Catalytic Properties of Poly(4(5)-vinylimidazole-*co*-acrylic acid) and Its Low Molecular Weight Analogues in the Hydrolyses of Various Substituted Phenyl Acetates

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ABSTRACT: The catalytic activities of poly(4(5)-vinylimidazole-*co*-acrylic acid) and its low molecular weight analogues in the hydrolyses of various substituted phenyl acetates in 4.35 vol % EtOH–aqueous solutions containing no salt have been studied. The hydrolysis of every substrate used here followed second-order kinetics and the data followed a straight line in the Bronsted plot. This indicates that hydroxyl and carboxyl groups did not work directly in the course of hydrolysis. The nucleophilicity of the imidazolyl group of every catalyst had the principal effect on both the nucleophilic attack upon the substrate and the breakdown of the addition intermediate. The slope in the Bronsted plot for the polymer catalysts was steeper than that for low molecular weight catalysts. This can be explained by the electrostatic effect in the vicinity of the polymer; the addition intermediate which is thought to be more polar than the neutral substrate is stabilized in the high dielectric field and high ionic strength and the leaving of ArO^- from the addition intermediate is facilitated by the electrostatic repulsion between the leaving ArO^- and the anionic field in the polymer. The existence of the electrostatic field was supported by the following facts: The addition of LiCl to the polymer solution in the NMR titration caused the decrease of the pK_{Im} value of the imidazolyl group of the polymer. The n_{AA} value of the carboxyl group in the potentiometric titration was larger than unity. Also, that the anionic field owed to carboxylate moieties and the position of the counterions to those in polymer catalysts had remarkable effect upon the nucleophilicity of the imidazolyl group was confirmed by the CNDO/2 calculation.

Up to the present many studies on catalytic hydrolyses of esters by imidazolyl derivatives and polymers which contain imidazolyl group have been made.[1–11] It has been observed that several of the polymers have high catalytic activity because of the cooperation between imidazolyl group and the other group in them. In particular, the cooperation between imidazolyl and carboxyl groups is of interest in connection not only with the catalysis by α-chymotrypsin, but also as an organic catalyst. Investigations of catalytic activity of poly(4(5)-vinylimidazole-*co*-acrylic acid) in hydrolyses of 3-acetoxy-*N*-trimethylanilinium iodide (ANTI), a cationic substrate, *p*-nitrophenyl acetate (PNPA), a neutral one, and 3-nitro-4-acetoxybenzoic acid (NABA), an anionic one, were done by Overberger and Maki,[3] followed by the present authors.[8] Those results suggest that the imidazolyl group cooperates with the carboxyl group. Both studies show that the catalytic activity of the imidazolyl group in the polymer is influenced by the content of the carboxyl group in the polymer. The investigation also shows that the slope in the Bronsted plot for the hydrolytic catalysis by the polymers was much larger than that by a series of low molecular weight imidazolyl derivatives. This result also suggests that some cooperation between imidazolyl and carboxyl groups in the polymers takes place. In addition, the catalytic activity of the terpolymer which contains imidazolyl, carboxyl and hydroxyl groups is higher than that of poly(4(5)-vinylimidazole-*co*-acrylic acid) and poly(4(5)-vinylimidazole-*co*-vinyl alcohol). And the terpolymer which contains the above mentioned three-functional groups in definite order has much higher catalytic activity than that which contains the groups at random.[9] These results suggest that cooperation among the three functional groups takes place.

In the present study, we attempt to clarify the catalytic property of poly(4(5)-vinylimidazole-*co*-acrylic acid) through a comparison with low molecular weight imidazolyl derivatives.

