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Polymerization of *N*-Vinylcarbazole, *N*-Vinyl-5*H*-benzo[*b*]carbazole, and *N*-Vinyl-7*H*-benzo[*c*]carbazole

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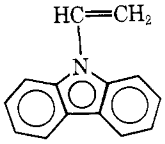
ABSTRACT: *N*-Vinyl-5*H*-benzo[*b*]carbazole and *N*-vinyl-7*H*-benzo[*c*]carbazole (V5BCz and V7BCz, respectively) having more bulky pendant groups than *N*-vinylcarbazole (VCz) were synthesized and polymerized. From the NMR spectra, the glass transition temperatures, and the solubility of the polymers, it was clarified that the stereoregularity depends on the polymerization method. This is opposite to the currently accepted concept for the vinyl polymers with large pendant aromatic groups. By cationic polymerization at low temperatures, V5BCz gives only the low molecular weight polymer (DP $\leq$ 9) in a high yield. The high molecular weight polymer (DP = 50) is prepared only by bulk polymerization initiated with azobisisobutyronitrile. V7BCz is easily polymerized free radically and cationically, as is the case with VCz. Both methylene and methine protons of these three polymers show doublet signals, of which the higher field peaks may be assigned to the isotactic sequence and the lower field peaks to the syndiotactic one. According to this assignment, it was estimated that the cationic polymers have the largest amount of the isotactic sequence (50%), and that the free-radical polymers have the smallest amount (25%). The effect of polymerization temperature on the stereoregularity is different from the case of the usual cationic polymerization, but effect of solvent polarity is similar.

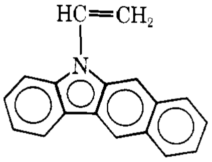
The polymerization of *N*-vinylcarbazole (VCz) has been widely investigated.[1] This monomer can be easily polymerized by many kinds of initiators such as free-radical, cationic, Ziegler–Natta, and electron acceptor ones. Heller et al. have pointed out that VCz with Ziegler–Natta catalyst systems did not undergo a coordination polymerization but merely underwent a cationic one.[2] The stereoregularity and the crystallinity of poly(*N*-vinylcarbazole) (PVCz) have been reported to be independent of the polymerization method from the NMR spectra and x-ray diffraction patterns.[3–6] Addition of a monomer onto a growing chain end has been, therefore, considered to be controlled sterically due to the bulkiness of the carbazolyl group, irrespective of the nature of the growing chain end.[3] This has been supported by the fact that poly(trityl methacrylate) prepared free radically has a pronounced isotacticity due to the steric hindrance of the pendant group.[7] On the other hand, this is clearly different from the polymerization behavior of *N*-acryloylcarbazole with a carbazolyl group connected a distance from a vinyl bond; the stereoregularity of this polymer has been reported to be dependent on the polymerization method.[8]

The present authors have recently found that the prompt and delayed fluorescences of PVCz differ between the cationic samples and the free-radical ones.[9] This seems to be attributable to a difference in the stereoregularity between them. It is, therefore, of interest to investigate in detail the relationship between the stereoregularity of the vinyl polymers containing large pendant π-electron groups and the polymerization method.

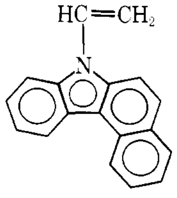
In the present paper, *N*-vinyl-5*H*-benzo[*b*]carbazole (V5BCz) and *N*-vinyl-7*H*-benzo[*c*]carbazole (V7BCz), which have more bulky pendant groups than VCz, were synthesized and polymerized by free-radical, cationic, and Ziegler–Natta initiators. The solubility, the glass transition temperatures, and the NMR spectra of PVCz, poly(*N*-vinyl-5*H*-benzo[*b*]carbazole) (PV5BCz), and poly(*N*-vinyl-7*H*-benzo[*c*]carbazole) (PV7BCz) were examined.



