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Studies on Special Type Surfactants. XVI. Preparation of Telomer-Type Surfactants Containing 4-Vinylpyridine and Oxidative Polymerization of 2,6-Xylenol Using Their Copper Complexes

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(Received January 13, 1986)

The polymerization of 2,6-xylenol (XOH) was catalyzed by using a copper complex of a telomer-type surfactant containing 4-vinylpyridine, 1-benzyl-4-vinylpyridinium chloride, and methyl acrylate or styrene (L-VP-Q, L-VP-Q-MA, L-VP-St, and L-VP-Q-St). A copper complex of L2.5VP3.9Q2.2MA catalyzed an emulsion polymerization of XOH more than that of L-VP-Q, 4-vinylpyridine polymer (VP-Q), or pyridine. Furthermore, the oxidative polymerization of XOH in several organic solvents was more effective than emulsion polymerization. The copper complexes formed reversed-micelles in water (3—10 vol%)-DMSO, and the catalytic actions were in the following order: L-VP-Q>VP-Q>pyridine. The acceleration by the L-VP-Q complex was considered to be due to the adsorption of XOH on reversed micelles.

Telomer-type surfactants have been characterized by the terminal alkyl group and polyfunctional groups.[1] Telomer-type surfactants bearing 4-vinylpyridine and 1-benzyl-4-vinylpyridinium chloride (L-VP-Q), oriented at the interface of water and an immisible organic solution, emulsify these solutions.[2] The emulsion polymerization of XOH using the L-VP-Q–copper complex was more catalytically active than that using the corresponding polymer (VP-Q) complex or a pyridine(py) complex in a water–benzene solvent.[2]

The oxidative polymerization of XOH was studied in detail by Tsuchida et al. using a VP-Q polymer complex and several solvents.[3,4] The catalytic activity was accelerated by a nonpolar field in the polymer ligand[3] and the nonpolar solvent.[4] Therefore, a telomer-type surfactant is expected to be an excellent catalyst since the surfactant forms a nonpolar field consisting dodecyl groups; a highly condensed catalytic active site consists of pyridyl groups above the critical micelle concentration (cmc). However, the oxidative polymerization of XOH using a catalyst of a surfactant-copper complex has not yet been seen. In this study, cotelomer-type surfactants bearing 4-vinylpyridine, 1-benzyl-4-vinylpyridinium chloride, and methyl acrylate or styrene were prepared and the oxidative polymerization of XOH using their copper complexes were examined in comparison with the VP-Q polymer or the py ligand for obtaining information regarding the catalytic character of a telomer-type surfacant.

Experimental

Syntheses of Cotelomer-Type Surfactants. The L-VP-Q telomer-type surfactants and the VP-Q polymer were obtained as described in a previous paper.[2] The cotelomer-type surfactants bearing 4-vinylpyridine, 1-benzyl-4-vinylpyridinium chloride, and methyl acrylate (L-VP-Q-MA) or styrene (L-VP-Q-St) were derived from the corresponding 4-vinylpyridine cotelomers (L-VP-MA, L-VP-St).

The preparation of L-VP-Q-MA was as follows: 4-Vinylpyridine (26.3—27.3 g), methyl acrylate (15.5—54.2 g), and 0.5 wt% of 2,2′-azobisisobutyronitrile (per weight of the mixed monomers) were added to 1-dodecanethiol (30.3—44.4 g); then, the reaction mixture was stirred at 70 °C for 6 h. After cooling to room temperature, the light-brown L-VP-MA was precipitated by adding hexane to the solution mixture. The crude L-VP-MA was reprecipitated twice with hexane after dissolving in chloroform. Then, benzyl chloride (1.0—1.2 g) was added dropwise to 100 cm^3 of a 2% L-VP-MA methanolic solution and the mixture was refluxed for 24 h. After cooling to room temperature, the reaction mixture was poured into 200 cm^3 of ether. The resulting precipitate, L-VP-Q-MA, was filtered and rinsed with ether. The cotelomer-type surfactant-bearing 4-vinylpyridine, 1-benzyl-4-vinylpyridinium chloride, and styrene, L-VP-Q-St, was obtained with styrene instead of methyl acrylate by the same procedure as the preparation of L-VP-Q-MA.

