The oxidation of hydroquinone catalysed by poly(4-vinyl pyridine-co-N-vinyl pyrrolidone)-Cu(II) complexes: effect of the copolymer composition distribution on the catalytic activity

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4-Vinyl pyridine–N-vinyl pyrrolidone copolymers having various copolymer compositions and composition distribution were prepared. The latter was estimated by means of Spinner's equation. The copolymer prepared during the early stage of copolymerization was a random like copolymer, and the polymer polymerized completely was a blend like copolymer. Cu(II) complexes of the prepared copolymers had sufficient catalytic activity for the oxidation of hydroquinone, depending upon their composition distribution and the composition. The Cu(II) complex of the random like copolymer showed a higher catalytic activity than that of the blend like copolymer, even if the copolymers had a similar composition.

INTRODUCTION

A biopolymer catalyst, such as an enzyme, exhibits high selectivity and activity for several reactions *in vivo*. It is well known that their specificities are caused by an intramolecular co-operative catalysis between functional groups in the enzyme. Recently, artificial polymer catalysts having the intramolecular co-operative effect between their functional groups were synthesized[1-5]. To study the intramolecular co-operative effect, it is important to consider the effect of the composition distribution of the functional groups in the polymer catalysts on their catalytic activity as well as the effect of their composition. However, there have been few studies on the relationship between the distribution of the functional groups in the polymer catalyst and their activity[2].

Previously, we reported that the distribution of the functional groups in 4-vinyl pyridine (VPy)–N-vinyl pyrrolidone (NVP) copolymers such as random, graft, block and blend copolymers affected the catalytic activity of their Cu(II) complexes for the oxidation of hydroquinone (HQ)[6,7], where the NVP units around the VPy units as catalytic sites increased the catalytic activity of VPy–NVP copolymer–Cu(II) complexes. However, even if the copolymer catalysts are random copolymers having the same copolymer composition, when the monomers have different monomer reactivity ratios, the prepared copolymers have different composition distributions. Therefore, each functional group in the random copolymer catalysts does not exist in the polymer main chain at random. In this paper, we report the composition distribution of VPy–NVP random copolymers estimated by means of Spinner's equation[8], and clarify the relationship between the distribution of the functional groups along the random copolymers and their catalytic activities.

EXPERIMENTAL

Materials

Vpy and NVP were purified by distillation just before polymerization. 2,2'-Azobisisobutyronitrile (AIBN) was purified by recrystallization twice from methanol (MeOH). Dimethyl sulfoxide (DMSO) was distilled over calcium hydride. HQ and $CuSO_4 \cdot 5H_2O$ were obtained commercially and used without further purification.

Radical copolymerization of VPy with NVP

A given amount of VPy, NVP, AIBN and DMSO were charged in a Pyrex ampoule. The ampoule was then degassed by the conventional freeze–thaw technique, and was sealed off under vacuum. Polymerization was carried out at 60°C for a given time. The content of the ampoule was then poured into excess diethyl ether. The precipitated polymers were purified twice by reprecipitation from a MeOH/diethyl ether system. The copolymer composition was determined by the absorbance of pyridine units at 256 nm in MeOH by using a Hitachi-U-2000 spectrophotometer.

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Oxidation of HQ

The polymer–Cu(II) complex was prepared by stirring VPy polymers and CuSO$_4$ at 25°C for 30 min in H$_2$O/MeOH just before oxidation. Then pure oxygen was bubbled into the solution. The oxidation started immediately after HQ was added. The pseudo first-order rate constant (k_{obsd}) of the oxidation was estimated by the increase of the absorbance at λ_{max} (245 nm) of benzoquinone (BQ).

Potentiometric titration

The concentration of free Cu(II) ions was measured by a Horiba M-8 pH meter equipped with a Horiba 8006-06T Cu(II) electrode; $[Cu(II)]_0 = 4.4 \times 10^{-5}$ M, in H$_2$O/MeOH (1/1 v/v) mixed solvent.

RESULTS AND DISCUSSION

Copolymerization of VPy with NVP

DMSO solution copolymerization of VPy with NVP was performed with AIBN at 60°C. The results of the copolymerization during the early stage ($\leqslant 4\%$ conversion) are shown in *Table 1*. The comonomer–copolymer composition curves are shown in *Figure 1*.

