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Esterolyses of *p*-nitrophenyl esters catalyzed by dialkylaminopyridines attached to polyorganosiloxane

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SUMMARY

The present study describes the preparation of polyorganosiloxanes containing dialkylaminopyridines in their side chains (POS-DAAPs) and the use of them as catalysts for esterolyses of *p*-nitrophenyl esters of $CH_3(CH_2)_nCOOH$ (n=0-5). The POS-DAAPs (**4**, **5**) were prepared from poly[(3-chlorocarbonylpropyl)methylsiloxane] (PCCPMS, **1**) and two pyridine derivatives, such as 4-[(2-hydroxyethyl)methylamino]pyridine (HEMAP, **2**) and 4-[4-(2-hydroxyethyl)piperidino]pyridine (HEPP, **3**). Pyridyl groups of POS-DAAPs **4** and **5** were partially quaternized with dimethylsulfate (**6**, **7**) in order to carry out esterolysis in homogenious systems. The esterolyses were examined in methanol/tris(hydroxymethyl)-aminomethane-hydrochloric acid buffer solution (vol. ratio 2/1, pH of buffer solution: 7.5) and analyzed following Michaelis-Menten like kinetics. The second-order rate constants (k_2/K_m) of the esterolyses catalyzed by POSs **6** and **7** were 22-38 fold values of those catalyzed by the corresponding monomolecular catalysts **2** and **3**. In addition, the effects of POSs were discussed from the kinetic, thermodynamic, and activation parameters.

INTRODUCTION

Recently, it has been reported that polymeric catalysts containing 4-aminopyridine supernucleophiles similar to 4-(dimethylamino)pyridine, 4-pyrrolidinopyridine, and 4-piperidinopyridine have been employed to esterolyses of active esters,[1-5] as well as acylation reaction[3,5-12] or various reactions.[8] Mathias *et al.* have reported[5] that copolymers of 4-(diallylamino)pyridine with neutral, anionic, or cationic monomer catalyze the esterolyses of active esters and the esterolyses follow the Michaelis-Menten like kinetics.

On the other hand, polyorganosiloxanes (POSs) have particular characteristics, such as flexibility of the main chain and hydrophobicity of the alkyl side chains.[13,14] We have studied functionalities resulting from introduction of various functional groups into side chains of a POS.[15-18] One of applications which have attracted our interests is the use of POS as a polymeric catalyst, since POSs are considered to be effective in the formation of hydrophobic surroundings and the inclusion of substrates due to the above mentioned characteristics. However, there are the limited number of reports in which a linear POS was used as polymeric catalysts.[19-26] Recently, we have reported[26] homogenious hydroquinone oxidation catalyzed by linear POSs with pendant pyridyl groups complexed with Cu(II) ion and have discussed the efficiency of POS from Michaelis-Menten kinetic, thermodynamic, and activation parameters. The large value of rate constant for electron transfer step was concluded to be due to the hydrophobicity and flexibility of POS.

With these suggestions in mind, in the present article we describe the preparation of POSs with dialkylaminopyridyl moieties from poly[(3-chlorocarbonylpropyl)methylsiloxane] (PCCPMS, **1**) and pyridine derivatives such as 4-[(2-hydroxyethyl)methylamino]pyridine (HEMAP, **2**), 4-[4-(2-hydroxyethyl)piperidino]pyridine (HEPP, **3**) as shown in Scheme 1. In addition, we also report the use of these POSs as polymeric catalysts for the esterolyses of *p*-nitrophenyl esters, which have different length of alkyl chain ($CH_3(CH_2)_nCOOPhNO_2$, n=0-5) and discuss the effect of POS in these esterolyses.