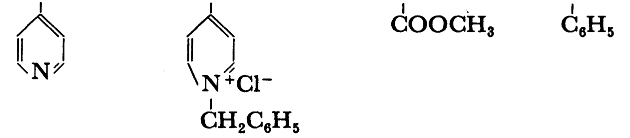
The compositions of the cotelomers (L-VP-MA, L-VP-Q-MA, L-VP-St, and L-VP-Q-St) were determined by means of molecular-weight (Corona 114 vapor-pressure osmometer) and the analytical data of nitrogen from elementary analyses. Detailed descriptions for preparing L-VP-MA and L-VP-St were reported in a preceding paper.[5] Then, the L-VP-Q-MA and L-VP-Q-St that quaternized with benzyl chloride were confirmed by the pyridinium absorption at 1640 cm^{-1} in the IR spectrum and the benzyl peak of 7.2 ppm in the NMR spectrum. The quaternized percent was calculated from the absorption ratio of the IR spectrum[2] or the integrated values of the NMR spectrum. The benzyl chloride reacted with the pyridyl groups of L-VP-MA in 90—95% yields. The chemical formulas and the elementary analyses of the cotelomers are shown in Table 1. The calculated values of C, H, and N based on the chemical formulas agreed with the analytical data.

Polymerization of XOH. The polymerization rate was measured in terms of the oxygen consumption.[2] The polymerization of XOH in an organic solution was as follows: The copper ($CuCl_2$ or CuCl) complex of telomer-type surfactant and the equimolar sodium hydroxide dissolved in a 10 cm^3 of organic solution was added to a 10 cm^3 of organic solution containing the known amount of XOH in a 100 cm^3 flask. The mixed solution was thermostated at 30 °C and shaken until a termination of oxygen absorption. Then, the solution was first added to 450 cm^3 of methanol and the resulting diphenoquinone (DQ) was filtered out. Then, 50 cm^3 of 35%-hydrochloric acid was added to the methanol. The resulting polyphenylene oxide (PPO) was

Table 1. Elementary Analyses of Cotelomers

Cotelomer	Composition[a)]	Calcd[b)] (Found) (%) C	H	N	Molecular weight (Found)
L4.0VP1.6MA	L-$VP_{4.0}$-$MA_{1.6}$	73.46	8.45	7.39	760
		(73.63)	(8.60)	(7.25)	(749)
L6.4VP2.2MA	L-$VP_{6.4}$-$MA_{2.2}$-$H_2O_{0.2}$	73.89	7.98	8.41	1067
		(73.63)	(8.20)	(8.41)	(1059)
L7.7VP9.4MA	L-$VP_{7.7}$-$MA_{9.4}$-$H_2O_{1.3}$	67.47	7.60	5.85	1842
		(67.90)	(7.72)	(5.85)	(1820)
L6.8VP2.5St	L-$VP_{6.8}$-$St_{2.5}$-$H_2O_{2.0}$	78.90	8.12	7.86	1212
		(78.61)	(8.31)	(7.84)	(1206)
L0.8VP3.2Q1.6MA	L-$VP_{0.8}$-$Q_{3.2}$-$MA_{1.6}$-$H_2O_{1.9}$	68.98	7.56	4.68	1198
		(68.08)	(7.42)	(4.60)	(—[c)])
L2.5VP3.9Q2.2MA	L-$VP_{2.5}$-$Q_{3.9}$-$MA_{2.2}$-$H_2O_{3.2}$	69.13	7.35	5.55	1614
		(68.55)	(7.12)	(5.19)	(—[c)])
L1.5VP6.2Q9.4MA	L-$VP_{1.5}$-$Q_{6.2}$-$MA_{9.4}$-$H_2O_{8.2}$	64.12	7.18	3.92	2750
		(63.28)	(7.13)	(4.55)	(—[c)])
L3.1VP3.7Q2.5St	L-$VP_{3.1}$-$Q_{3.7}$-$St_{2.5}$-$H_2H_{10.6}$	69.05	7.73	5.19	1835
		(68.81)	(7.18)	(5.18)	(—[c)])

a) L: $C_{12}H_{25}S$–; VP: –(CH_2CH)–; Q: –(CH_2CH)–; MA: –(CH_2CH)–; St: –(CH_2CH)–. b) Calculated values based on the composition. c) The molecular weight could not be measured because of the chloroform-insoluble compound.