Table 1 Copolymerization of VPy with NVP[a]

Monomers				Copolymers
[VPy] (M)	(NVP) (M)	Time (min)	Conv. (%)	[VPy][b] (mol%)
0.25	4.75	75	2.9	58
0.50	4.50	60	3.0	69
1.00	4.00	55	1.9	81
1.50	3.50	50	2.2	89
2.00	3.00	45	3.9	91
2.50	2.50	25	1.0	93
3.00	2.00	22	1.9	97
3.50	1.50	20	2.1	99
4.00	1.00	17	3.4	98
4.50	0.50	15	2.8	100

[a] Polymerized in DMSO (10 ml) at 60°C, [AIBN] $= 1.0 \times 10^{-2}$ M
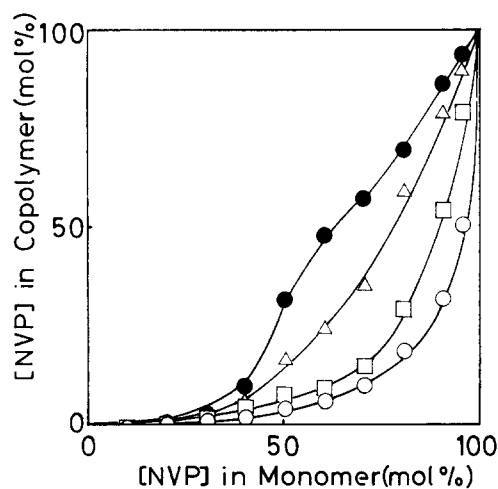[b] Determined by absorbance of pyridine units at 256 nm

Figure 1 Comonomer–copolymer composition curves for the copolymerization of VPy with NVP. Polymerization carried out at 60°C in DMSO (10 ml), [AIBN] = 0.01 M, [monomer] = 5 M. Conversion: (O) 10.0±1.7%; (□) 25.0±2.1%; (△) 52.0±5.1%; (●) 73.0±2.9%

Table 2 Preparation of the same origin copolymers[a]

Time (h)	Conv. (%)	Copolymers [VPy][b] (mol%)
3.0	11.6	64
7.0	23.7	46
8.0	49.1	22
9.5	75.1	14

[a,b] As in *Table 1*, except for [VPy] = 4.5 M, [VPy] = 0.5 M

Monomer reactivity ratios of VPy and NVP were determined from the results in *Table 1* by using the non-linear least squares method[9]. The obtained values ($r_{VPy} = 15.46$, $r_{NVP} = 0.02$) are approximately equal to the values ($r_{VPy} = 9.06$, $r_{NVP} = 0.05$) calculated from the reported e values ($e_{VPy} = -0.28$, $e_{NVP} = -1.14$) and Q values ($Q_{VPy} = 1.00$, $Q_{NVP} = 0.14$)[10].

A non-conjugative monomer (NVP) hardly participated in the early stage of the copolymerization with a conjugative monomer (VPy). However, as the copolymerization proceeded, the NVP content in the copolymers increased in response to the residual NVP monomer content. These results indicated that the composition of the copolymer prepared during the early stage of copolymerization differed greatly from that of the copolymer prepared during the final stage.

Copolymer composition distribution

In order to prepare copolymers with various compositions and composition distributions, VPy was copolymerized with NVP by the following three methods:

1. Copolymers having several copolymer compositions were prepared under the same initial conditions, i.e. the same initial comonomer composition (VPy = 10 mol%). We call these copolymers 'same origin' copolymers.
2. Copolymers having several compositions were prepared at low conversion (< 10%). We call these copolymers 'low conversion' copolymers.
3. Copolymers having similar VPy content (~70 mol%) were prepared at several copolymer conversions. We call these copolymers 'same grade' copolymers.

The results of the copolymerization of same origin copolymers are shown in *Table 2*. The copolymers prepared during the early stage of the copolymerization had high VPy content, but when the copolymerization was performed to high conversion (75%), the copolymers had a similar composition ([VPy] = 14 mol%) to the initial comonomer composition ([VPy] = 10 mol%).