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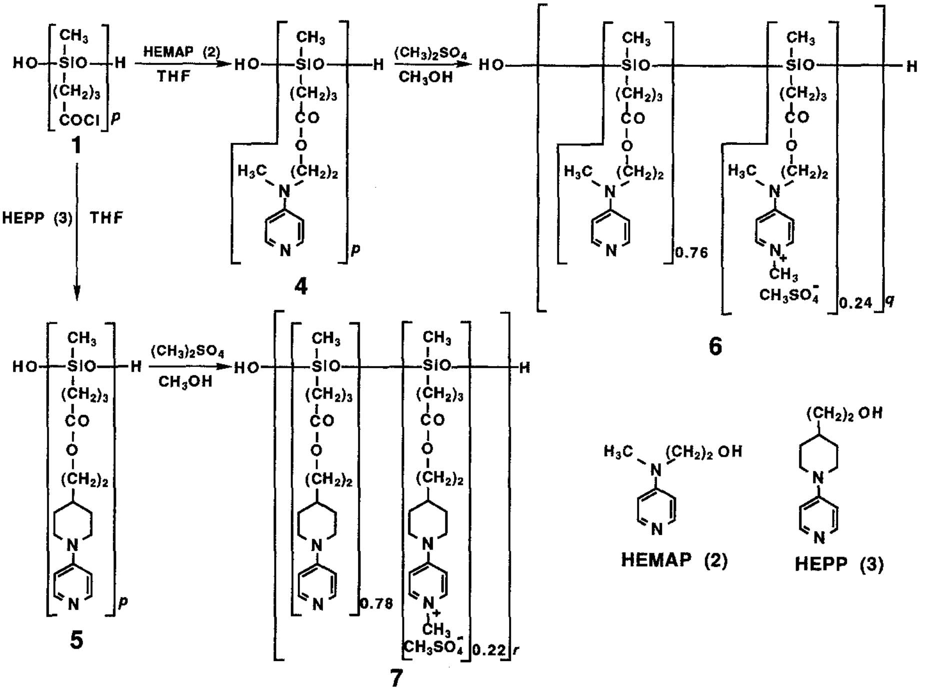

Scheme 1. Pathways for the preparation of POS-DAAPs

EXPERIMENTAL

Materials: All solvents were purchased from Kanto Chemical Co., Inc. and were purified by distillation on suitable dehydrating reagents before use. Water was used after deionization and distillation. Tris(hydroxymethyl)aminomethane and hydrochloric acid, which were used for control of pH, were purchased from Kanto Chemical Co., Inc. and used without further purification. HEMAP (**2**) and HEPP (**3**) were prepared following the method reported by Deratani *et al.*[10] pK_a of **2**: 8.88 (15°C), 8.71 (25°C), 8.65 (35°C); pK_a of **3**: 8.85 (15°C), 8.68 (25°C), 8.63 (35°C) (determined from titration in methanol/water (vol. ratio: 2/1, [KCl]: 5.0 X 10^{-2} mol dm^{-3})). Preparation of PCCPMS (**1**, M_n: 2590, M_w/M_n: 1.49 determined by gel permeation chromatography (GPC) performed on Waters μ-STYRAGEL 10^3 and 10^4 Å using polystyrene standards in THF eluent at ambient temperature) was performed following the method reported elsewhere.[15] *p*-Nitrophenyl acetate (PNPAC, n=0) was purchased from Tokyo Kasei Kogyo Co., Ltd. and purified by twice recrystallization from chloroform. Propanoic, butanoic, pentanoic, hexanoic, and heptanoic acids were obtained from Tokyo Kasei Kogyo Co., Ltd. and used without further purification. *p*-Nitrophenol was purchased from Kanto Chemical Co., Inc. and used without further purification.

Preparation of substrates: Substrates, *p*-nitrophenyl esters of carboxylic acids, except PNPAC were prepared from *p*-nitrophenol and the corresponding carboxylic acid chlorides, which were obtained by distillation from the mixture of carboxylic acid and thionyl chloride. *p*-Nitrophenyl propanoate (PNPPR, n=1) was purified by twice recrystallization from chloroform. *p*-Nitrophenyl butanoate (PNPBU, n=2), *p*-nitrophenyl pentanoate (PNPPE, n=3), *p*-nitrophenyl hexanoate (PNPHX, n=4), and *p*-nitrophenyl heptanoate (PNPHP, n=5) were purified by three time column chromatography packed with silica gel in chloroform eluent.