Experimental Section

Catalysts. 4(5)-Ethylimidazole (EI) was synthesized via bromomethyl ethyl ketone from propionyl bromide,[12] followed by the Weidenhagen synthesis. β-(4(5)-Imidazoly)-α-hydroxypropionic acid (Oh),[13] β-(4(5)-imidazolyl)-α-chloropropionic acid (Ic),[14] *trans*-urocanic acid (t-U),[14] 4(5)-vinylimidazole (VIm),[15] histaminol (HI),[16] and *cis*-urocanic acid (c-U)[17] were synthesized according to the literature. β-(4(5)-Imidazolyl)propionic acid (Ip) was synthesized quantitatively from *trans*-urocanic acid in the presence of Raney-Ni under 50 atm of H_2 during 24 h at the temperature of 25 °C. Poly(4(5)-vinylimidazole-*co*-acrylic acid) was synthesized as was described in the preceding paper.[8]

Substrates. 2,4-Dinitrophenyl acetate,[18] 2-nitro-4-chlorophenyl acetate,[19] and *p*-chlorophenyl acetate[20] were obtained from corresponding phenols and acetic anhydride. *p*-Cresyl acetate[21] was obtained from *p*-cresol and acetyl chloride. The others were obtained commercially.

Determination of pK_{Im}. Aqueous solution of the above-mentioned imidazolyl derivative which contains 0.01 M imidazole moiety and 0.01 M HCl was titrated by 0.1 M NaOH aqueous solution, then the pK_{Im} value of the imidazole moiety and the *n* value were obtained by the modified Henderson–Hasselbach plot.

The pK_a values of various phenol derivatives were determined by the method of spectrophotometric titration at 30 ± 0.5 °C. Optical densities of about 5×10^{-4} M phenol derivatives in 4.35 vol % EtOH–aqueous solutions were measured at various pH's at the following wavelengths: 360 nm for 2,4-dinitrophenol, 430 nm for 2-nitro-4-chlorophenol, 402 nm for *p*-nitrophenol, 245 nm for *p*-chlorophenol, 235 nm for phenol, and 237 nm for *p*-cresol, respectively.

NMR Titration. NMR spectra (220 MHz) of 0.63 M A-81 (for the imidazole moiety) were measured in D_2O at several pD at room temperature, using 2,2-dimethylsilapentane 5-sulfonic acid (DSS) as an internal standard. The pD was adjusted with DCl or NaOD and read with the Radiometer Model 28 pH meter equipped with a combination microelectrode. Uncorrected meter readings are given in all cases.

Kinetics. The kinetical measurement was performed at 30 ± 0.5 °C at pH 8.0. The reaction solution consisted of 3.48×10^{-4} M catalyst and 8.70×10^{-4} M substrate in the 4.35 vol % EtOH–aqueous solution at the initial time. The apparent rate constant of the second-order reaction, k_{cat}, is obtained according to the following equation at the initial stage,

$$k_{cat} = (V_{cat} - V_0)/[Cat][S]$$

where V_{cat} and V_0 indicate reaction rates both in the presence and the absence of the catalyst, respectively, and [Cat] and [S] represent concentrations of the catalyst and the substrate, repectively. $(V_{cat} - V_0)$ was proportional to the product of [Cat] and [S]. The reaction rate at a certain pH is obtained from the volume of titrant, 0.001 M NaOH in the 4.35 vol % EtOH–aqueous solution, needed to neutralize the produced acetic acid and phenol derivative, using the Radiometer type TT2b titrator equipped with an automatic buret and a recorder.

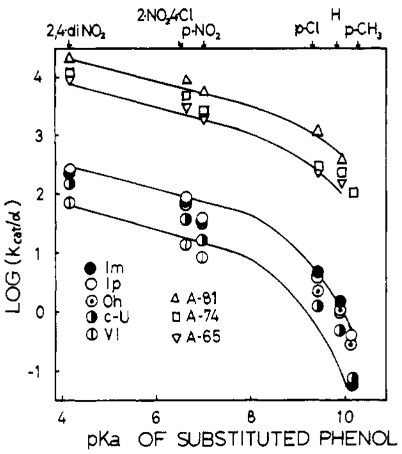

Figure 1. Rate of the hydrolyses of substituted phenyl acetates with various catalysts against pK_a of the leaving phenols ([Cat] = 4×10^{-3} M, [S] = 2×10^{-2} M).

