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OXIDATION OF HYDROQUINONE BY (*N*-VINYLPYRROLIDONE)-(4-VINYLPYRIDINE) BLOCK AND GRAFT COPOLYMERS

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ABSTRACT

A-B Type block copolymer of *N*-vinylpyrrolidone (NVP) and 4-vinylpyridine (VPy) [poly(NVP-*b*-VPy)] and graft copolymers of VPy onto copolymers of NVP with 4-vinylbenzyl *N,N*-diethyldithiocarbamate (VBDC) [poly(NVP-*g*-VPy)] were synthesized by the iniferter method. The compatibility between NVP and VPy units in the copolymers was evaluated from the glass transition temperature of these copolymers. Hydroquinone was then oxidized by the synthesized NVP-VPy copolymers–Cu(II) complex catalysts. The influence of the distribution of each monomer unit in copolymers on the catalytic activity was studied by comparing the activity of these copolymers. The catalytic activity of these copolymers increased in the order: NVP-VPy blend polymer, poly(NVP-*b*-VPy), poly(NVP-*g*-VPy), random copolymer [poly(NVP-*ran*-VPy)]. This order parallels the compatibility between NVP units and VPy units in these copolymers.

INTRODUCTION

Block copolymers and graft copolymers are considered very important in the field of material science, since these copolymers have physical properties widely different from those of homopolymers or random copolymers in their melting temperatures, glass transition temperatures, solubilities, etc. [1, 2]. Graft and block copolymerizations enable two incompatible polymers on a polymer chain to be dispersed and the distribution of each monomer unit in a copolymer to be controlled. However, these copolymers were mainly studied for their physical properties.

In the field of polymeric reagents and polymeric catalysts, block and graft copolymers were employed to study the solubility and mobility of functional groups on the polymer backbone [3, 4]. However, concerning catalytic activity, there was no study of the influence of the distribution of each functional monomer unit, which work cooperatively in the reaction, as far as we know.

We reported earlier that poly(NVP-*ran*-VPy)-Cu(II) complex catalyst had higher activity than a homoPVPy-Cu(II) complex catalyst in the oxidation of hydroquinone (HQ) and that the activity increased with an increase of NVP monomeric units in the copolymer [5]. This NVP unit effect did not appear in the oxidation by a mixture of homoPVPy-Cu(II) with homoPNVP or *N*-methylpyrrolidone. From this fact it was considered that the NVP unit near the VPy unit affected the catalytic activity of NVP–VPy copolymers complexes and that the activity may be affected by the distribution of both functional groups (pyrrolidone unit and pyridine unit) in a copolymer chain.

In this article we report the syntheses of NVP–VPy block and graft copolymers, and describe the influence of the distribution of NVP and VPy units in a copolymer chain on the catalytic activity for HQ oxidation. The block and graft copolymers were synthesized by the photoiniferter method, which was found to be effective for the construction of the desired structures of various polymers with functional groups [6].

EXPERIMENTAL

Material

4-Vinylbenzyl *N,N*-diethyldithiocarbamate (VBDC) and benzyl *N,N*-diethyldithiocarbamate (BDC) were synthesized according to previously described procedures [6, 7]. VPy and NVP were purified by distillation just before polymerization. HQ and other reagents were obtained commercially and used without further purification. The polymeric ligands, homo-polyVPy and NVP-VPy random copolymer, were synthesized by following previous methods [5].

Polymerization

Photopolymerization of NVP with BDC was carried out in a sealed Pyrex tube at 30°C under irradiation by a Toshiba SHL-100UV lamp from a distance of 3 cm. After polymerization for a given time, the content of the tube was poured into a large amount of diethylether (ether) to isolate the polymer. The precipitated polymers were purified by the reprecipitation method from a methanol (MeOH)-ether system.

A similar procedure was employed for the synthesis of block and graft copolymers. The resulting block and graft copolymers were purified by fractional precipitation from a MeOH–H_2O system. The compositions of the copolymers were determined by elemental analysis of S and/or by the absorbance of pyridine units at 256 nm in MeOH. T_g was determined with a Rigaku PTC-10A differential scanning calorimeter at 10 K/min.