***Introduction of HEMAP and HEPP into side chains of POS*:** Under a dry nitrogen atmosphere, a dry tetrahydrofuran (THF) solution (100 ml) of 10.26 mmol of HEMAP (**2**) or HEPP (**3**) with 3.42 mmol of 4-(dimethylamino)pyridine was added dropwise to a dry THF solution (30 ml) of 1.65 g (6.84 mmol) of PCCPMS (**1**), and the reaction mixture was stirred for 4 h at ambient temperature. After an addition of 15 ml of water, the clear solution was dialyzed with cellulose tube against water. The produced precipitate was dissolved in 10 ml of chloroform. The solution was dried over anhydrous sodium sulfate and poured into 200 ml of diethylether. Finally, the precipitate was washed with diethylether and dried at ambient temperature *in vacuo*. The complete introduction of **2** or **3** into **1** was confirmed with a comparison of signal areas of ^{1}H-NMR spectra of **4** and **5**. ^{1}H-NMR of **4** ($CDCl_3$, δ, ppm): 0.1 (s, 3H, CH_3-Si), 0.3-0.7 (m, 2H, Si-CH_2-), 1.3-1.9 (m, 2H, Si-CH_2-$\underline{CH_2}$-), 2.1-2.5 (t, 2H, CH_2-COO-), 3.0 (s, 3H, CH_3-N-), 3.4-3.8 (t, 2H, -CH_2-N), 4.0-4.5 (t, 2H, COO-CH_2-), 6.4-6.7 (d, 2H, pyridyl), 8.0-8.4 (d, 2H, pyridyl); IR of **4** (film on NaCl, cm^{-1}, s): 2956, 1734, 1602, 1522, 1389, 1261, 1078, 911, 804; T_g of **4**: -20°C (determined by differential scanning calorimetry (DSC) performed on a Shimadzu DSC-50 at heating rate of 10 °C/min and a helium flow rate of 20 mL/min). ^{1}H-NMR of **5** ($CDCl_3$, δ, ppm): 0.1 (s, 3H, CH_3-Si), 0.3-0.7 (m, 2H, Si-CH_2-), 1.0-2.0 (m, 7H, Si-CH_2-$\underline{CH_2}$- and piperidine), 2.2-2.5 (t, 2H, CH_2-COO-), 2.6-3.1 (t, 2H, -$\underline{CH_2}$-piperidine), 3.3-4.0 (m, 4H, piperidine), 4.0-4.3 (t, 2H, COO-CH_2-), 6.5-6.9 (d, 2H, pyridyl), 8.0-8.5 (d, 2H, pyridyl); IR of **5** (film on NaCl, cm^{-1}, s): 2926, 1732, 1594, 1515, 1394, 1259, 1080, 929, 804; T_g of **7**: -12°C.

***Partial quaternization of POSs 4 and 5*:** Partial quaternization of POS **4** or **5** was carried out in methanol with dimethylsulfate by stirring the reaction mixture at ambient temperature for 12 h. After the reaction, the concentrated solution was poured into diethylether and the products were dried at ambient temperature *in vacuo*. This quaternization reaction proceeds stoichiometrically. The degree of quaternization of pyridyl group was determined from a comparison of signal areas of ^{1}H-NMR spectrum. ^{1}H-NMR of **6** (CD_3OD, δ, ppm): 3.1 (s, $CH_3SO_4^-$), 3.9 (s, CH_3-N^+(pyridyl)), 6.8-7.1 (d, quaternized pyridyl) , and the other signals are as for **4**; pK_a of **6**: 7.90 (15°C), 7.32 (25°C), 7.22 (35°C) (determined from titration in methanol/water (vol. ratio: 2/1, [KCl]: 5.0×10^{-2} mol dm^{-3})). ^{1}H-NMR of **7** (CD_3OD, δ, ppm): 3.1 (s, $CH_3SO_4^-$), 3.9 (s, CH_3-N^+(pyridyl)), 6.9-7.2 (d, quaternized pyridyl), and the other signals are as for **5**; pK_a of **7**: 7.93 (15°C), 7.37 (25°C), 7.25 (35°C).