The copolymer composition distribution, dm/dF_1, at a given copolymer composition was estimated statistically based on the determined monomer reactivity ratios, r_{VPy} and r_{NVP}, by using Spinner's equation:

$$\frac{dm}{dF_1} =$$

$$\frac{(1-m)[f_1^2(2-r_1-r_2)-2f_1(1-r_2)-r_2]^3}{[f_1^2(r_1+r_2-2r_1r_2)-2f_1r_2(1-r_1)+r_2][f_1(2-r_1-r_2)-(1-r_2)]f_1(1-f_1)}$$

where m is the copolymer conversion to time t, F_1 is an instantaneous polymer mole fraction for M_1, f_1 is an instantaneous monomer mole fraction for M_1, and r_1 and r_2 are the monomer reactivity ratios for monomers M_1 and M_2, respectively. The resulting normalized composition distributions are shown in *Figure 2*. The

copolymers prepared during the early stage of the copolymerization had a narrow composition distribution (*Figure 2a*). Then, the distribution spread as the copolymerization proceeded. Finally, the copolymer became a mixture of a small amount of copolymer having high VPy content and a large amount of copolymer like homo PNVP (*Figure 2d*), so that it had high NVP content. These calculated results are in agreement with the experimental results shown in *Table 2*.

The low conversion copolymers were prepared under several conditions. The results are shown in *Table 3*. Their copolymer composition distributions were estimated and are shown in *Figure 3*. Their distributions spread with a decrease in VPy content in the copolymers (*Figure 3d*). The broadening, however, was small compared with that of the same origin copolymers.

The results of the copolymerization of the same grade copolymers are shown in *Table 4*, and their estimated composition distributions are shown in *Figure 4*. They had a similar copolymer composition, but their distributions differed greatly from each other. The copolymer (*Figure 4a*) had a narrow copolymer composition distribution around 70 mol% VPy (*Figure 4a*), when it was prepared under conditions where the initial mole fraction of VPy was low ([VPy] = 10 mol%). However, when the copolymer was prepared under conditions where the initial mole fraction of VPy was 70 mol%, it was a blend copolymer of homo PNVP and copolymer with high VPy content (≥90 mol%) (*Figure 4d*).
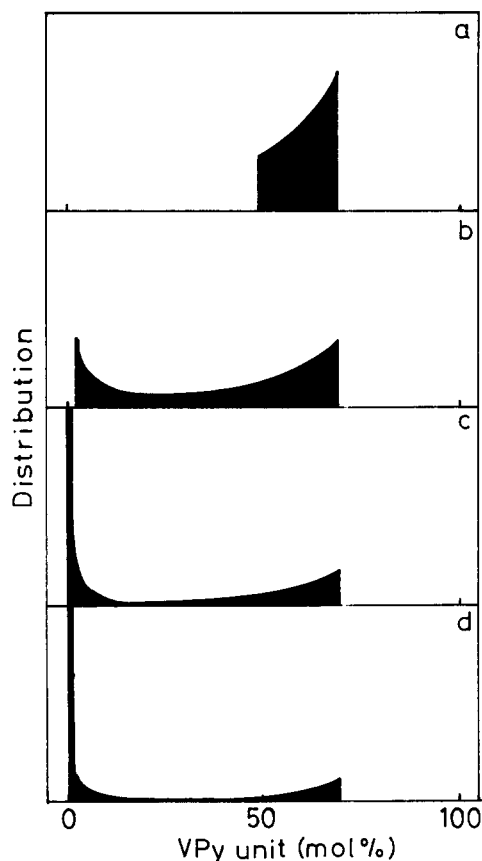
Table 3 Preparation of the low conversion copolymers[a]

Monomers				Copolymers
[VPy] (M)	(NVP) (M)	Time (min)	Conv. (%)	[VPy] (mol%)
1.00	4.00	2.1	8.5	81
0.50	4.50	3.0	9.5	68
0.25	4.75	3.5	9.3	50
0.15	4.85	2.1	9.3	33

[a] Polymerized in DMSO (10 ml) at 60°C, [AIBN] = 1.0×10^{-2} M

Table 4 Preparation of the same grade copolymers[a]

Monomers				Copolymers
[VPy] (M)	[NVP] (M)	Time (min)	Conv. (%)	[VPy] (mol%)
0.5	4.5	3.0	9.5	68
1.0	4.0	9.8	28.8	71
1.5	3.5	14.0	47.4	66
2.5	2.5	20.5	75.7	69
3.5	1.5	45.0	99.3	70