VCz



V5BCz



V7BCz

Experimental Section

***N*-β-Chloroethyl-5*H*-benzo[*b*]carbazole (CE5BCz)** was synthesized from 5*H*-benzo[*b*]carbazole, which was prepared from sodium 2-naphthol-1-sulfonate.[10] 5*H*-Benzo[*b*]carbazole was suspended

Table I
Characterization of PVCz Prepared by Various Methods

		Polymerization method					$I_{H/L}$[b]	
Sample	Solvent	Concn, M	Initiator (mol %)	Temp, °C	T_g, °C	M_n,[a] ×10^4	-CHR-	$-CH_2-$
A	Benzene	0.5	AIBN (1)	70	228	20	0.35	0.38
B	Bulk		Thermally	80	226		0.46	
C	Toluene	0.26	BF_3OEt_2 (1)	20	248	10	0.97	0.83
D	$(CH_2Cl)_2$	0.09	BF_3OEt_2 (1)	20	238	11	0.58	0.60
E	Toluene	0.09	BF_3OEt_2 (1)	−78	244	77	1.00	
F	Toluene	0.2	$AlEt_3/TiCl_4$ (2/2)	20	245	33	0.73	

[a] Determined from the specific viscosity.[13] [b] See text. The $I_{H/L}$ value for methylene signal could not be obtained from the spectra measured in $CDCl_3$ at 60 °C because of the broadness.

Table II
Polymerization Results of V5BCz

No.	Initiator (mol %)	Concn, M[a]	Time, h	Temp, °C	Yield, %	T_s, °C	M_n
1	BF_3OEt_2 (2)	0.14	4	40	14	212–219	
2	BF_3OEt_2 (2)	0.14	4	−20	83	230–240	1750
3	BF_3OEt_2 (2)	0.42	3	−33	85	248–258	2000
4	BF_3OEt_2 (2)	0.42	3	−40	85	258–268	2030
5	BF_3OEt_2 (1)	0.14	4	−78	93	264–274	2120
6	BF_3OEt_2 (2)	0.10	6	−90	93	260–272	2030
7	$AlEtCl_2$ (2)	0.14	4	−78	86	243–253	1770
8	$AlEt_3/TiCl_4$ (2/2)	0.20	10	20	71	245–250	
9	BPO (2)	0.35	15	80	0		
10	BPO (2)	Bulk	24	100	37	200–208	
11	AIBN (2)	0.34	48	75	30	230–240	3060
12	AIBN (2)	0.40	35	80	47	240–248	
13	AIBN (2)	Bulk	48	100	56	290–300	12000
14	None	Bulk	48	100	Trace		

[a] Solvent: ethylene chloride for No. 3 and toluene for the others.

in 400 ml of acetone; 20 g of β-chloroethyl *p*-toluenesulfonate and a solution of 10 g of NaOH in 7.5 ml of water were added with stirring. The mixture was stirred at 60 °C for 10 h; then another 10 g of β-chloroethyl *p*-toluenesulfonate and a solution of 4 g of NaOH in 1.5 ml of water were added and stirring was continued for an additional 10 h. The precipitate was filtered off. After the unreacted β-chloroethyl *p*-toluenesulfonate was separated off, the filtrate was evaporated and the residue chromatographed on silica gel using benzene to give 7 g (54%) of the product. Recrystallization from methanol gave CE5BCz as colorless needles: mp 121–122 °C; NMR ($CDCl_3$) τ 1.62 (s, 1, aromatic); 1.90–2.18 (m, 3, aromatic); 2.45–2.90 (m, 6, aromatic); 5.44–5.58 (t, 2, $-CH_2-$); 6.15–6.30 (t, 2, CH_2Cl). Anal. Calcd for $C_{18}H_{14}NCl$: C, 77.28; H, 5.01; N, 5.01. Found: C, 76.99; H, 4.97; N, 5.10.