$-(CH_2\underset{COOCH_3}{CH})-$; $-(CH_2\underset{C_6H_5}{CH})-$

centrifuged, reprecipitated twice with a 35%-hydrochloric acid (10 vol%)-methanol (90) mixture after dissolving in chloroform, and dried.

Results and Discussion

Emulsion Polymerization of XOH. It is known that a plot of the volume of oxygen consumption against the amount of resulting PPO gives a straight line for a large excess of XOH.⁶⁾ Therefore, the polymerization rate can be determined by a measurement of the oxygen-consumption rate, with an error of about 2 $mm^3 min^{-1}$.

The emulsion polymerization of XOH using the L-VP-Q-copper complex was more catalytically active than that using the VP-Q polymer complex in a water-benzene solvent.²⁾ Moreover, the polymerization rate (66 $mm^3 min^{-1}$) using a L2.5VP3.9Q2.2MA complex which contains methoxycarbonyl groups was 1.4-times faster than that (47 $mm^3 min^{-1}$) using the L3.0VP5.0Q complex at pH 7.5. The acceleration was considered to be due to a slight increase in the nonpolarity formed by the methoxycarbonyl groups³⁾ in addition to the emulsification.²⁾ However, the resulting PPO were 3100—5100 of molecular weight and the by-product, DQ, yielded more than 10%. Consequently, the following polymerizations were carried out in a DMSO or a methanol-*o*-dichlorobenzene (DCB) mixture.

Oxidative Polymerization in DMSO. The high molecular weight of PPO and a small amount of DQ were obtained for the above-mentioned solvents by Tsuchida et al. using a VP-Q polymer complex.⁷⁾ The polymerization rate was accelerated under alkaline conditions because of the low oxidation potential of XOH; however, a higher pH made the copper complex hydrolysis.⁶⁾ Therefore, equimolar sodium hydroxide was added to a copper complex.

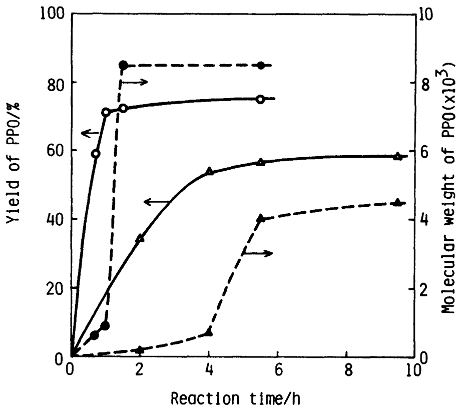


Fig. 1. Effect of reaction time.
XOH: 0.5 mol dm^{-3}; $CuCl_2$: 0.01 mol dm^{-3}; [VP unit]/[Cu]=2; [py]/[Cu]=20. Solvent: 20 cm^3 of water(10 vol%)-DMSO(90) mixture; Temp: 30 °C; Oxidation: under aerobic conditions.
○,● L5.1VP8.7Q, △,▲ Pyridine.

The polymerization of XOH in a water (10 vol%)-DMSO(90) mixture was examined using the L5.1VP8.7Q or pyridine complex. The effects of the reaction time are indicated in Fig. 1. The yield of PPO increased with the passage of time, while the molecular weight of PPO increased steeply near the conclusion of the reaction (the oxygen consumption ceased). Therefore, the reaction was allowed to continue twice as long as