[a] Polymerized in DMSO (10 ml) at 60°C, [AIBN] = 1.0×10^{-2} M

Figure 2 Calculated copolymer composition distributions of the same origin copolymers: (a) [VPy in copolymer] = 64 mol%, conversion = 11.6%; (b) [VPy in copolymer] = 46 mol%, conversion = 23.7%; (c) [VPy in copolymer] = 22 mol%, conversion = 49.1%; (d) [VPy in copolymer] = 14 mol%, conversion = 75.1%
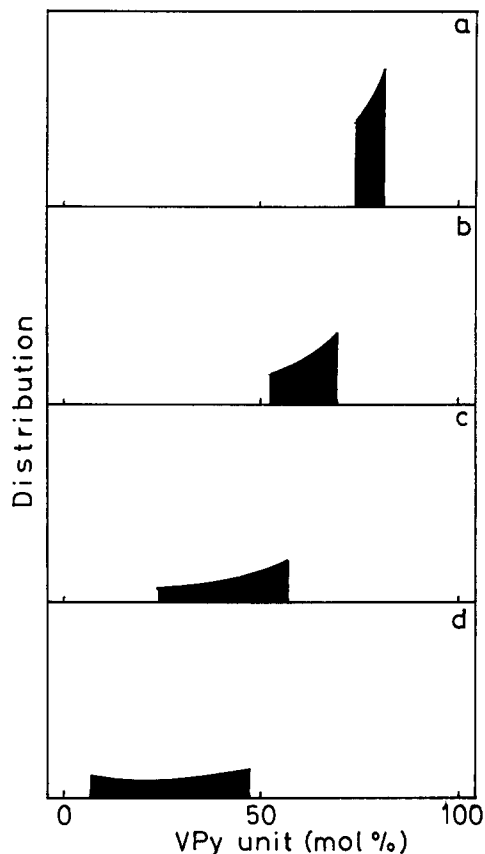

Figure 3 Calculated copolymer composition distributions of the low conversion copolymers. [VPy in copolymer]: (a) 81 mol%; (b) 68 mol%; (c) 50 mol%; (d) 33 mol%

These results show that there is a remarkable difference between the composition of the copolymers prepared during the early stage of the copolymerization and that of the copolymer prepared during the final stage, when VPy is copolymerized with NVP having a very different monomer reactivity ratio from that of VPy. The
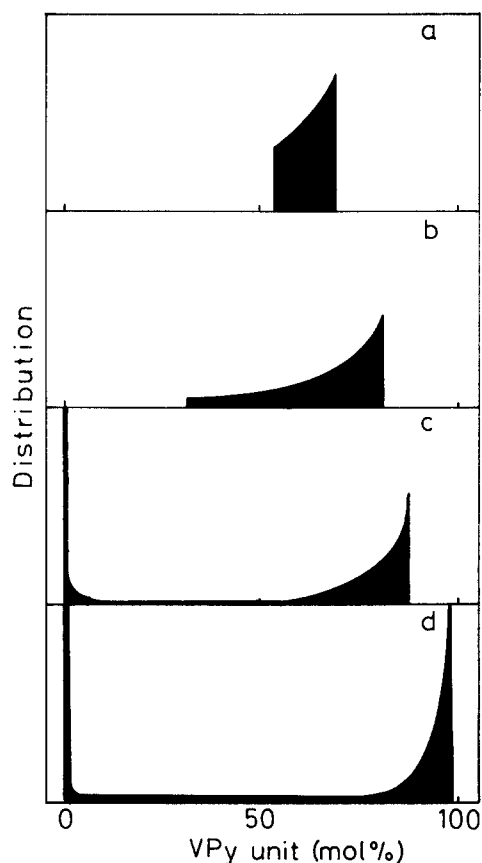
Figure 4 Calculated copolymer composition distributions of the same grade copolymers ([VPy in copolymers] = 69 ± 3 mol%): (a) [VPy in monomers] = 10 mol%, conversion = 9.5%; (b) [VPy in monomers] = 20 mol%, conversion = 28.8%; (c) [VPy in monomers] = 30 mol%, conversion = 43.4%; (d) [VPy in monomers] = 70 mol%, conversion = 99.3%

copolymer polymerized until the final stage is a blend copolymer consisting of copolymers with several compositions. It became clear that the VPy–NVP copolymers prepared under several conditions had several composition distributions, even if they had a similar copolymer composition.

Influence of composition distribution on catalytic activity

All of the Cu(II) complexes of the prepared VPy–NVP copolymers had sufficient catalytic activity for the oxidation of HQ. The catalytic activities of the low conversion copolymers and the same origin copolymers are plotted as a function of NVP content in *Figure 5*. The catalytic activity of the low conversion copolymers increased with increase of NVP content similar to previous results[6], indicating that the influence of the NVP units on the catalytic activity appears in the oxidation catalysed by the copolymer having a narrow composition distribution.