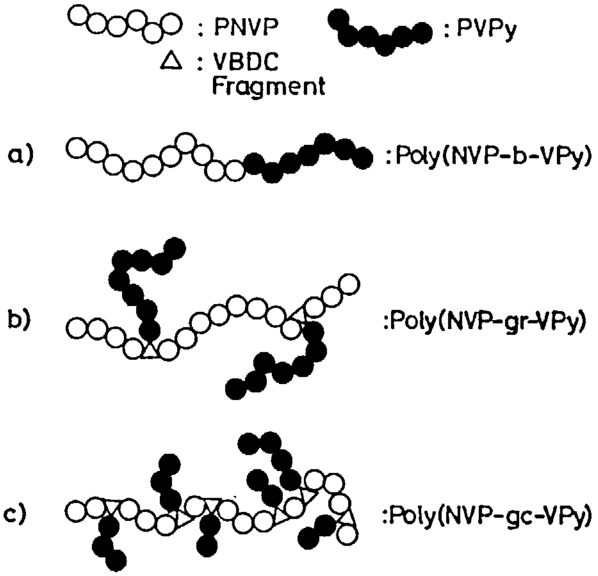
Kinetic Procedure of the Oxidation

Polymer–Cu(II) complexes were prepared by stirring polymeric ligands and $CuSO_4$ in H_2O/MeOH (volume ratio 1/3) solvent for 30 min just before oxidation at 25°C. Then pure oxygen was bubbled into the solution. The oxidation started immediately after HQ was added. Pseudo-first-order rate constants (k_{obsd}) of the oxidation were obtained from the absorbance at λ_{max} of benzoquinone by using a Hitachi-U-2000 spectrophotometer.

RESULTS AND DISCUSSIONS

Molecular Designs of Polymer Catalysts by Iniferter Method

We synthesized a NVP–VPy A-B type block copolymer, poly(NVP-*b*-VPy) (Scheme Ia), and NVP–VPy graft copolymers by the iniferter method under UV irradiation. VPy was grafted onto two parent copolymers of NVP with VBDC; that is, poly(NVP-*ran*-VBDC) (2) and poly(NVP-*ran*-VBDC) (30), in which (2) and (30) mean the mol% of VBDC monomeric units. As the consequence, two kind of graft copolymers were obtained from the two parent copolymers: a roughly grafted copolymer which had



SCHEME 1.

a long VPy chain was obtained from poly(NVP-*ran*-VBDC) (2) [poly (NVP-*gr*-VPy)] (Scheme Ib), and another with short VPy chains was obtained from poly(NVP-*ran*-VBDC) (30) [poly(NVP-*gc*-VPy)] (Scheme Ic).

Syntheses of Block Copolymers

The parent NVP homopolymers, which had abilities as polymeric photo-iniferters, were synthesized by the photopolymerization of NVP with BDC (e.g., as shown Table 1, Run 1). The resulting NVP homopolymers were purified by reprecipitation from the MeOH/ether system in order to remove the iniferter. Figure 1 shows the conversion–η_{sp}/C relation in the photopolymerization of NVP with BDC. The molecular weights assigned by η_{sp}/C increase as a function of conversion. This shows that the polymerization proceeds via a living radical mechanism, and that the resulting homoPNVP has a dithiocarbamate group at its chain end [6].

The results of the block copolymerization of VPy with this homoPNVP as a polymeric photo-iniferter are shown in Table 2. The yield

TABLE 1. Syntheses of Polymeric Photoiniferters

	Monomer				Parent polymers	
Run	[VBDC], *M*	[NVP], *M*	Time, h	Temperature, °C	Yield, g	[VBDC],[a] mol%
1	–	5.00	4	30	1.26[b]	–
2	0.05	4.95	25	60	4.80[c]	2
3	0.05	4.35	8	60	3.37[c]	30

[a] Determined by elemental analysis of sulfur.

[b] Polymerized in DMSO (10 mL) under UV irradiation from a 3-cm distance; [BDC] = 1.0 × 10^{-2} *M*.

[c] Polymerized in DMSO (10 mL) with AIBN (1 × 10^{-2} *M*).

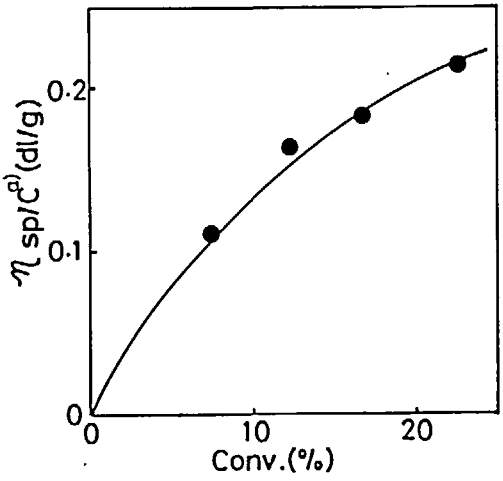


FIG. 1. Conversion-η_{sp}/C relation in photopolymerization of NVP with BDC. [BDC] = 1 × 10^{-2} *M*, [NVP] = 5 *M* in DMSO at 30°C under UV irradiation at a distance of 3 cm. a): [C] = 0.5 g/dL in MeOH at 30°C.