The apparent rates of the reaction (V_{cat} and V_0) were obtained from the slope of the plot of the volume of the titrant against the reaction time. The volume of the titrant was almost proportional to the reaction time up to about 10% hydrolysis. The data were obtained from the slope of the volume of the titrant–reaction time curve, when a certain volume of the titrant was consumed.

Calculation. All calculations have been carried out by the CNDO/2 method in its original parametrization.[22] We used the proton affinity (PA)[23] or superdelocalizability (Sr)[24] of the N-3 of the imidazole moiety as a measure of the basicity of it. PA and Sr are defined as follows

$$PA = E_{BH^+} - (E_{H^+} + E_B)$$

$$Sr = 2 \sum_{j}^{occ} \frac{c_{jr}^{2}}{m_j}$$

where c_{jr} and m_j indicate the coefficient of the rth AO in the jth MO and that of jth MO, respectively. The former represents the measure of the energy needed to add one proton to the base, while the latter represents the measure of the facility being attacked by electrophilic reagent on the concerned atom, where the electrophilic reagent was H^+ in the present study.

Results and Discussion

Figure 1 shows catalytic activities of low molecular weight imidazolyl derivatives and of the polymers which contain the imidazolyl group in the hydrolyses of various substituted phenyl acetates of which leaving groups have different activities. At pH 8.0, the catalytic activity is mainly attributed to the neutral imidazolyl group. Because the cationic imidazolyl group has no catalytic activity[10] and the pK_a value in the change between neutral and anionic imidazolyl groups is high,[25] the concentration of anionic imidazolyl group is very low at this pH condition. Therefore, the catalytic activity can

$$\mathrm{Im} \overset{K_a}{\rightleftharpoons} \mathrm{Im}^- + \mathrm{H}^+$$

be regarded as that of the neutral imidazolyl group. The rate constant in the hydrolysis by every catalyst decreases with an increase of basicity of the leaving group of the substrate, ArO^-. It also shows a precipitous fall in the rate when the basicity of ArO^- is stronger than a certain value. The figure is classified roughly into a polymer group and a low molecular weight group. There is no remarkable difference between each group in the tendency. In the present study, the precipitous fall in the rate at a certain basicity of ArO^- suggests either steric hindrance owed to the substituent in the ortho position or a change in the transition state that is expected for the rate-determining process. It is thought that the latter is plausible. Kirsch and Jencks[26] showed, in the investigation of imidazole-catalyzed and alkaline hydrolyses of a series of acetates (leaving groups of pK_a = 4–16), that the attack of imidazole onto the acetate is the rate-determining process with a good leaving group and that the breakdown of an addition intermediate is the rate-determining process with a poor leaving group.

With a series of phenyl acetates of which pK_a values of leaving groups are small, the nucleophilic attack is the rate-determining process in the hydrolysis, and in this range, both the low molecular weight and the polymer catalysts have similar slopes in the rate profile. This fact may suggest that both catalysts have a similar mechanism in their hydrolytic reactions. That there is no remarkable difference in the hydrolyses of those substrates by the respective low molecular weight catalysts indicates that both the carboxyl group and the hydroxyl group have not had such cooperative action, as these groups assist the nucleophilic attack of the imidazole moiety onto the substrate. Consequently, it is suggested that the carboxyl group in the polymer also does not assist the nucleophilic attack of the imidazole moiety onto the substrate.

