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STUDIES OF POLYMER-METAL CATALYSTS. ISOTACTIC AND ATACTIC POLYACRLAMIDOXIME–Co(II) CHELATES AS CATALYSTS FOR THE OXIDATIVE COUPLING OF 2,6-XYLENOL

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ABSTRACT

The catalytic behavior of isotactic (isot) and atactic (at) PAAO-Co(II) chelates as catalysts for oxidative coupling of 2,6-xylenol has been examined. The experimental results show that these reactions follow the Michaelis-Menten mechanism and may be described by

$$E + S_0 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} E{\cdot}S \xrightarrow{k_2} E' + P.$$

Compound E′ is quickly oxidized to E. The second reaction is the rate-determining step. At 30, 35, and 40°C, the rate constant k_2 equals 0.274, 0.304, and 0.450 min^{-1} for 2,6-xylenol-isot-PAAO-Co(II) and 0.189, 0,284, and 0.335 min^{-1} for 2,6-xylenol-at-PAAO-Co(II), respectively. It is obvious that the isotactic chelate is more catalytically active than the atactic one. The negative values found for ΔG show that the formation of the catalyst-substrate complexes may take place spontaneously. This may be mainly attributed to the entropy increase. On the other hand, since the main chains of isot-PAAO-Co(II) are more regularly helicoidal in the reactions, it has lower entropy in the initial

state (E) and the end state (E′) than at-PAAO-Co(II). Thus, ΔS is larger and $\Delta S^{\ddagger}$ is lower for 2,6-xylenol-isot-Co(II) than for 2,6-xylenol-at-PAAO-Co(II).

INTRODUCTION

Polymeric catalysts are often regarded as models of enzymes [1, 2]. It is known that the basic components of enzymes are proteins, the molecules of which are more or less helicoidal. Thus, it is very interesting to examine the effects of conformation of polymer catalysts on their catalytic activities. Drago [3] and Wöhrle [4] found that polymer-supported amine-Co(II) and Schiff's base-Co(II) chelates exhibited good product selectivity or high activity for the oxidative coupling of 2,6-xylenol. It is our purpose to compare the catalytic behavior of isotactic and atactic PAAO-Co(II) chelates as catalysts for the oxidative coupling of 2,6-xylenol.

EXPERIMENTAL

The isotactic polyacrylonitrile (isot-PAN) was prepared by low-temperature close-radiation polymerization (-78°C; γ-rays 4 370 rd/h; 6 X 24 h). The atactic polyacrylonitrile (at-PAN) was prepared by solution polymerization (50°C; solvent DMF; 48 h). The isotactic and atactic polyacrylamidoximes (isot-PAAO and at-PAAO) were obtained by the reaction of isot-PAN and at-PAN with NH_2OH in DMF (50°C; 24 h). The isot- and at-PAAO-Co(II) chelates were prepared by reaction of isot- and at-PAAO with $CoCl_2$ in CH_3OH. All of these compounds and chelates were characterized by IR, NMR, Raman, and x-ray photoelectron spectroscopy (XPS), as well as x-diffraction. The initial oxidative reaction rates were determined by measuring the oxygen consumption.

RESULTS AND DISCUSSION

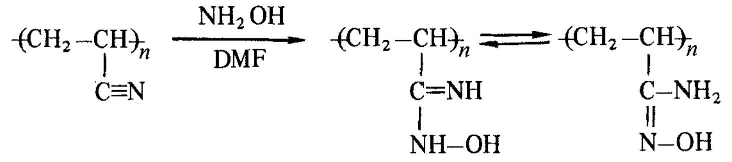
The ^{13}C and [^{1}H] NMR spectra of isot-PAN and at-PAN show the difference between them. The triad microtacticities calculated from the strength of these peaks are shown in Table 1, which confirm that isot-PAN has the higher isotacticity [5]. From the ^{1}H NMR spectra of isot-PAAO and at-PAAO, it is seen that, after substituting H with D_2O, the characteristic peaks of the NH_2 and OH groups disappeared.