***Kinetic measurements*:** Esterolysis of *p*-nitrophenyl ester was carried out in methanol/tris(hydroxymethyl)aminomethane-hydrochloric acid buffer solution (pH 7.5, vol. ratio 2/1) with 5.0×10^{-2} mol dm^{-3} of potassium chloride at 15, 25, 35 ± 0.2 °C. First, a solution of a POS-DAAP (5.0×10^{-4} mol dm^{-3} pyridyl unit) and a methanol solution of a substrate were prepared. The concentrations reported were those of the final reaction mixture. 3 mL of a catalyst solution and 1 mL of a buffer solution was mixed in a quartz cell of 1 cm optical pathlength. Next, 2 mL of a methanol solution of a substrate was added to the quartz cell. The esterolysis, which produces carboxylic acid and *p*-nitrophenol, was followed spectrophotometrically on a thermostated Hitachi Model U-2000 spectrophotometer by monitoring the absorption at 400 nm. The velocity of the esterolysis (V_0)was evaluated from

$$V_0 = [p\text{-nitrophenol}]/t = (A_t - A_0) / (\varepsilon \times d \times t) - V_{\mathrm{blank}} , \qquad (1)$$

where A_t is the observed absorption at time t, A_0 is the observed absorption at t=0, ε is the extinction coefficient of *p*-nitrophenol at 400 nm: 5920 dm^3 mol^{-1} cm^{-1}, d is the pathlength in cm, and V_{blank} is the velocity in the absence of a catalyst. It has been confirmed that V_{blank} was negligible compared with the velocity in the presence of a catalyst in all cases. The initial esterolysis rate was evaluated from [*p*-nitrophenol]/t in the range where variation in absorption follows a straight line.

RESULTS AND DISCUSSION

***Preparation of 4 and 5*:** The pathways for the syntheses of POSs with pendant DAAP groups and the compositions of POS-DAAPs **4**-**7** are shown in Scheme 1. Introduction of **2** or **3** into side chains of **1** was performed with the introduction ratio of 100%. This may be due to the strong nucleophilicity of **2** and **3**. Polymers **4** and **5** are soluble in chloroform, THF/ water (vol. ratio 9/1), and swelling in methanol and THF, but insoluble in the solvent for esterolysis, methanol/buffer solution (*p*H 7.5, vol. ratio 2/1). For the purpose of increasing the solubility in the solvent for esterolysis, pyridyl groups of polymers **4** and **5** were partially quaternized with dimethylsulfate. By the way, POS-DAAPs **4** and **5** have the relatively low grass transition temperatures (see EXPERIMENTAL), though the bulky moieties such as HEPP are introduced, due to the long flexible spacers between a polymer backbone and a pyridyl group in the end of the side chain.

***Esterolyses of p-nitrophenyl esters*:** The kinetics of esterolyses of *p*-nitrophenyl esters catalyzed by POSs **6** and **7** was examined at three temperatures with [*p*-nitrophenyl ester] » [catalyst]. Under these conditions, the esterolyses catalyzed by polymeric catalysts follow a Michaelis-Menten relationship involving formation of a catalyst-substrate complex (Eq. 2).

$$C \quad + \quad S \quad \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \quad C{\bullet}S \quad \xrightarrow{k_2} \quad C \quad + \quad P \qquad (2)$$

where C, S, and P represent catalyst, substrate, and product, respectively, k_1 is the rate constant for formation of a catalyst-substrate complex, k_{-1} is that for the reverse reaction, and k_2 is that for product formation. As an example, Fig. 1 shows the dependence of the velocity (V_0) of esterolysis of PNPAC (n=0) catalyzed by polymer **7** on the substrate concentration ($[S]_0$) at three temperatures. The data were analyzed by the double reciprocal V_0^{-1} versus $[S]_0^{-1}$, Lineweaver-Burk plots, with

$$1/V_0 = K_m / (k_2[C]_0[S]_0) \ + \ 1/(k_2[C]_0) \qquad (3)$$

$$K_m = k_1 / (k_{-1} + k_2) \qquad (4)$$

where $[C]_0$ is the initial effective concentration of the POS-DAAP catalyst and K_m is Michaelis constant defined by Eq. 4. Lineweaver-Burk plots of Fig. 1 are shown in Fig. 2, which provide straight lines. It has been confirmed that the esterolyses of the other *p*-nitrophenyl esters in this report also provide straight lines in V_0^{-1} versus $[S]_0^{-1}$ plots. Kinetic parameters at 25 ± 0.2°C obtained from Lineweaver-Burk plots are given in Tab. 1.