In the study of complexation of Cu(II) ions by using a Cu(II) ion selective electrode, homo PVPy ligand was found to bind more Cu(II) ions than poly(VPy-*co*-NVP) (71) ligands (*Figure 6*). It was reported that four pyridine units co-ordinated rapidly with one Cu(II) ion in the homo PVPy–Cu(II) system[11], and that a complete complexation of four pyridine units with a Cu(II) ion may be unfavourable for the one electron transfer to the Cu(II) ion from HQ[12]. Since the NVP units near the pyridine units may hinder the formation of the stable

complex of pyridine units with Cu(II) ions, the VPy–NVP copolymers become unsaturated complexes which are highly active complex catalysts. Contrary to these results, the catalytic activity of the same origin copolymers was independent of their copolymer composition.

To clarify these phenomena by means of their composition distribution, the composition distributions of only VPy units in the same origin copolymers are shown in *Figure 7*. These results show that most of the VPy monomers were consumed during the early stage of the copolymerization, showing that the copolymers were a mixture of copolymers having similar VPy contents, acting as true catalytic sites, and homo PNVP, with no catalytic activity. Therefore, their catalytic activities may be independent of the copolymer composition. In comparison with the same origin copolymers, the low conversion copolymers had narrow composition distributions (*Figure 3*), so that their NVP units affect neighbouring VPy–Cu(II) complex units as catalytic sites and their catalytic activities increased with increase of NVP content.

The catalytic activities of the same grade copolymers are shown in *Figure 8*. Their catalytic activities decreased with increasing copolymer conversion despite their
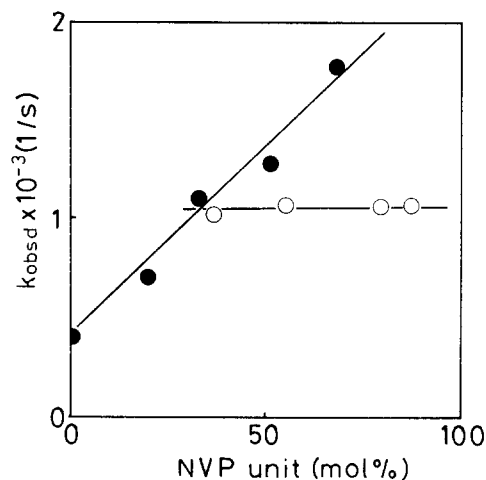

Figure 5 Catalytic activity of the same origin copolymers (○) and the low conversion copolymers (●) oxidized at 25°C in $H_2O/MeOH(1/3)$. [VPy unit] = 4.4 × 10⁻⁴ M, [VPy unit]:[HQ]:[CuSO₄] = 10:10:1
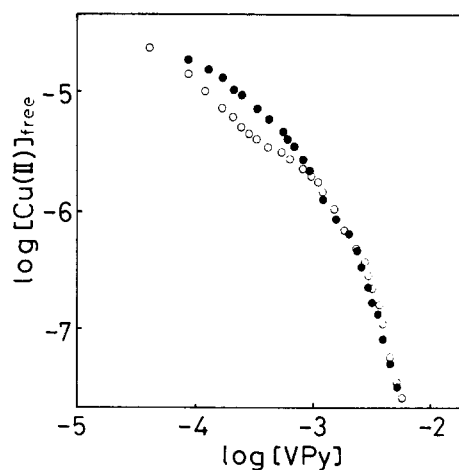

Figure 6 Relationship between $-\log[Cu(II)]_{free}$ and $-\log[Py\ unit]$ in $H_2O/MeOH(1/1)$ at 25°C. $[Cu(II)]_0 = 4.4 × 10^{-5}$ M. (○) Homo PVPy; (●) poly(VPy-*co*-NVP) (71)

Table 5 Kinetic parameters for oxidation of HQ[a]

Ligands	Conv.[b] (%)	K_m ($\times 10^{-3}$) (M)	k_{cat} ($\times 10^{-2}$) (s^{-1})	k_{cat}/K_m (s^{-1} M^{-1})	k_{obsd}[c] ($\times 10^{-4}$) (s^{-1})
Poly(VPy-*co*-NVP) (68)	9.5	1.2	8.4	67	11.0
Poly(VPy-*co*-NVP) (71)	28.8	1.3	6.7	51	8.5
Poly(VPy-*co*-NVP) (69)	75.7	1.4	5.3	39	6.1
Homo PVPy	–	1.4	4.3	31	4.7

