVCZs with higher molecular weights, is caused by the flexible part becoming entangled in a random manner. In our studies the diminution of the extinction coefficient could not be explained by the hypochromism and could only be in relation to some regular orientation of the carbazole rings of the polymer with a highly isotactic sequence. A low mole extinction coefficient arises mainly from isotactic sequences which could have an efficient absorbance of light quantum, resulting in low energy excition which is very important for the organic electroluminescent contained in the PVCZ layer [20]. It was reported that the extinction coefficient of the charge transfer complex formed from PVCZ with TCNQ (tetracyanoquinodimethane) was 1310 $M^{-1}\cdot cm^{-1}$ which is good photoconductivity [21]. It is well known that the spectral properties of biological macromolecules, such as nucleic acids and proteins, differ considerably from those of monomeric chromophores. The optical density of these polymers decreases when the molecules are transformed from a random-coiled conformation to a helical one [22, 23]. In addition, hypochromism of polystyrene with a much smaller pendant π-electron system is observed in the isotactic polymer and is regarded as being due to the coulombic dipole-dipole interaction in the neighboring chromophores because of the retention of the local ordered helix structure in solution [24].

Molecular Weight Distribution

It is generally accepted that an equilibrium exists between the free ions and ion-pairs species dissociated from the organic salts in a nonaqueous solvent for which the dissociation constant and degree of dissociation (fraction of free ions) are listed in Table 1 of a previous paper [11]. The molecular weight distributions (MWD)s of PVCZ obtained from organic salts are shown in Fig. 3. (The MWs as measured by GPC have lower values compared to those measured by viscosity due to calibration with standard polystyrene.)

The polymers obtained show bimodal MWDs which are attributed to the free ions vs ion-pairs propagation for $Ph_3{}^*C^+(+)CSA^{*-}$ and $(-)Sp^{*+}(+)CSA^{*-}$

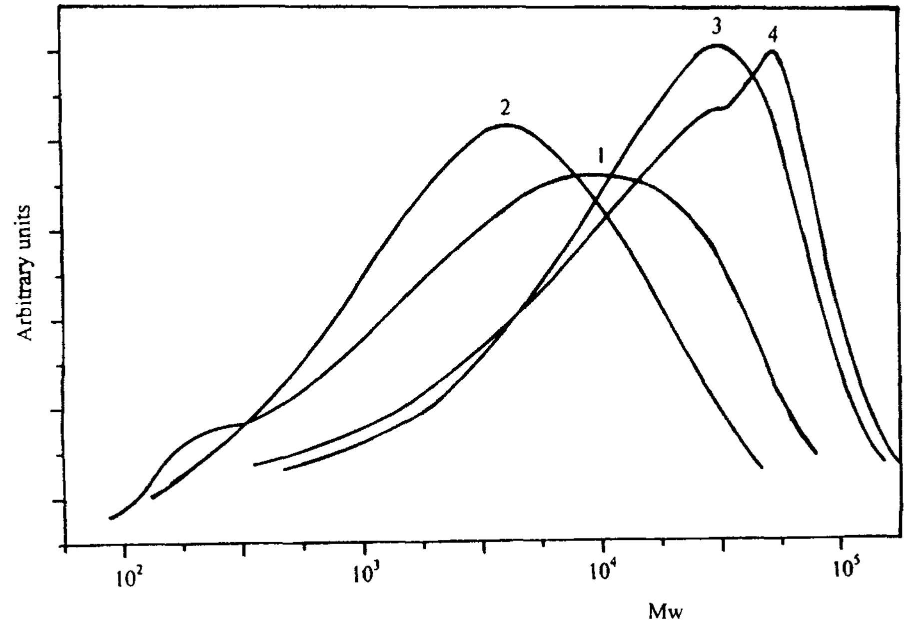


FIG. 3. Molecular weight distributions of the PVCZs obtained: (1) at 40°C in THF by $(-)Sp^{*+}(+)CSA^{*-}$; (2) at 25°C in DCE by $(-)Sp^{*+}ClO_4^-$; (3) at 40°C in THF by $(+)CSA^{*-}$; (4) at 25°C in DCE by $Ph^*{}_3C^+(+)CSA^{*-}$.

catalytic systems, and unimodal MWDs are attributed mainly to the free ions for (+)CSA* and (−)Sp*$^+$ClO$_4^-$ initiator systems. The equal reactivities of free ions and the corresponding ion-pairs in cationic polymerization involving large counterion were studied by Penezek et al. [25]. But it is well known that ion-pairs, which generally are without specific solvation effects, are less reactive than free ions. The greater capability of free ions to polarize monomer molecules, e.g., *N*-vinylcarbazole, is due to their greater effective charge density. A bimodal MWD indicates the presence of two different propagating species (free ion and ion-pair) which, by virtue of their different rates of propagation and termination, produce a polymer with a different MWD [26]. The bimodal MWDs of the PVCZ obtained could involve the initiating and growing mechanism of both the free ions and the ion-pairs. This will be studied in a future paper.