In the case of the hydrolysis of the ester of which the pK_a value of the leaving group is high, i.e., a breakdown of the addition intermediate is rate determining, there is no remarkable difference in slopes among the respective catalyses by the low molecular weight catalysts. This fact suggests that both the carboxyl group and the hydroxyl group do not assist the imidazole moiety in the breakdown of the addition intermediate in the low molecular weight catalysts. Slopes of the curves in the polymer catalysts are lower than slopes in the low molecular weight catalysts in this region. This is presumably owed to higher pK_a values of polymer catalysts than the low molecular weight catalysts. Jencks and Gilchrist[27] showed, in the investigation of the reactions of water and of nucleophiles of pK_a = 3.1–15.8 with a series of acetate esters with leaving groups of pK_a = 2–10, that the decrease in the hydrolyses of the esters, of which the pK_a's of the leaving groups were high, became small according to the nucleophilicity of the nucleophile.

In general, if the nucleophilicity of the catalyst has no effect on the breakdown of the addition intermediate, the rate of leaving of ArO^- from the addition intermediate should depend only upon the nature of the leaving substituted phenols, ArO^-'s. Generally, the rate of the nucleophilic attack is affected by the nucleophilicity of the catalyst as well as the nature of the leaving substituted phenols. In those cases, the bending points in the curves move to lower pK_a values of the leaving groups as the pK_a values of the catalysts are higher. In the present study, Figure 1 shows that the bending points for all catalytic systems appear at almost the same pK_a value of the leaving group of the ester. Therefore, nucleophilicities of catalysts must have an effect upon the breakdown of the addition intermediate as well as upon the nucleophilic attack onto the esters. Further, Stauffer[28] showed the change in the relative importance in the transition state of proton donation to the anilide, $\equiv$C–N–, with a basicity of the aniline moiety, in the investigation of the hydrolyses of a number of ring-substituted trifluoroacetanilides by imidazole. In the present study, the change in the transition state of proton donation to the phenolic oxygen on the breakdown of the addition intermediate may contribute to the rate of the reaction.

Figure 2 shows the Bronsted plot of the hydrolyses, that is the plot of the logarithm of the rate constant against the pK_{Im} value of the nucleophile. Slopes in the hydrolyses of *p*-cresyl, phenyl, and *p*-chlorophenyl acetates in which the breakdowns of the addition intermediates are rate determining and those in the hydrolyses of *p*-nitrophenyl, 2-nitro-4-chlorophenyl, and 2,4-dinitrophenyl acetates in which the nucleophilic attacks are rate determining are similar. This result suggests that the nucleophilicity of the nucleophile affects both the breakdown of the addition intermediate and the nucleophilic

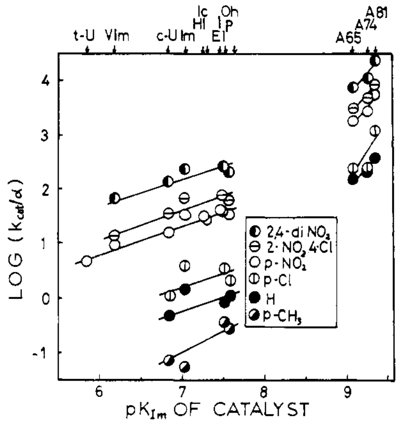

Figure 2. Bronsted plots of hydrolyses of esters by poly(4(5)-vinylimidazole-*co*-acrylic acid) and low molecular weight imidazolyl derivatives.

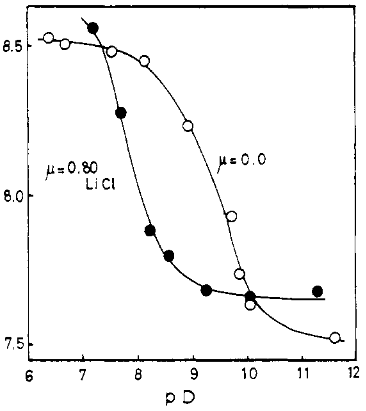

Figure 3. Plots of δ values of the C-2 proton of the imidazole moiety in poly(4(5)-vinylimidazole-*co*-acrylic acid), A-81, against pD (0.63 M equiv for imidazole moiety; room temperature).