TABLE 2. Block Copolymerization of 4-VPy with BDC-PNVP[a]

BDC-PNVP, g	Time, h	Total yield, g	HomoPVPy, g	Block copolymers Yield, g	Block copolymers [VPy],[b] mol%
0.5	0.5	0.63	0.09	0.55	49
0.5	2.0	1.34	0.46	0.88	81
0.5	6.0	2.50	0.15	2.35	94
—	6.0	0.25	0.25	—	—

[a] Polymerized in DMSO (15 mL) at 30°C under UV irradiation from a 3-cm distance; [VPy] = 5.0 *M*.

[b] Determined by the absorbance of the pyridine unit at 256 nm in MeOH.

of block copolymers and the VPy contents in the copolymer increase with irradiation time. Under these conditions, VPy is scarcely photopolymerized without the NVP parent polymer (Table 2). These results indicate that block copolymers, poly(NVP-*b*-VPy), are undoubtedly synthesized.

Syntheses of Graft Copolymers

We reported that the reactivity of VBDC in radical polymerization was similar to styrene (St); that VBDC acted as a photo-iniferter of the living radical polymerization of St, methyl methacrylate (MMA), and VPy; and that graft copolymerizations of MMA or VPy onto VBDC polymers were easily performed under UV irradiation [7, 8]. The results of the syntheses of polymeric photo-iniferters [(NVP-*ran*-VBDC) copolymers] by this method are shown in Table 1 (Runs 2 and 3). These copolymers contained 2 and 30 mol% VBDC units, respectively. Graft copolymerization of VPy onto these polymeric photo-iniferters was carried out in DMSO at 30°C under UV irradiation (Table 3). In order to avoid deactivation and coupling of growing end groups in these polymerizations, we added tetraethylthiuramdisulfide (TD) which could generate the same thiyl radical as did VBDC on UV irradiation. In this copolymerization the yield of graft copolymers and the content of VPy units in the copolymer increased as a function of polymerization time. Poly(NVP-*gc*-VPy) may

TABLE 3. Graft Copolymerization of 4-VPy onto VBDC–NVP Copolymers[a]

VBDC–NVP copolymer						Graft copolymer	
Grams	[VBDC], mol%	[NVP], mol%	Time, h	Total, yield, g	HomoPVPy, g	Yield, g	[VPy], mol%
0.5	30	70	1.0	1.22	0.34	0.88	59[b]
0.5	30	70	2.0	2.18	0.52	1.66	76[b]
0.5	30	70	4.0	3.74	1.20	2.54	84[b]
0.5	2	98	0.5	1.04	0.10	0.94	60[c]
0.5	2	98	1.0	1.60	0.22	1.38	78[c]

[a] Polymerized in DMSO (15 mL) at 30°C under UV irradiation from a 3-cm distance. [VBDC] = [TD] = 6.4×10^{-2} *M* (poly(VBDC-*ran*-NVP) (30)) = 5.8×10^{-3} *M* (poly(VBDC-*ran*-NVP) (2)); [VPy] = 5.0 *M*.

[b] Determined by elemental analysis of sulfur.

[c] Determined by absorbance of the pyridine unit at 256 nm in MeOH.

have many VPy side chains on the NVP main chain, because there are many initiating points in the parent copolymer. On the other hand, poly(NVP-*gr*-VPy) may have a few long VPy side chains on the main chain.

Compatibility between NVP and VPy Units in the Copolymers

In a previous article [8], structural analyses of the graft copolymers synthesized by the iniferter method were performed by using the glass transition temperature (T_g). The T_gs of block and graft copolymers are known to be influenced by chemical structure and by the way in which the graft chain on the main chain is generated [2, 9]. Therefore, we had utilized T_g as an indicator of copolymer structures.

The T_gs of VPy homopolymer and each copolymer, which had nearly the same VPy content (about 80 mol%), are shown in Table 4 and Fig. 2. Since an endothermic peak for the NVP domain at T_g was too indistinct to evaluate the environment around the NVP domain in the copolymer, only a sharp peak of the VPy domain was used as an indicator of the copolymer structures.