TABLE 1. Microtacticity as Determined by NMR in DMSO-d_6

		Triad microtacticity, %		
Polymer	Group	Isotactic	Atactic	Syndiotactic
isot-PAN	$-C{\equiv}N$	46.42	39.91	13.67
	$-CH-$	47.13	37.50	15.37
at-PAN	$-C{\equiv}N$	23.77	52.40	23.84
	$-CH-$	26.48	48.50	25.02

XPS examination of isot-PAAO-Co(II) and at-PAAO-Co(II) show that, compared with that in $CoCl_2$, the chemical shift of $Co2P_{3/2}$ decreased by 1.0 and 0.9 eV for isot-PAAO-Co(II) and at-PAAO-Co(II), respectively, and the chemical shift of Cl2P decreased 1.6 eV for both. These results indicate that chelates have been formed in both cases [6] and that the Cl^- is in a more free state after chelate-formation, in agreement with the reference data [7].

Both isotactic poly-α-olefins and isotactic vinyl polymers, below their melting points T_m, are theoretically regularly helicoidal and, in general, they can crystallize in the solid state. The structure parameters of most isotactic vinyl polymers indicate that they are helicoidal. The x-diffraction spectra of isot-PAN and at-PAN show that the former has the higher crystallinity. Therefore, the isot-PAN should also be helicoidal to some extent. The reaction for preparation of isot-PAAO takes place on the cyano carbon, not on an asymmetrical carbon:



$$\underset{\substack{|\\ C\equiv N}}{\left(CH_2-CH\right)_n} \xrightarrow[\text{DMF}]{NH_2OH} \underset{\substack{|\\ C=NH\\ |\\ NH-OH}}{\left(CH_2-CH\right)_n} \rightleftharpoons \underset{\substack{|\\ C-NH_2\\ \|\\ N-OH}}{\left(CH_2-CH\right)_n} \qquad (1)$$

Since the steric factor is one of the main factors that determine the conformation of organic compounds, the isot-PAAO doubtless contains some helicoidal chain sequences, especially in the solid state. The Raman spectra of isot-PAAO and at-PAAO are shown in Fig. 1. The differences observed between the two PAAO's (e.g., peak shape and strength) agree with those between helicoidal and random biopolymers [8]. On the other hand, at-PAN and at-PAAO are un-