Table 2. Polymerizations in Water-DMSO Mixture

	Water	Polymerization rate	PPO	
			Yield	Molecular weight
	vol%	mm^3 min^{-1}	wt%	
L0.8VP3.2Q1.6MA	3	25.5	70	8000
L0.8VP3.2Q1.6MA	10	8.0	64	10700
L0.8VP3.2Q1.6MA	50	4.5	77	8000
L1.5VP6.2Q9.4MA	3	14.2	84	10300
L5.1VP8.7Q	10	18.8	65	14800
L5.1VP8.7Q	50	6.5	45	7700
62VP26Q	3	9.0	0[a)]	—[a)]
62VP26Q	10	6.8	0[a)]	—[a)]
62VP26Q	50	6.6	7	2000

a) XOH: 0.5 mol dm^{-3}; CuCl$_2$: 0.01 mol dm^{-3}; [VP unit]/[Cu]=1.5. Solvent: 20 cm^3 of water-DMSO mixture; pH: 13.5; Temp: 30 °C; Oxidation: under aerobic conditions. a) PPO did not precipitate from methanol, which molecular weight seemed low.

the time necessary for a consumption of oxygen (the polymerization rate reduced nearly to zero). PPO was yielded in 75% with the L5.1VP8.7Q complex and 58% with the pyridine complex, and DQ yielded in 6% with the L5.1VP8.7Q complex and 8% with the pyridine complex.

Then, the effect of the water content in a DMSO solution was examined (Table 2). On the whole, the polymerization rates were not so fast at pH 13.5 when the VP-unit ratio to copper was 1.5 (the Cu complex is not hydrolyzed). However, the polymerization rate using the surfactant-copper complex was highly affected by the water content: L0.8VP3.2Q1.6MA 25.5 mm^3 min^{-1} at 3 vol% water in DMSO, 26.0 mm^3 min^{-1} at 5 vol%, 22.0 mm^3 min^{-1} at 7 vol%, 8.0 mm^3 min^{-1} at 10 vol%, and 4.5 mm^3 min^{-1} at 50 vol%. On the other hand, the polymerization rates using the 62VP26Q polymer complex were nearly constant in 3—50 vol% of water contents (9.0 mm^3 min^{-1} at 3 vol%, 7.5 mm^3 min^{-1} at 5 vol%, 7.0 mm^3 min^{-1} at 7 vol%, 6.8 mm^3 min^{-1} at 10 vol%, and 6.6 mm^3 min^{-1} at 50 vol%). Similar results had been obtained by Tsuchida et al.[7)] Usually, a surfactant in a nonaqueous solution tends to aggregate or to form reversed micelles, and the structure varies with the water content.[8)] The cmc of L5.1VP8.7Q-copper complex was actually confirmed in a water (5vol%)-DMSO(95) mixture by conductometric titration (cmc 4.8×10^{-4} mol dm^{-3}); however, that of the L5.1VP8.7Q complex in a water (50 vol%)-DMSO (50) mixture and those of 34VP51Q complex in a water (5 vol%)-DMSO(95) and a water (50 vol%)-DMSO(50) mixture were not found. The XOH anion would adsorb on the cationic reversed micelles or the cationic aggregated-surfactants in 3—10 vol% of water contents. The K_1 (the reciprocal of the Michaelis constant K_m) calculated from the Lineweaver-Burk plots were py-Cu 22 dm^3 mol^{-1},[7)] VP-Q-Cu 190,[7)] and L-VP-Q-Cu 800—900, which means the affinity of the catalyst for the substrate.[9)] Therefore, the rate using the telomer-type surfactants would become fast in the 3—10 vol% of water contents because the XOH was more condensed to the reversed micelles (about 40-times that of py) in addition to the nonpolar effect of the dodecyl group. The catalytic action of L5.1VP6.2Q9.4MA was more active than that of L0.8VP3.2Q1.6MA in the water (3 vol%)-DMSO(97) mixture. This difference is probably due to the extent of nonpolarity based on the methoxycarbonyl groups.