Table I
Result of Potentiometric Titration

Copolym	% VIm	pK_{Im}	n_{Im}	pK_{AA}	n_{AA}
A-81	19	9.36	1.00	6.18	1.48
A-74	26	9.27	1.00	6.28	1.28
A-65	35	9.10	1.28	6.33	1.02

attack. This suggestion is consistent with the discussion on the bending points that we discussed above. The point for the low molecular weight catalysts fall on a straight line. These results suggest that the catalytic activity of the low molecular weight catalyst is mainly caused by the nucleophilicity of the imidazole moiety and that carboxyl and hydroxyl groups do not cooperate with the imidazole moiety in the low molecular weight catalysts. They merely make the pK_{Im} value of the imidazolyl group change. The points for the polymer catalysts also fall on a straight line, but the slope of the line is much larger than that for the low molecular weight catalysts. These results suggest that the catalytic activity of the polymer catalyst is caused by the nucleophilicity of the imidazole moiety and an additional positive effect which cannot be seen in the low molecular weight catalyst. From these results, it will be expected that the carboxyl group in the polymer catalyst has some positive effect on the catalytic activity of the imidazolyl group without a change in the catalytic mechanism.

The slope in the Bronsted plot corresponds to the exponent term in the Bronsted catalyst law,

$$k_{cat} = G_{Im}(K_{Im})^{\beta}$$

The slope in the polymer catalyst is much larger than that in low molecular weight catalyst, so that it would be thought that several imidazolyl groups come together and that they constitute one cavity. On the other hand, as is shown in Table I, n values of the imidazolyl groups in the potentiometric titration are 1.00, 1.00, and 1.28 for A-81, A-74, and A-65 polymer catalysts, respectively. This means that one imidazolyl group practically participates in give-and-take of one proton. It is not likely that several imidazolyl groups gather and constitute the cavity when the substrate approaches the polymer catalysts, though the potentiometric titration is related to the proton. Therefore it is difficult to interpret the larger slope in the Bronsted plot for the polymer catalysts by adopting the concept of the cavity.

Mandel and Jenard[29] showed in the investigation of the dielectric behavior of aqueous polyelectrolyte solution that the dielectric constant of the solution of ionized polymethacrylic acid was larger than that of pure water on account of bound ions. The pK_{AA} values of the carboxyl groups of the polymer catalysts ranged from 6.18 to 6.33, so most carboxyl groups in the polymer catalysts are dissociated at pH 8. Therefore it is thought that the dielectric character and the ionic strength increase in the vicinity of the polymer catalysts. In addition, Kotliar and Morawetz[30] showed that in the titration of poly(acrylic acid) the addition of simple electrolytes drastically reduces the value of the electrostatic free energy of the ionization and that the value increases with the ionization of the carboxyl group. These facts lead to the opinion that the electrostatic effect in the vicinity of the polymer contributes to the increase in the catalytic activity of the poly(4(5)-vinylimidazole-*co*-acrylic acid). That is to say, the addition intermediate which is thought to be more polar than the neutral substrate is stabilized in the high dielectric field and high ionic strength in the vicinity of the polymer, and the leaving of ArO^- from the addition intermediate is facilitated by the electrostatic repulsion between the leaving ArO^- and the carboxylate anions in the polymer. It is expected that these factors will presumably contribute to the increase in the slope in the Bronsted plot for the polymer catalysts. The following facts actually support the existence of the strong anionic field. The n_{AA} values of carboxyl groups in Table I become larger with the content of the carboxyl moiety, where the deviation of the n value from unity is the measure of the magnitude of the electrostatic effect. This shows that the strong anionic field owed to carboxylate anions exists in the polymers.