[a] Oxidized at 25°C in H_2O/MeOH (1/3 v/v), [VPy unit] = 8.9 $\times 10^{-5}$ M, [CuSO$_4$] = 8.9 $\times 10^{-6}$ M
[b] Copolymer conversion
[c] [VPy unit] = [HQ] = 4.4 $\times 10^{-4}$ M, [CuSO$_4$] = 4.4 $\times 10^{-5}$ M
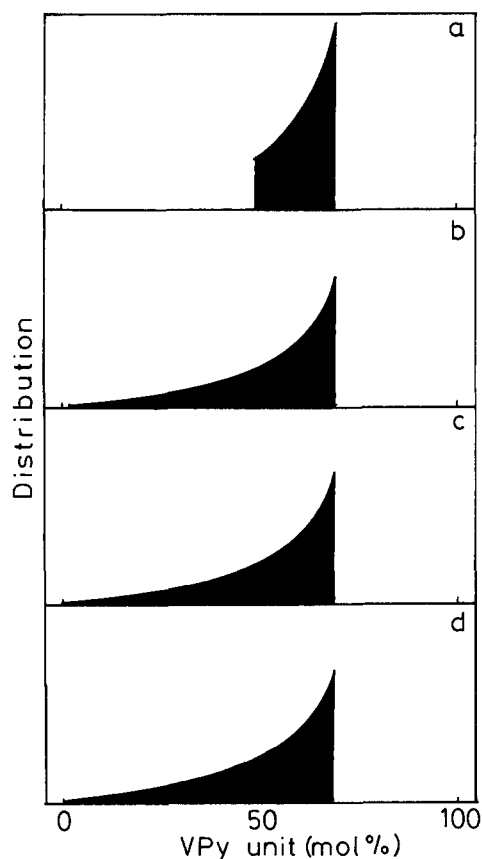

Figure 7 Modified calculated copolymer composition distributions of the same origin copolymers. [VPy in copolymers]: (a) 64 mol%; (b) 46 mol%; (c) 22 mol%; (d) 14 mol%
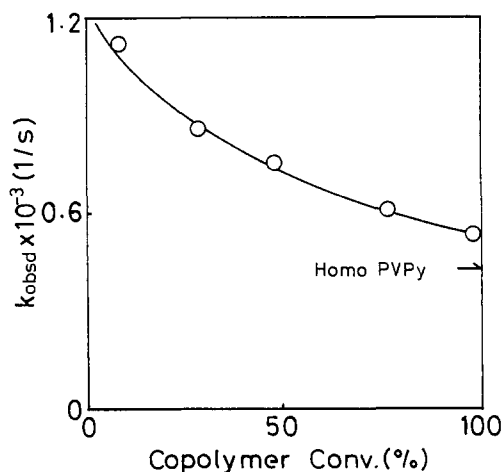

Figure 8 Catalytic activity of the same grade copolymers ([VPy] = 69 ± 2%) oxidized at 25°C in H_2O/MeOH(1/3). [VPy unit] = 4.4 $\times 10^{-4}$ M, [VPy unit]:[HQ]:[CuSO$_4$] = 10:10:1

similar compositions. The activity of the copolymer having a 99.3% conversion was approximately that of the homo PVPy. *Figure 4* shows that their copolymer composition distribution spread as the copolymerization proceeded. Finally, the copolymer became a mixture of homo PNVP having no activity and copolymer which consisted almost entirely of homo PVPy. Therefore, the copolymer may have a similar catalytic activity to that of homo PVPy.

It was reported that an oxidation of HQ by Cu(II) ion complex catalysts proceeded via a typical Michaelis–Menten type mechanism[13,14]. *Table 5* shows Michaelis–Menten kinetic parameters for the oxidation of HQ by the same grade copolymers. There are no large differences in the K_m values for all of the polymer catalysts. In contrast to the K_m values, the turn over number, k_{cat}, increased with increase of the compatibility between the VPy and NVP units in the copolymer catalysts. It was clear that the copolymer composition distribution of the polymer catalysts did not affect the binding of the substrate but the catalytic activity of the Cu(II)–copolymer complexes.

In conclusion, the composition and its distribution of VPy–NVP copolymers affected the catalytic activity of the Cu(II) complexes in the oxidation of HQ even if the copolymer catalysts were random copolymers. The catalytic activity of some VPy–NVP copolymers increased with increase in compatibility between the VPy and NVP units similar to our previous results[7]. These results showed that careful attention should be paid to the distribution of functional groups in the study of polymer catalysts and reagents.

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