V5BCz. CE5BCz (7.2 g; 0.026 mol) was suspended in 360 ml of ethanol and 75 ml of 25% KOH–methanol solution was added. The mixture was refluxed for 15 h and poured into water. After standing over a night, the precipitate was filtered and washed with water. Repeated recrystallizations from methanol gave V5BCz (4.0 g, 62%) as pale yellow needles: mp 89.5–90.5 °C: NMR ($CDCl_3$) τ 1.70 (s, 1, aromatic); 1.88–2.20 (m, 4, aromatic and $-CH{=}$); 2.55–2.96 (m, 6, aromatic); 4.45–5.00 (q, 2, $=CH_2$); ir (KBr) 952 and 880 cm^{-1} (terminal vinyl). Anal. Calcd for $C_{18}H_{13}N$: C, 88.89; H, 5.35; N, 5.76. Found: C, 88.91; H, 5.23; N, 5.82.

***N*-β-Chloroethyl-7*H*-benzo[*c*]carbazole (CE7BCz)** was synthesized from 7*H*-benzo[c]carbazole[11] by the procedure described in the synthesis of CE5BCz. The crude product was chromatographed on silica gel using a mixture of *n*-hexane–benzene (1:2) and then recrystallized twice from methanol. Yield: 62%; colorless needles; mp 105–106.5 °C. Anal. Calcd for $C_{18}H_{14}NCl$: C, 77.28; H, 5.01; N, 5.01. Found: C, 77.19; H, 4.84; N, 4.95.

V7BCz was synthesized from CE7BCz by the procedure described in the synthesis of V5BCz. The product was recrystallized twice from methanol. Yield: 56%; colorless plates; mp 88–89 °C; NMR ($CDCl_3$) τ 1.25–1.60 (q, 2, aromatic); 2.08–3.00 (m, 9, aromatic and $-CH{=}$); 4.40–4.87 (q, 2, $=CH_2$); ir (KBr) 960 and 873 cm^{-1} (terminal vinyl). Anal. Calcd for $C_{18}H_{13}N$: C, 88.89; H, 5.35; N, 5.76. Found: C, 89.06; H, 5.20; N, 5.74.

Polymerization Procedures. All polymerization reactions were carried out using standard procedures under nitrogen or under vacuum.[12] Reagents were carefully purified and dried. Polymers were isolated by precipitation with methanol and purified by repeated reprecipitations followed by drying under vacuum.

Polymer Characterization. The polymer molecular weights (M_n) were determined in ethylene chloride solution at 40 °C by a vapor pressure osmometer. Glass transition temperatures (T_g) were determined with a Shimadzu DSC-20 differential scanning calorimeter at heating rates of 10–15 °C/min. The T_g for each sample was taken as the average of four or five determinations. NMR spectra were measured in deuteriochloroform at 60 °C and in tetradeuterioethylene bromide at 60–140 °C with a JEOL MH-100 spectrometer.

Results and Discussion

Polymerization of VCz. Representative results are shown in Table I. All of the PVCz samples are soluble in ordinary solvents irrespective of the polymerization method. The clear differences in T_g are, however, observed between the samples prepared free radically, cationically in a polar solvent, and cationically in a nonpolar one; the T_g increases in this order. The T_g is supposed to be independent of the M_n in the range of $M_n > 100\,000$.[14] It is considered that there is no serious difference in molecular weight distribution between these samples.[15] Therefore, the differences in T_g are not attributable to the differences in M_n, but to some differences in the stereoregularity which will be discussed below.