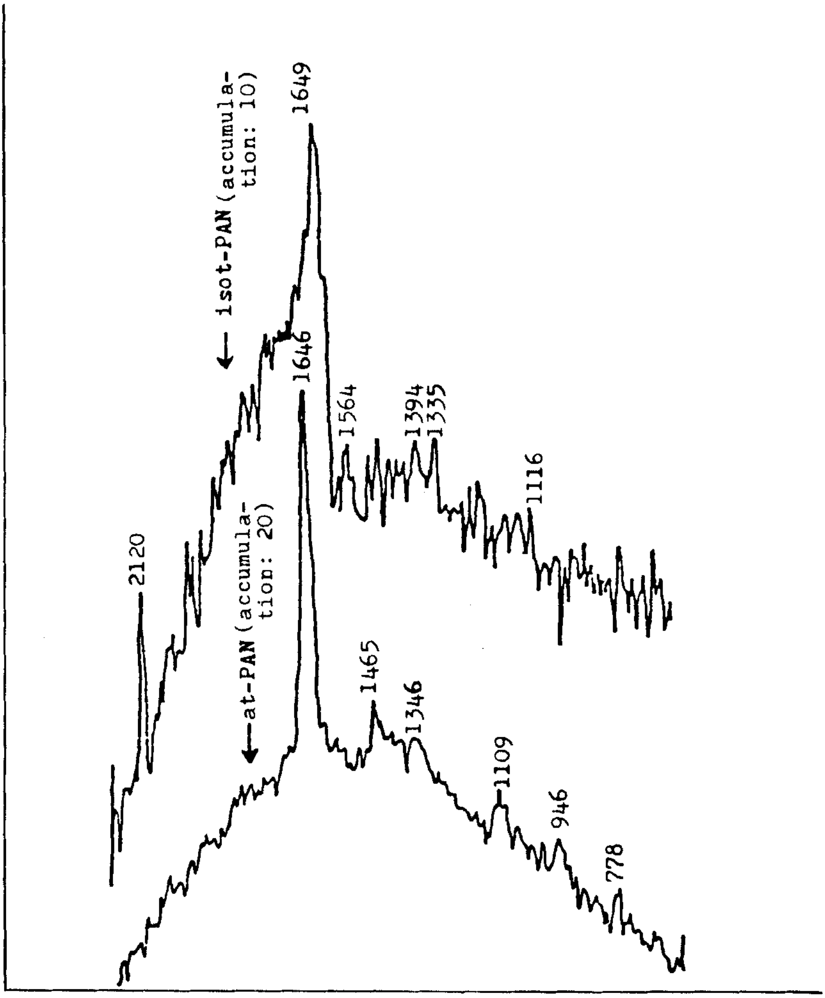


FIG. 1. Raman spectra of isot-PAAO (top) and at-PAAO (bottom).

doubtedly randomly coiled. Since both Co(II) chelates were prepared from polymers in the solid state, they should maintain their original conformation.

We have studied the kinetic behavior of the oxidative coupling of 2,6-xylenol with isot-PAAO-Co(II) and at-PAAO-Co(II) as catalysts. Figures 2(A)