Figure 3 shows the plots of chemical shifts of the C-2 proton of the imidazolyl group of A-81 against pD. The addition of 0.80 M LiCl leads to the drastic decrease of the pK_{Im} value of the imidazolyl group. This fact also supports the existence of the strong anionic field owed to the carboxylate anions in these polymers. The pK_{Im} value in this NMR titration without LiCl is 9.15. This value is lower by 0.21 than the value shown in Table I. Taking into account D_2O solution and the much higher concentration of the polymer in the NMR titration, this result seems to be reasonable.[31]

As stated above, the pK_{Im} values of the imidazolyl groups in the poly(4(5)-vinylimidazole-*co*-acrylic acid) are much larger than that of low molecular weight imidazolyl derivatives. In order to make clear theoretically the cause of this fact, the calculation has been done, adopting *cis*-urocanic acid–counterion, β-(5-imidazolyl)propionic acid–counterion, and 5-methylimidazole–acetate systems as models of the polymers. In general, the anionic moiety increases and induces the nucleophilicity of the nucleophile directly and indirectly. The fact that the temporary organized water molecules in the vicinity of the polymer transfer the electronic influence

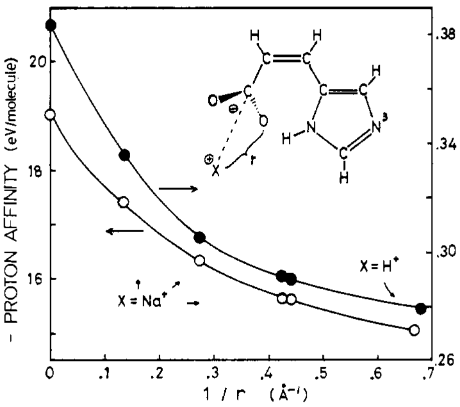

Figure 4. Plots of the proton affinity and the superdelocalizability of the N-3 in *cis*-urocanic acid against the reciprocal of the distance between O of the carboxylate and the counterion. (Counterion = H^+, Na^+. The angle between the plane composed of the carboxylate and that composed of imidazole moiety is 90°.)

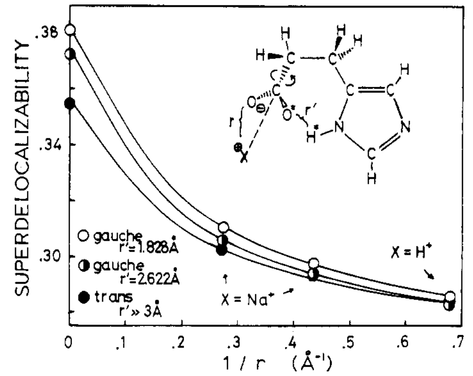

Figure 5. Plots of the superdelocalizability of the N-3 in β-(5-imidazolyl)propionic acid against the reciprocal of the distance between the O of the carboxylate and counterion (counterion = H^+, Na^+).

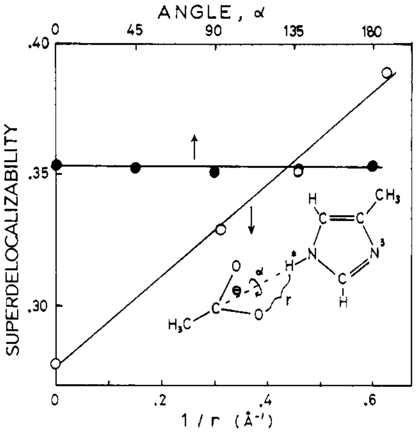

Figure 6. Effects of the distance between H* and O and the angle between the plane composed of carboxylate and that composed of imidazole moieties on the superdelocalizability of the N-3.

smoothly should not be neglected. However, it is plausible that the carboxylate ion affects the -NH in the imidazolyl group predominantly, in the present case. Therefore, we adopted the case that the carboxylate affects the -NH in the imidazolyl group in the calculation.