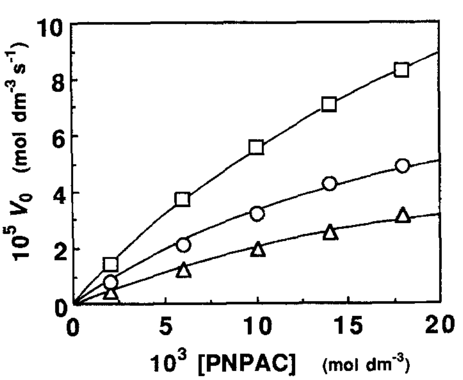

Figure 1. Dependence of the velocity of esterolysis of PNPAC (n=0) catalyzed by POS **7**; (△): 15°C, (○): 25°C, (□): 35°C.

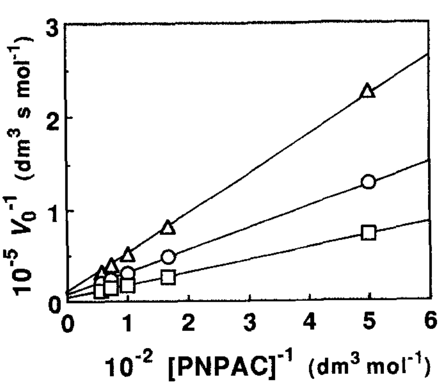

Figure 2. Lineweaver-Burk plots of Fig.1; (△): 15°C, (○): 25°C, (□): 35°C

Table 1. Kinetic parameters for the esterolyses of *p*-nitrophenyl esters catalyzed by POS-DAAPs

Cat.	n[a]	$10^2 K_m$ mol dm^{-3}	$10 k_2$ s^{-1}	k_2/K_m dm^3 mol^{-1} s^{-1}
6	0	6.70	3.00	4.48
6	1	7.50	2.81	3.75
6	2	8.80	1.96	2.23
6	3	10.1	2.24	2.22
6	4	8.30	2.29	2.76
6	5	8.28	2.38	2.87
7	0	3.72	3.04	8.17
7	1	6.89	2.62	3.80
7	2	11.1	2.47	2.23
7	3	10.8	2.49	2.31
7	4	9.30	2.57	2.76
7	5	9.74	2.55	2.62

[a] Number of methylene group of a substrate ($CH_3(CH_2)_nCOOPhNO_2$)

Table 2. Second-order rate constants for the esterolyses of *p*-nitrophenyl esters catalyzed by **2** and **3**

Cat.	n[a]	$10 k$ dm^3 mol^{-1} s^{-1}
2	0	1.59
2	1	1.42
2	2	0.98
2	3	1.00
2	4	1.04
2	5	0.94
3	0	2.17
3	1	1.36
3	2	1.00
3	3	1.01
3	4	1.10
3	5	0.94

[a] See footnote a in Table 1

Table 3. Activation parameters for the esterolyses of *p*-nitrophenyl esters at 25 ± 0.2 °C