Polymerization of V5BCz. V5BCz is easily polymerized

Table III
Polymerization Results of V7BCz

	Polymerization method					Characterization of polymers					
								Solubility^b		$I_{H/L}$^{c}	
No.	Initiator (mol %)	Concn, M^a	Time, h	Temp, °C	Yield, %	T_g, °C	M_n	Bz	THF	-CHR-	-CH$_2$-
1	AIBN (2)	0.10	5	75	39		11 000	○	○		
2	AIBN (2)	0.28	5	75	65	271	14 000	○	○	0.32	
3	AIBN (2)	0.56	5.5	75	92	271	15 000	○	○	0.33	0.39
4	BF_3OEt_2 (2)	0.14	1.5	−78	99	283	>25 000	○	○	0.54	0.52
5	BF_3OEt_2 (2)	0.14	1	−55	98	288	>25 000	○	○		
6	BF_3OEt_2 (2)	0.14	1.5	−40	99	292		×	△		
7	BF_3OEt_2 (2)	0.05	1	−78	19		10 000	○	○		
8	BF_3OEt_2 (2)	0.05	3	−50	92	280	16 000	○	○	0.63	
9	BF_3OEt_2 (2)	0.05	1	−40	99	287	20 000	○	○	0.68	
10	BF_3OEt_2 (2)	0.05	1	0	93	287	14 000	◑	○		
11	BF_3OEt_2 (2)	0.05	1	10	94		8 500	◑	○	0.99	
12	BF_3OEt_2 (2)	0.05	1	25	93	291		×	△		
13	BF_3OEt_2 (1)	0.15	3	10	99	289		△	○	0.92	0.78
14	BF_3OEt_2 (1)	0.10	1	10	93	278		○	○	0.54	0.50
15	$AlEt_3/TiCl_4$ (1/1)	0.20	10	20	91	292		×	△		
16	$AlEt_3/TiCl_4$ (3/2)	0.10	7	35	99			◑	○	0.56	
17	$AlEt_3/TiCl_3$ (1/1)	0.20	10	20	90	282		○	○	0.53	

[a] Solvent: ethylene chloride for No. 14 and toluene for the others. [b] (○) soluble; (◑) soluble but opaque in cold benzene; (△) swollen; (×) insoluble. [c] See Table I.

by cationic initiators, as is shown in Table II. The yields, softening ranges (T_s), and M_n of the polymers increase with a decrease in polymerization temperature. At the temperatures below −40 °C, the polymers are obtained almost quantitatively and the M_n values are constant at 2000–2100 (DP = 8–9). These polymers are readily soluble in ordinary solvents such as benzene and THF, and the T_s and T_g of them are 260–270 and 235 °C, respectively. All attempts to obtain the high molecular weight polymer by cationic initiators were unsuccessful. Ziegler–Natta initiators also give the low molecular weight polymers in high yields.

V5BCz is also polymerized by free-radical initiators, although the yields are very low as compared with those of cationic polymerizations. Benzoyl peroxide (BPO) gives the polymer having a low value of T_s only in bulk polymerization. Azobisisobutyronitrile (AIBN) gives the polymers even in solution. The yields increase with an increase in monomer concentration up to 50% in the saturated solution (0.4 M), but the T_s and probably also the M_n hardly increase. The AIBN-initiated bulk polymerization at 95–100 °C gives the fairly high molecular weight polymer (DP = 50) in an about 50% yield. The polymer thus obtained is pale yellow, and soluble in THF, etc., but not in benzene, etc., and the T_g of it is 271 °C. It is noted that the T_s values of the cationic polymers are much larger than those of the free-radical polymers with the corresponding M_n values.

V5BCz is not polymerized by anionic initiators. This is the same reason as the case with VCz.[16]

Polymerization of V7BCz. V7BCz is easily polymerized by free-radical initiators. Some polymerization results are shown in Table III. The yields and the M_n depend a little both on monomer concentration and on temperature. The M_n values are much larger than those of the PV5BCz samples prepared under the similar conditions, but much smaller than those of the PVCz ones.

V7BCz is polymerized by cationic initiators in high yields with an exception of No. 7 in Table III. The T_g, M_n, and solubility of the cationic polymers vary remarkably with the polymerization condition. The M_n increases with an increase in the concentration of monomer or initiator, and there is an optimal polymerization temperature of the M_n at about −40 °C. The T_g increases with an increase in polymerization temperature and decreases with an increase in the solvent polarity. The T_g of the cationic polymers are much higher than those of the free-radical ones. These results are not explained by the differences in the M_n, although the T_g depends a little on the M_n even in the range of fairly high M_n. The polymers prepared at temperatures below −40 °C are readily soluble in ordinary solvents. However, the solubility becomes poor with an increase in the temperature, in spite of a decrease in the M. The polymers insoluble in all of the solvents examined are obtained at temperatures above a critical one, which is raised with an increase in the concentration of initiator or monomer. The solubility is also dependent on the solvent polarity; ethylene chloride gives the polymer having better solubility than toluene. Thus, there is a roughly parallel relationship between the T_g and the solubility.