Figure 4 shows the effect of the approach of the counterion to the carboxylate anion. PA of the N-3 of the imidazole moiety almost runs parallel with Sr of it. This result suggests that PA is almost the same in precision as Sr as the measure of the acidity. As the counterion goes away from the carboxylate anion, −PA and Sr of the N-3 of the imidazole moiety become larger, i.e., the basicity becomes stronger. This result is consistent with the decrease of the pK_{Im} value of the imidazolyl group owing to the addition of LiCl to the A-81 solution, where the addition of LiCl facilitates the approach of the counterions to the carboxylate anions in the polymer. In addition, Figure 5 shows the effect of the approach of the counterion in the β-(5-imidazolyl)propionic acid–counterion system. As the counterion goes further from the carboxylate anion, Sr of the N-3 of the imidazole moiety becomes larger, in any case where a plausible conformation takes place. It will be reasonable to conclude that also in the polymer the approach of the counterion to the carboxylate moiety will cause the decrease of the pK_{Im} value of the imidazolyl group. The smaller the distance between O* of the carboxylate moiety and H* attached to the imidazole moiety is, the larger the Sr of the N-3 of the latter becomes. This result suggests that both the relative position between imidazole and carboxylate moieties and the orientation of the carboxylate moiety have an effect upon the pK_{Im} value of the imidazolyl group as well as upon the position of the counterion.

Figure 6 shows the effect of the electrostatic field owed to the approach of AcO^- on the basicity of the imidazolyl group. The approach of AcO^-, i.e., the approach of the anionic field, contributes to the increase of the basicity of the imidazolyl group, irrespective of the angle between the plane composed of the carboxylate moiety and that composed of the imidazole moiety. This result supports the importance of the anionic field in poly(4(5)-vinylimidazole-*co*-acrylic acid). And it seems to be reasonable that the Sr of the N-3 of the imidazole moiety is almost independent of the angle, taking into account that the variation of the angle little affects the distance between the imidazole moiety and the carboxylate moiety.

It is suggested that the cooperative action of the carboxyl groups in both the low molecular weight and polymer catalysts is not the direct action upon the esters. In the polymer catalysts, the carboxyl groups cause the electrostatic interaction which promotes both the nucleophilic attack of the imidazolyl group on the ester and the breakdown of the addition intermediate, and further cause the increase of the pK_{Im} value of the imidazole moiety. Consequently, the carboxyl groups may have a large effect upon the catalytic activity of poly(4(5)-vinylimidazole-*co*-acrylic acid). In this connection, the importance and the cooperative effect of the strong anionic field in the polymer catalyst containing the imidazolyl group are presented.

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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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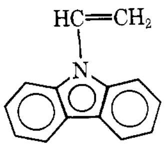
ABSTRACT: *N*-Vinyl-5*H*-benzo[*b*]carbazole and *N*-vinyl-7*H*-benzo[*c*]carbazole (V5BCz and V7BCz, respectively) having more bulky pendant groups than *N*-vinylcarbazole (VCz) were synthesized and polymerized. From the NMR spectra, the glass transition temperatures, and the solubility of the polymers, 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.

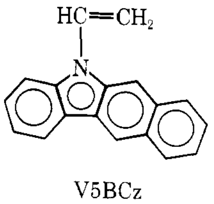
The polymerization of *N*-vinylcarbazole (VCz) has been widely investigated.[1] This monomer can be easily polymerized by many kinds of initiators such as free-radical, cationic, Ziegler–Natta, and electron acceptor ones. Heller et al. have pointed out that VCz with Ziegler–Natta catalyst systems did 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.

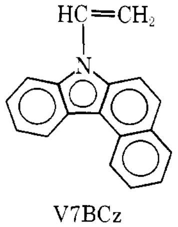
In the present paper, *N*-vinyl-5*H*-benzo[*b*]carbazole (V5BCz) and *N*-vinyl-7*H*-benzo[*c*]carbazole (V7BCz), which have more bulky pendant groups than VCz, were synthesized and polymerized by free-radical, cationic, and Ziegler–Natta initiators. The solubility, the glass transition temperatures,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