The thermograms of blend polymer and poly(NVP-*b*-VPy) show sharp T_gs (with smaller ΔT_g) at temperatures similar to that of homoPVPy. These results indicated that the microphases of the VPy and NVP domains are well developed, and that the phase boundaries are reasonably sharp. In contrast to the blend and block copolymer, the graft and ran-

TABLE 4. Thermal Properties of NVP–VPy Copolymers

Polymer	T_g(VPy),[a] °C	ΔT_g(VPy),[a] °C
HomoPVPy	150	6
Blend Polymer (PNVP–PVPy)	152	5
Poly(NVP-*b*-VPy) (81)	152	7
Poly(NVP-*gr*-VPy) (78)	149	6
Poly(NVP-*gc*-VPy) (76)	143	8
Poly(NVP-*ran*-VPy) (83)	144	20

[a] Defined in Fig. 2.

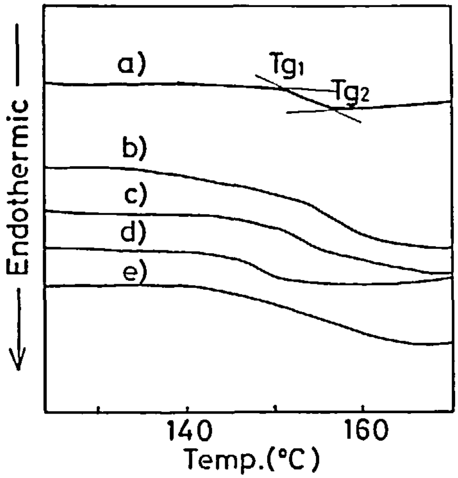


FIG. 2. DSC thermograms of NVP–VPy copolymers: a) HomoPVPy, b) poly(NVP-*b*-VPy) (81), c) poly(NVP-*gr*-VPy) (78), d) poly(NVP-*gc*-VPy) (76), e) poly(NVP-*ran*-VPy) (83). $T_g = T_{g_1}$, $\Delta T_g = T_{g_2} - T_{g_1}$.

dom copolymers had lower T_gs and larger ΔT_gs than homoPVPy. These results show that the compatibility between the VPy and NVP domains in the copolymer increase in the order: blend polymer, block, rough graft, close graft, random copolymer.

Oxidation Reaction

HQ was oxidized by the use of these NVP-VPy copolymers–Cu(II) complex catalysts in H_2O/MeOH (1/3) solvent under O_2 atmosphere. Figure 3 presents plots of pseudo-first-order rate constants vs NVP unit contents in the copolymers. Except for the case of the blend polymer, the catalytic activity of the copolymer complexes increased as the NVP contents in the copolymers increased. It was reported that a homoPNVP scarcely had binding ability for Cu(II) ions and catalytic activity in the oxidation of HQ [5]. The catalytic activity of these copolymers increased in the order: blend, block, rough graft, close graft, and random copolymers. This order is the same as the order of compatibility between NVP and VPy units in these copolymers.

From the above results, only the NVP groups close to the pyridine units promoted the activation of this oxidation. Since the NVP units near

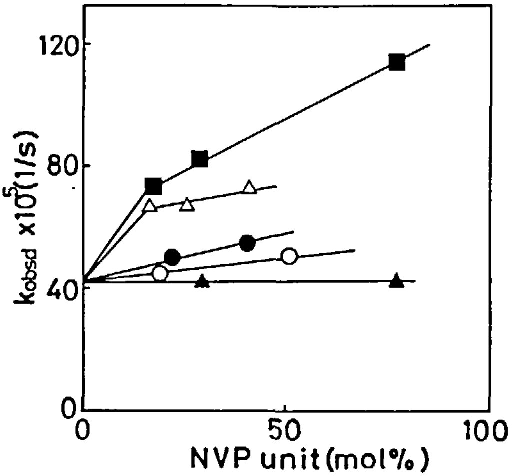


FIG. 3. Relation between the oxidation rate constants and NVP contents, Oxidized in H_2O/MeOH (v/v : 1/3) at 25°C, [VPy unit] = 4.4 × 10^{-4} *M*, [VPy unit]:[HQ]:[$CuSO_4$] = 10 : 10 : 1. (▲) Blend polymer, (○) poly(NVP-*b*-VPy), (●) poly(NVP-*gr*-VPy), (△) poly(NVP-*gc*-VPy), (■) poly(NVP-*ran*-VPy).