V7BCz is easily polymerized by Ziegler–Natta initiators, but not polymerized anionically.

These three monomers are rich both in the electron-resonance stabilization and in the electron-donating character of the pendant groups, of which the magnitudes are considered to be in the order of V5BCz > V7BCz > VCz. They were, therefore, predicted to be easily polymerized free radically and cationically to the high molecular weight polymers. In the case of free-radical polymerization, both the yields and the M_n are in the order of VCz > V7BCz > V5BCz. This is opposite to the order predicted from the electron resonance stabilization. The radical reactivity of these monomers seems to be controlled by the steric hindrance effect rather than by the resonance effect.

In the case of cationic polymerization, the yields are almost quantitative and the M_n is in the order of VCz > V7BCz ≫ V5BCz. The cationic reactivity of the growing chain end is predicted to be in the inverse order of that of the monomer, as is the case with vinyl ethers.[17] This may be a reason for the latter fact (the order of M_n), if the approach of an incoming monomer to the growing chain end followed by the separation of the counterion is not the rate-determining step of the propagation reaction. However, this assumption seems very

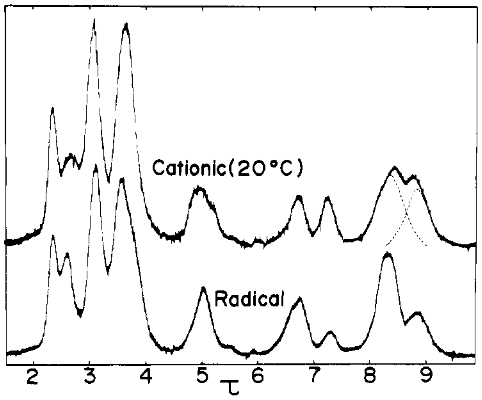


Figure 1. NMR spectra (100 MHz) of PVCz in tetradeuterioethylene bromide at 125 °C. The upper and lower curves are for the samples of No. C and A in Table I, respectively.

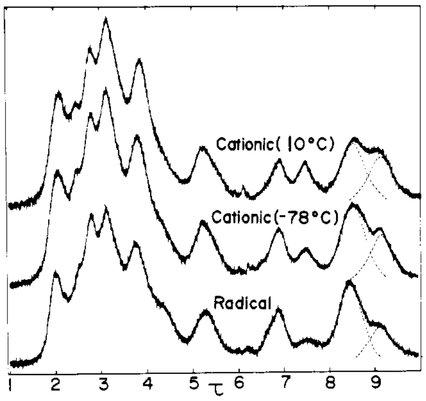


Figure 3. NMR spectra (100 MHz) of PV7BCz in tetradeuterioethylene bromide at 125 °C. The upper, middle, and lower curves are for the samples of No. 13, 4, and 3 in Table III, respectively.

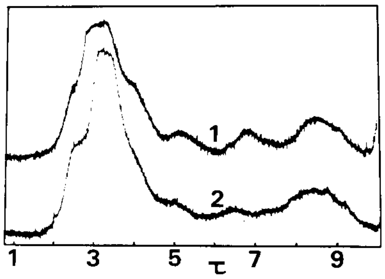


Figure 2. NMR spectra (100 MHz) of PV5BCz in deuteriochloroform at 60 °C. 1 and 2 are for the samples of No. 13 and 5 in Table II, respectively.

Table IV
Chemical Shifts (τ) of Protons[a]

Sample	Aromatic	Methine	Methylene
PVCz (cationic)	2.3–3.7, 4.95	6.7, 7.25	8.35, 8.83
PVCz (radical)	2.3–3.6, 5.0	6.73, 7.27	8.3, 8.85
PV7BCz (cationic)	2.0–3.8, 5.15	6.8, 7.4	8.4, 9.05
PV7BCz (radical)	1.9–3.7, 5.2	6.8, 7.4	8.36, 9.0
PV5BCz (radical)	2.3–3.9, 5.1	6.75	8.4

[a] The spectra were measured in tetradeuterioethylene bromide at 125 °C.

unlikely for these monomers. Therefore, the order of M_n suggests that the cationic reactivity of the growing chain end may be controlled by the steric hindrance effect rather than by the electron-donating effect. The cationic polymerization of V5BCz, the most bulky monomer among these used, gives only the low molecular weight polymer in a high yield. This suggests that the cationic reactivity of the growing chain end decreases drastically with increasing sequence of the growing chain, resulting in the transfer reaction to a counterion and/or a monomer.