Cat.	n	$\Delta G^{\neq}$[a] kJ mol^{-1}	$\Delta H^{\neq}$[a] kJ mol^{-1}	$\Delta S^{\neq}$[a] J mol^{-1} K^{-1}
6	0	69.3 ± 0.1	31.0 ± 0.8	-128 ± 4
6	1	69.8 ± 0.1	7.16 ± 0.23	-209 ± 3
6	2	71.1 ± 0.1	0.68 ± 0.10	-235 ± 3
6	3	71.0 ± 0.1	1.33 ± 0.10	-235 ± 3
6	4	70.5 ± 0.1	2.05 ± 0.12	-230 ± 3
6	5	70.4 ± 0.1	22.0 ± 0.7	-162 ± 3
7	0	67.8 ± 0.1	41.6 ± 1.0	-88 ± 4
7	1	69.7 ± 0.1	4.00 ± 1.36	-220 ± 6
7	2	71.1 ± 0.1	1.56 ± 0.09	-223 ± 2
7	3	71.0 ± 0.1	1.02 ± 0.08	-233 ± 2
7	4	70.5 ± 0.1	2.55 ± 0.11	-227 ± 2
7	5	70.6 ± 0.1	22.3 ± 0.6	-162 ± 3
2	0	77.6 ± 0.1	20.7 ± 0.5	-191 ± 3
2	1	77.9 ± 0.1	4.88 ± 0.16	-245 ± 2
2	2	78.8 ± 0.1	0.58 ± 0.06	-262 ± 1
2	3	78.7 ± 0.1	1.02 ± 0.06	-260 ± 2
2	4	78.6 ± 0.1	0.92 ± 0.07	-260 ± 2
2	5	78.8 ± 0.1	14.4 ± 0.4	-216 ± 2
3	0	76.8 ± 0.1	20.2 ± 0.5	-190 ± 3
3	1	78.0 ± 0.1	3.70 ± 0.13	-249 ± 1
3	2	78.7 ± 0.1	0.55 ± 0.07	-262 ± 1
3	3	78.7 ± 0.1	0.17 ± 0.06	-263 ± 2
3	4	78.5 ± 0.1	2.89 ± 0.11	-254 ± 2
3	5	78.9 ± 0.1	13.7 ± 0.4	-219 ± 3

[a] In the case of cat. **6** and **7**, activation parameters $\Delta X^{\neq}$ were evaluated as the sum of ΔX_m and $\Delta X_2^{\neq}$ calculated from K_m and k_2 at different temperatures, respectively (X= G, H, or S). In the case of **2** and **3**, activation parameters were evaluated from k in Tab. 2 at different temperatures.

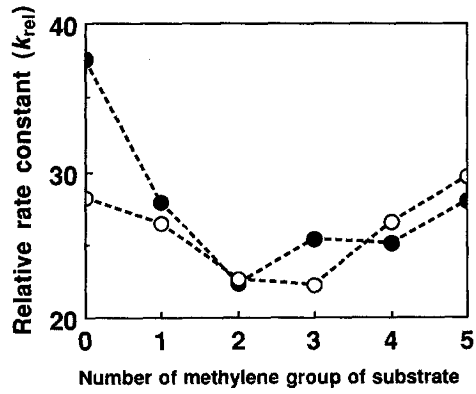

Figure 3. Dependence of relative rate constant (k_{rel}) on number of methylene group of substrate (n); (○): **6**, (●): **7**.

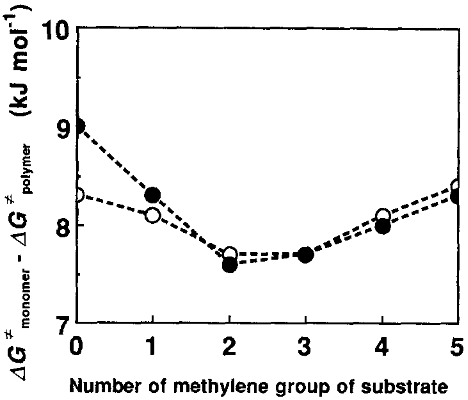

Figure 4. Plots of difference in activation free energy between monomeric and polymeric catalysts *versus* number of methylene group of substrate (n); (○): **6**, (●): **7**.