the pyridine units may hinder the formation of the stable complex with Cu(II) ion, the VPy-NVP copolymers become unsaturated complexes, which are known to form a highly active complex catalyst with Cu(II) ions [10]. In the study of a complexation of Cu(II) ions employing the Cu(II) ion-selective electrode, the proportions of complexed Cu(II) ions with homoPVPy or poly(NVP-*ran*-VPy) (71) were found to be 98.2 and 88.9%, respectively [11]. These results show that complexes of NVP-VPy copolymer are less stable than that of homoPVPy. In the oxidation by NVP-VPy copolymer, the nearer the NVP units are to the pyridine units, the less stable and more active the copolymer complexes become.

In order to study the above consideration in detail, we carried out the Michaelis-Menten kinetic treatment because it has been reported that the Cu(II) complex catalyzed oxidation of HQ proceeds via a typical Michaelis-Menten mechanism [12, 13]. Figure 4 presents plots of the reciprocal of the rate vs the reciprocal of the substrate concentration (Lineweaver-Burk plot) in H_2O/MeOH (volume ratio 1/3) solvent. In the oxidation using these NVP-VPy copolymers, each plot gave a straight line (correlation coefficient $R > 0.99$). This shows that the kinetic treatment

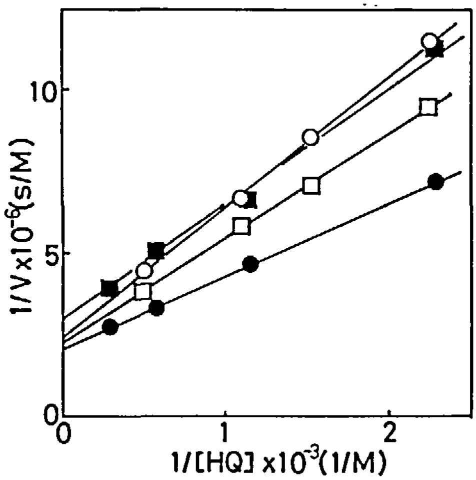


FIG. 4. Lineweaver-Burk plot for the oxidation of HQ. [VPy unit] = 8.89 × 10^{-5} *M*, [$CuSO_4$] = 8.86 × 10^{-5} *M*. (●) Poly(NVP-*ran*-VPy) (71), (□) poly(NVP-*gr*-VPy) (78), (○) poly(NVP-*b*-VPy) (81), (■) homoPVPy.

based on the Michaelis-Menten mechanism is also appropriate for oxidation by these catalysts.

K_m and k_{cat} values calculated from the slopes and intercepts of the straight lines in Fig. 4 are summarized in Table 5. Each catalyst has a nearly constant K_m value, but as mentioned above, the k_{cat} values increase with an increase of compatibility between NVP units and VPy units, in the same way as do the k_{obsd} values.

In conclusion, the poly(NVP-*ran*-VPy)-Cu(II) complex catalyst had the highest activity among the copolymers, and the blend polymer (PNVP and PVPy) had the same activity as the homo-PVPy complex catalyst. These results indicate that NVP–VPy copolymers which have NVP units near VPy ligand groups have a higher catalytic activity. Now, even in the field of polymer reagents and catalysts, it is clear that block and graft copolymers have activities between those of blend and random copolymers, and that the distribution of each monomer unit in copolymers affects the catalytic activity in the oxidation of HQ.

TABLE 5. Kinetic Parameters for the Oxidized HQ[a]

Polymer ligand	K_m, 10^{-3} M	k_{cat}, 10^{-2}/s	k_{cat}/K_m, 1/sM
HomoPVPy	1.35	4.27	30.85
Poly(NVP-*b*-VPy) (81)	1.55	4.46	28.90
Poly(NVP-*gr*-VPy) (78)	1.49	5.23	35.24
Poly(NVP-*gc*-VPy) (76)	1.17	5.66	48.60
Poly(NVP-*ran*-VPy) (71)	1.16	5,78	50.06

[a] Oxidized in H_2O/MeOH (v/v : 1/3) at 25°C. [$CuSO_4$] = 8.89×10^{-6} M, [Py unit] = 8.86×10^{-5} M.

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M-8 pH meter equipped with a Horiba 8006-06T cupric electrode; $[Cu(II)]_0 = 0.98 \times 10^{-4}$ *M*, [Py unit] = 9.80×10^{-4} *M* in MeOH/H_2O (v/v : 1/1) cosolvent.
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