NMR spectra of PVCz, PV5BCz, and PV7BCz. The T_g and solubility data mentioned above suggest that the stereoregularity and/or the crystallinity of these polymers vary depending on the polymerization method. The ir, NMR, and x-ray diffraction spectra of these polymers were also examined. The ir and x-ray diffraction spectra are essentially the same, irrespective of the polymerization method. All of the samples which were precipitated from solution and have never experienced heat treatment are of low crystallinity. The 100-MHz NMR spectra are shown in Figures 1–3. The spectra of PV5BCz and PV7BCz were assigned according to the case of PVCz.[5,18] The assignment is listed in Table IV. Both positions and relative intensities of all the signals are independent of temperature in the range of 60 to 140 °C, although the resolution of the signals of methylene protons are appreciably improved with an increase in temperature.

In the case of PVCz and PV7BCz, the aromatic regions of the spectra ($\tau < 6.0$) vary only a little with the polymerization method. The intensity of a peak appearing at about τ 5 always corresponds to about one proton. On the other hand, the methylene and methine regions of the spectra composed of two peaks respectively vary appreciably with the polymerization method; the intensity ratio of the higher field peak to the lower field one ($I_{H/L}$) is dependent on it, as is shown in the last columns in Tables I and III, although the positions of the signals are hardly dependent on it. The $I_{H/L}$ value for methylene protons is in agreement with that for a methine proton, taking into consideration the error (±5%) in resolving a methylene signal *into two components*. In both PVCz and PV7BCz, the samples prepared cationically in a nonpolar solvent at room temperature have the largest $I_{H/L}$ value (unity) and the free-radical samples have the smallest value (a third). In the cationic polymerization, the $I_{H/L}$ value decreases appreciably in going from toluene to ethylene chloride. As the temperature decreases, it decreases down to about 0.50 at −78 °C in the case of PV7BCz, but does not vary in the case of PVCz. Thus, it varies with the polymerization method in a manner similar to the case of both the T_g and the solubility; the sample having a higher T_g and poorer solubility has a larger $I_{H/L}$ value. However, this relationship does not hold for the samples prepared by Ziegler–Natta initiators; the $I_{H/L}$ values are relatively small, in spite of the high T_g and the poor solubility.

In the case of PV5BCz, there seems to be a similar difference in the $I_{H/L}$ value between the cationic and the free-radical samples, but no quantitative discussion can be done because of the highly unresolved spectra.

Both the doublet signals of methylene and methine protons in the 100-MHz spectra are independent of measuring temperature but dependent on the polymerization method. On the other hand, Williams has reported that the 220-MHz NMR spectrum of PVCz shows clearly the multiplicity of the signals of methylene and methine protons and that the methylene signal in the 220-MHz spectrum varies with temperature owing to temperature-dependent conformational effects.[5] We have also measured the 220-MHz spectra of PVCz in several solvents and at a series of temperatures. The resolution of the spectrum of methylene protons varies with both on solvent and on temperature. In some cases, the 220-MHz spectra are unresolved rather than the 100-MHz spectra. However, the highly resolved spectra of methylene protons are composed of four peaks in both cases of the cationic and free-radical samples; the two higher field peaks and the two lower field ones correspond to the higher field peak and the lower field one in the 100-MHz spectra, respectively.[19] Moreover, the intensity ratios of the two higher field peaks to the two lower field ones (for example, 0.35 and 0.89 for samples A and C, respectively) are in good agreement with the $I_{H/L}$ values of the corresponding samples listed in Table I. Therefore, the differences in $I_{H/L}$ values are attributable to some difference in the stereochemical configuration of the polymer chain.