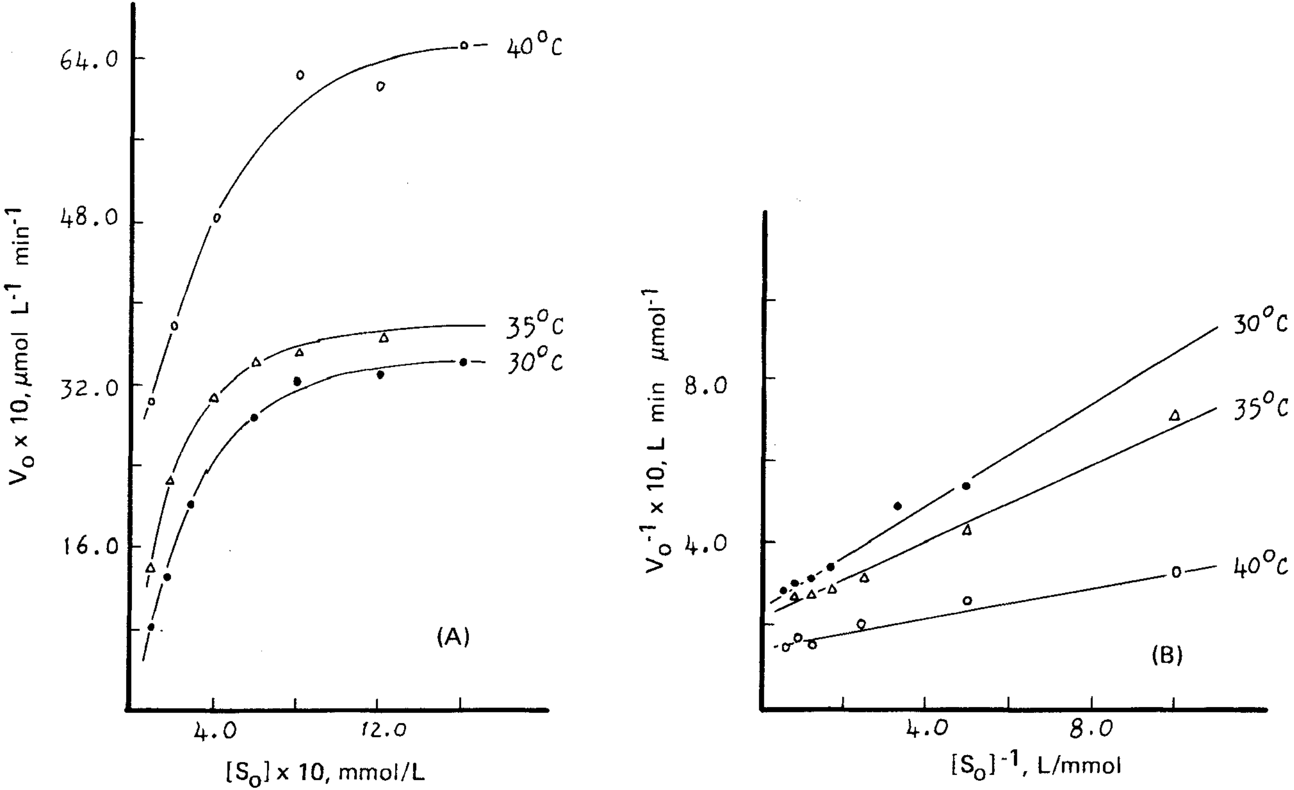


FIG. 2. (A) Catalytic behavior of isot-PAAO-Co(II) for the oxidative coupling of 2,6-xylenol at various temperatures. (B) Lineweaver-Burk plot of (A). pH = 10.5, [Co(II)] = 15 μmol/L.

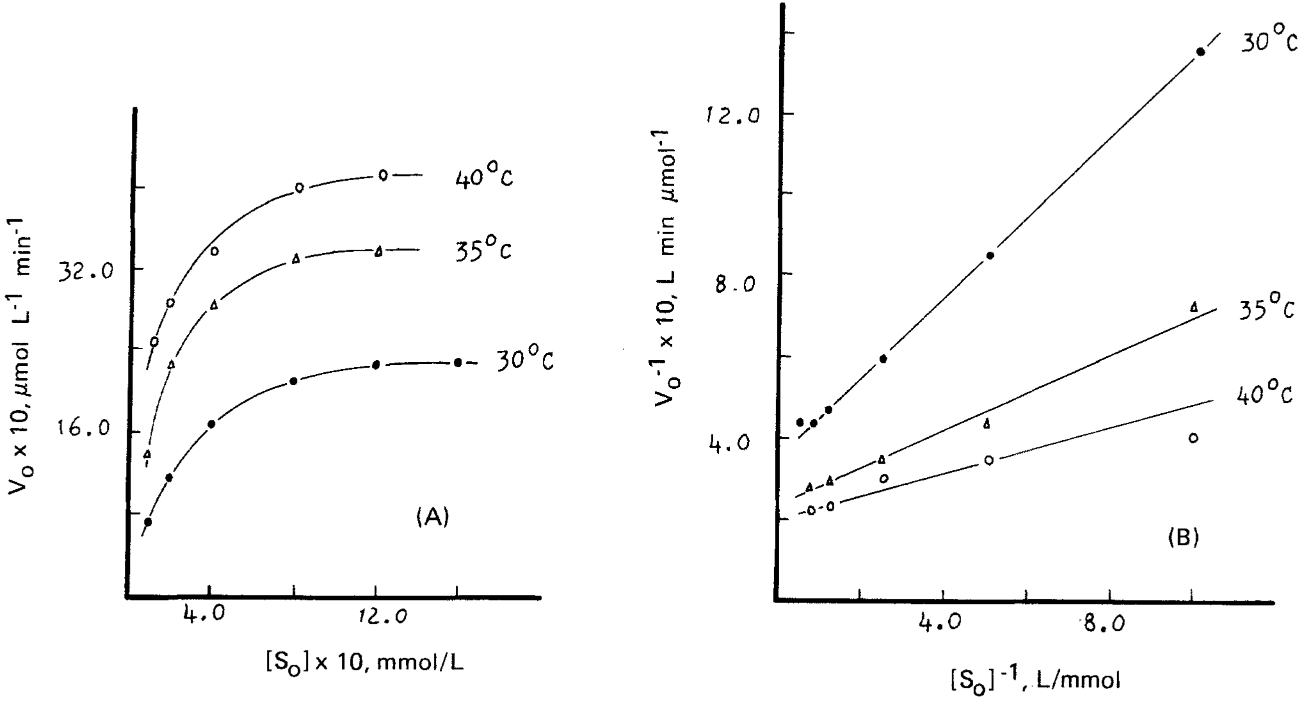


FIG. 3. (A) Catalytic behavior of at-PAAO-Co(II) for the oxidative coupling of 2,6-xylenol at various temperatures. (B) Lineweaver-Burk plot of (A). pH = 10.5, [Co(II)] = 15 μmol/L.