CONCLUSION

The steric microstructure of PVCZ can be controlled by using organic salts with chiral or stereodifferentiating ligands during asymmetrically stereoselective induction polymerization. The extinction coefficients decreased with an increase of the isotactic diad mole fraction. The bimodal MWD of the polymers can be attributed to two growing species, i.e., free ions and ion-pairs of the growing species.

REFERENCES

[1] T. Higashimura and Y. Hirokawa, *J. Polym. Sci., Polym. Chem. Ed., 15,* 1137 (1977).
[2] (a) Y. Okamoto and E. Yashima, *Prog. Polym. Sci., 15,* 263 (1990). (b) T. Nakano, Y. Okamoto, and K. Hatada, *J. Am. Chem. Soc., 114,* 1318 (1992).
[3] C. Y. Ren, C. F. Chen, F. Xi, T. Nakano, and Y. Okamoto, *J. Polym. Sci., Part A, Polym. Chem., 31,* 2721 (1993).
[4] C. Chen, C. Ren, J. Zhang, and F. Xi, *Makromol. Chem. Phys., 195,* 1177 (1994).
[5] R. J. M. Nolte, A. J. M. van Beijnen, and W. Drenth, *J. Am. Chem. Soc., 96,* 5932 (1974).
[6] W. Drenth and R. J. M. Nolte, *Acc. Chem. Res., 12,* 30 (1979).
[7] L. S. Corley and O. Vogl, *Polym. Bull. (Berlin), 3,* 211 (1980).
[8] W. J. Harris and O. Vogl, *J. Macromol. Sci.—Chem., A26,* 1067, 1083 (1989).
[9] Y. Okamoto, K. Suzuki, K. Ohta, and H. Yuki, *J. Am. Chem. Soc., 101,* 4763 (1979).
[10] Y. Okamoto, E. Yashima, T. Nakano, and K. Hatada, *Chem. Lett.,* p. 759 (1987).
[11] C. Chen, Q. Su, W. Liu, Y. Chen, and F. Xi, *J. Macromol. Sci.—Pure Appl. Chem., A33*(8), 1017 (1996).
[12] G. Sitaramaiah and D. Jacobs, *Polymer, 11,* 165 (1970).
[13] T. Kawamura and K. Matsuzaki, *Makromol. Chem., 182,* 3003 (1981).
[14] D. R. Terrell and F. Evers, *Makromol. Chem., 183,* 863 (1982).

[15] (a) K. Okamoto, M. Yamada, A. Itaya, T. Kimura, and S. Kasabayashi, *Macromolecules, 9,* 645 (1976). (b) A. Kimura, S. Yoshimoto, Y. Akana, H. Hirata, S. Kusabayashi, H. Mikawa, and N. Kasai, *J. Polym. Sci., Part A-2, 8*, 643 (1970). (c) D. J. Williams, *Macromolecules, 3*(5), 602 (1970).

[16] D. R. Terrell and F. Evers, *J. Polym. Sci., Polym. Chem. Ed., 20,* 2529 (1982).

[17] J. R. Platt, *J. Chem. Phys., 17,* 484 (1949).

[18] K. Okamoto, A. Itaya, and S. Kusabayashi, *Chem. Lett.*, p. 1167 (1974).

[19] W. Rhodes, *J. Am. Chem. Soc., 83,* 3609 (1961).

[20] F. C. Deschryver, J. Vandentriessche, S. Toppet, K. Demeyer, and N. Boens, *Macromolecules, 15,* 406 (1982).

[21] A. Reabaum, A. M. Herman, and R. Heack, *J. Polym. Sci., Part A, 6*(7), 1955 (1968).

[22] H. R. Mahler, B. Kline, and B. D. Mahrotra, *J. Chem. Phys., 9,* 801 (1972).

[23] N. J. Leonard, H. Iwamura, and J. Eisinger, *Proc. Natl. Acad. Sci., US, 64,* 325 (1969).

[24] M. T. Vala and S. A. Rice, *J. Chem. Phys., 39,* 2348 (1963).

[25] K. Brzezinska, K. Matyjaszewski, and S. Penczek, *Makromol. Chem., 179,* 2387 (1978).

[26] R. W. Lenz and L. C. Westfelt, *J. Polym. Sci., Polym. Chem. Ed., 14,* 2147 (1976).

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