The splittings of both doublet signals of methylene and methine protons are too large to be attributable to some triad tacticity in a usual manner. Therefore, it may be necessary to assume the presence of two kinds of both methylene and methine protons having the quite different environments, that is, the stereoblock arrangements of isotactic 3/1 and syndiotactic 2/1 helixes, as have been proposed by Mikawa et al.[3]

Heller et al. investigated the NMR spectra of polyvinylaromatics such as polystyrene and poly-1-vinylnaphthalene (P1VN) in connection with the stereoregularity, and found that the aliphatic protons of P1VN have the following unusual behaviors probably owing to the bulkiness of the pendant group.[20] (1) Both the methylene and methine signals of the isotactic sample (9.02 and 7.52 τ, respectively) are remarkably upfield from the signals of the atactic one (8.57 and 7.24 τ). (2) The methine signals of both the samples are shifted appreciably downfield as compared with those of polystyrene etc.

In the present case, the aliphatic protons have the behaviors similar to those of P1VN. Therefore, the higher field peaks of both methylene methine protons may be tentatively assigned to the isotactic sequence, and the lower field peaks to the syndiotactic one. According to this assignment, the $I_{H/L}$ value is a measure of the relative amount of isotactic sequence to syndiotactic one of the polymer. In both PVCz and PV7BCz, the samples prepared cationically in a nonpolar solvent at room temperature have the largest amount of isotactic sequence (50%) and the free-radical samples have the smallest amount (25%). The difference in the amount of isotactic sequence explains reasonably the high T_g and poor solubility of the former samples as compared with the case of the latter ones, because the isotactic 3/1 helix is considered to be less flexible rather than the syndiotactic 2/1 helix. This is another evidence for the present assignment.

Crystal[6] and Griffiths[21] have reported that in the lamellar type or rod type crystals of PVCz prepared by appropriate heat treatments a polymer chain is composed of an isotactic 3/1 helix but not of a syndiotactic 2/1 helix, although the PVCz sample used by Griffith is considered to be a free-radical sample judging from the T_g (227 °C). This might suggest that the isotactic 3/1 helix segment is crystallized much more easily than the syndiotactic 2/1 helix segment, and that the latter segment is primarily present in the poor crystalline and amorphous phases. The sample with the crystallinity of 60% has been obtained from the PVCz sample used by Griffiths.[21] This might support assigning the lower field peaks of both methylene and methine protons to the syndiotactic sequence rather than the atactic one.

From the above-mentioned results and discussion, the polymerization behaviors of these vinyl monomers may be explained as follows. Monomers make addition onto a growing chain end in a way that the resulting polymer chain forms a helix in order to make the steric repulsion between neighboring bulky pendant groups as little as possible. The polymer chain is, therefore, composed of the isotactic and syndiotactic sequences rather than of the atactic one. The relative probability of isotactic and syndiotactic propagations varies with the nature of the growing chain end. The model proposed for the homogeneous cationic polymerization of common vinyl monomers[22] seems applicable to the present case. The syndiotactic propagation occurs preferentially in free-radical polymerization, because the steric repulsion between two bulky pendant groups of a growing terminal carbon and an incoming monomer is less in such propagation. On the other hand, the isotactic propagation occurs with an increased probability in cationic polymerization, because of the presence of the counteranion on the growing terminal carbon. This effect of counteranion decreases significantly with an increase in the solvent polarity because of dissociation of the growing ion pair. This is similar to the case of common vinyl monomers.[22] However, the effect of temperature on the stereoregularity in the cationic polymerization of these vinyl monomers is quite different from the case of common vinyl monomers; in the latter case, the isotactic polymers are obtained only at low temperatures.[22] In the present case, the fixation of the conformation of the growing chain end, which is crucial in enhancing the stereoregularity, may be maintained even at room temperature because of the considerable bulkiness of the pendant groups. As the pendant group becomes more bulky, the growing chain end becomes too stiff to reorganize conformationally at low temperatures after the monomer addition. This effect seems significant in the isotactic propagation rather than in the syndiotactic one. This might be a conceivable explanation of the temperature effect and also of the failure to prepare the high molecular weight polymer of V5BCz by cationic initiators.

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