and 3(A) show that substrate saturation takes place. The reactions may be described by

$$\begin{tikzcd} E + S_0 \arrow[r, shift left, "k_1"] & E{\cdot}S \arrow[l, shift left, "k_{-1}"] \arrow[r, "k_2"] & E' + P \arrow[ll, bend left, "k_3\ (O)"] \end{tikzcd} \tag{2}$$

E′ is quickly oxidized to E, and the second step is rate-determining. The corresponding reaction steps may be expressed by

$$\begin{aligned} V_0 &= \frac{V_m[S_0]}{k_m + [S_0]} \\ k_m &= \frac{k_3(k_{-1} + k_2)}{k_1(k_2 + k_3)} \\ V_m &= \frac{k_2 k_3}{(k_2 + k_3)}[E_0] \end{aligned} \tag{3}$$

in which V_0 is the initial reaction rate, V_m is the maximum reaction rate, k_m is the characteristic constant (as in enzyme catalysis), and $[S_0]$ is the initial substrate concentration. This may be transformed into

$$\frac{1}{V_0} = \frac{k_m}{V_m}\frac{1}{[S_0]} + \frac{1}{V_m} \tag{4}$$

Plots of substrate-velocity data according to the Lineweaver-Burk method give straight lines, as shown in Figs. 2(B) and 3(B). Thus, it is clear that these reactions follow a Michaelis-Menten mechanism.

At all temperatures, k_2 for 2,6-xylenol-isot-PAAO-Co(II) is always larger than for 2,6-xylenol-at-PAAO-Co(II) (Table 2). The differences between the k_2 values in the two cases are not very large, but quite real. Thus, it may be concluded that isot-PAAO-Co(II) is a more active catalyst than at-PAAO-Co(II). This may be attributed to the higher concentration of catalyst-substrate complexes which results from the so-called "cooperative effect" between neighboring groups in the former. That is, in isot-PAAO-Co(II), the main chain being helicoidal, the distribution of Co(II) is more regular than in

TABLE 2. Kinetic Parameters[a] for Oxidative Coupling of 2,6-Xylenol

	Catalyst					
	isot-PAAO-Co(II)			at-PAAO-Co(II)		
Temperature, °C:	30	35	40	30	35	40
k_m, mmol/L	0.274	0.220	0.132	0.282	0.201	0.159
V_m, μmol·L^{-1}·min^{-1}	4.11	4.56	6.75	2.84	4.26	5.02
k_2, min^{-1}	0.274	0.304	0.450	0.189	0.284	0.335

[a] Calculated from slopes and intercepts in Figs. 2(B) and 3(B).

at-PAAO-Co(II), and the cooperative effect of the adjacent Co(II) promotes the interaction of active centers with the substrate, resulting in a higher concentration of catalyst-substrate complexes.

The thermodynamic parameters of oxidative coupling reactions of 2,6-xylenol are summarized in Table 3. The negative values of ΔG show that the formation of catalyst-substrate complexes may take place spontaneously, on account of the entropy increase. Since the main chains of isot-PAAO-Co(II) are more regularly helicoidal, the isot-PAAO-Co(II) has lower ΔS values in the initial state (E) and in the end state (E′) than at-PAAO-Co(II). Thus, ΔS is larger and ΔS‡ is lower for 2,6-xylenol-isot-PAAO-Co(II) than for 2,6-xylenol-at-PAAO-Co(II).

The higher k_2 values and the ΔS and ΔS‡ differences agree with the predictions of theory. Thus the experimental facts tally with our suggested mechanism.

TABLE 3. Thermodynamic and Activation Parameters for Oxidative Coupling of 2,6-Xylenol at 30°C

Catalyst	ΔG, kcal/mol	ΔH, kcal/mol	ΔS, $\text{cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	$\Delta G\ddagger$, kcal/mol	$\Delta H\ddagger$, kcal/mol	$\Delta S\ddagger$, $\text{cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
isot-PAAO-Co(II)	-4.91	13.9	62.0	21.0	8.49	-41.0
at-PAAO-Co(II)	-4.93	10.8	52.0	21.2	9.51	-39.0

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