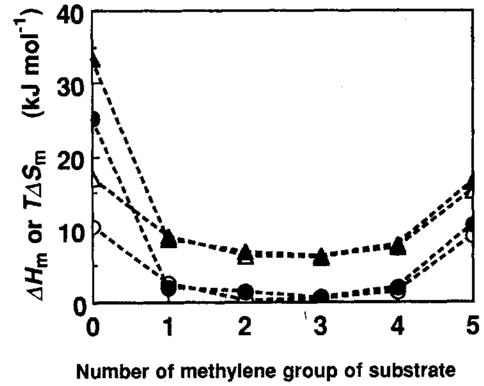

Figure 5. Dependence of enthalpy and entropy change for substrate-binding process on number of methylene group of substrate (n); (○): ΔH_m of **6**, (△): $T\Delta S_m$ of **6**, (●): ΔH_m of **7**, (▲): $T\Delta S_m$ of **7**.

Michaelis constants in the present report have relatively large values, i. e. the order of 10^{-1}-10^{-2} mol dm^{-3}. Tab. 2 provides the values of second-order rate constant of the esterolyses, which correspond to k_2/K_m in Tab. 1, catalyzed by low molecular weight analogues **2** and **3** at 25 ± 0.2°C. Fig. 3 shows relationship between the ratio of k_2/K_m to the corresponding second-order rate constants (k_{rel}) and number of methylene group of a substrate (n). The maximum value of k_{rel} in this report is 37.6 (Sub.: PNPAC (n=0), Cat.: POS **7**). Second-order rate constants in the case of low molecular weight analogue catalysts decreased with increase in length of alkyl chain of substrates. When POS catalysts were used, in the case of n=0-3, values of k_2/K_m and k_{rel} tend to decrease with increase in n, possibly due to the steric hindrance. On the other hand, in the case of n=4, 5, those of k_2/K_m and k_{rel} increase with increase in n. This may be because the effect of hydrophobic interaction between POS catalyst and a substrate with long alkyl chain become remarkable.

Tab. 3 gives activation parameters for the esterolyses. In the case of POS catalysts, activation parameters were evaluated as the sum of thermodynamic parameters for the substrate-binding process (ΔX_m, X=G: free energy, H: enthalpy, S: entropy) and activation parameters for the product formation step ($\Delta X_2^{\neq}$), which are calculated from the values of K_m and k_2 at three temperatures, respectively. In all cases in the present report, the values of activation free energy ($\Delta G^{\neq}$) for POS catalysts were smaller than those for the corresponding low molecular weight analogue catalysts. This finding is due to the negative free energy change for the substrate-binding process. Fig. 4 shows plots of difference in $\Delta G^{\neq}$ between monomeric and polymeric catalysts *versus n*, the trend of which is compatible with that of plots of $k_{\rm rel}$ *versus n*. Fig. 5 shows dependence of the thermodynamic parameters for the substrate-binding process on number of methylene group of a substrate (n). The values of $\Delta S_{\rm m}$ and $\Delta H_{\rm m}$ decrease with increase in n during small value of n, but in the case of n=4, 5, these values increase. This result may be interpreted as follows: in the substrate-binding process, inclusion of *p*-nitrophenyl esters more bulky than solvent molecules would require polymer conformation changes. A small amount of exchange of solvent molecules with substrates is considered to decrease the values of $\Delta H_{\rm m}$ and $\Delta S_{\rm m}$, possibly due to the steric hindrance of substrates. However, additional increase in the value of n would makes hydrophobic interaction between POS catalysts and substrates remarkable and result in increase in the values of $\Delta H_{\rm m}$ and $\Delta S_{\rm m}$.[27,28] Namely, the use of a substrate with long alkyl chain makes the effect of hydrophobicity of POS clearly appear.

CONCLUSIONS

In the present study, we achieved the preparation of polyorganosiloxanes with side-chain dialkylaminopyridyl moieties. These polymers are useful as catalysts for esterolyses of *p*-nitrophenyl esters. The second-order rate constants of the esterolyses catalyzed by them were 22-38 fold values of those catalyzed by the corresponding monomolecular catalysts. Relative rate constants decreased with increase in length of alkyl chain of a substrate during C_1-C_4, due to the steric hindrance. Additional increase in length of alkyl chain of a substrate, C_5, C_6, increased the relative rate constants, because hydrophobic interaction between a polymeric catalyst and a substrate become remarkable.

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