Then, the repeated use of telomer-type surfactants was examined. L0.8VP3.2Q1.6MA, the less active catalyst, was used repeatedly for the oxidative polymerization of XOH in a half scale of the abovementioned concentration (Table 2). Then, 60 cm^3 of 0.25 M (M=mol dm^{-3}) XOH in water (3 vol%)-DMSO (97) mixture was polymerized by 5×10^{-3} M CuCl$_2$ and 6.3×10^{-2} M L0.8VP3.2Q1.6MA at 30 °C under aerobic conditions. After the oxidative polymerization, the reaction mixture was divided in two parts; 10-cm^3 of the reaction mixture was used for a determination of PPO and 50 cm^3 of the remainder was subjected for further polymerization: 10 cm^3 of 0.5-M XOH in water (3 vol%)-DMSO mixture was added to 50 cm^3 of the reaction mixture. The resulting PPO were first 4800 of molecular weight in 64% yield, second 4800 in 69%, and third 4200 in 62%. In spite of the half-scale concentration, and the L0.8VP3.2Q1.6MA-copper solution was then diluted in series, the three findings were similar. Furthermore, the other telomer-type surfactants were confirmed their repeating use in similar reactivities.

Solvent Effects. The catalytic action of the VP-Q polymer complex was much affected by the solvent polarity.[4)] Therefore, the effects of solvent polarity were examined on the assumption that the dielectric constant of mixed solvent D is equal to the sum of the individual products of the dielectric constant of the mixing species and its volume ratio.[10)] The polarity was expressed as a dielectric parameter E; $E=(D-1)(2D+1)^{-1}$,[11)] The E values for the 3—50 vol% water in DMSO were 0.485—0.488 (Table 2). The tendency that the catalytic action increased with a decrease in the solvent polarity could be recognized, but the

Table 3. Effects of Solvents and Ligands on Polymerizations of XOH

Ligand	Polymerization rate	PPO Yield	PPO Reduced viscosity	DQ Yield
	$mm^3 min^{-1}$	wt%	($\eta_{sp}C^{-1}$)	wt%
Water (10 vol%)-DMSO(90) E=0.486				
L5.1VP8.7Q	70	75	0.24	10
L0.8VP3.2Q1.6MA	26	66	0.12	6
L-VP-Q-St	29	54	0.13	6
34VP51Q	25	0[a]	—[a]	0
py	20	58	0.15	8
MeOH(10 vol%)-DCB(90) E=0.441				
L5.1VP8.7Q	85	74	0.33	9
L-VP-Q-St	200	65	0.25	10
34VP51Q	70	62	0.16	6
py	60	62	0.78	4
MeOH(10 vol%)-DMSO(90) E=0.484				
L5.1VP8.7Q	23	45	0.05	9
MeOH(10 vol%)-Bz(90) E=0.371				
L5.1VP8.7Q	100	63	0.31	8

XOH: 0.5 mol dm^{-3}; $CuCl_2$: 0.01 mol dm^{-3}; [VP unit]/[Cu]=2. Volume: 20 cm^3; Temp: 30 °C: Oxidation: under aerobic conditions. a) PPO did not precipitate from methanol.

Table 4. Polymerizations of XOH by Cu(II) Complexes in MeOH-DCB-py Mixture

Ligand	Solvent Composition vol% (MeOH	-DCB	-py)	Solvent Dielectric parameter (E)	Polymerization rate $mm^3 min^{-1}$	PPO Yield wt%	PPO Reduced viscosity ($\eta_{sp}C^{-1}$)	DQ Yield wt%
L5.1VP8.7Q	10	90	0	0.441	85	74	0.33	8
L5.1VP8.7Q	10	87	3	0.441	100	80	0.74	4
L5.1VP8.7Q	10	10	80	0.449	64	59	0.43	2
None	10	87	3	0.441	0[a]	—[a]	—[a]	0
None	10	10	80	0.449	106	58	0.11	0.4

XOH: 0.5 mol dm^{-3}; $CuCl_2$: 0.01 mol dm^{-3}; [VP unit]/[Cu]=2. Volume: 20 cm^3; Dielectric parameter $E\{=(D-1)(2D+1)^{-1}\}$: 0.441, 0.449; Temp: 30 °C; Oxidation: under aerobic conditions. a) PPO did not precipitate from methanol.

range of the E values was too narrow to discuss. The polymerization using the L-VP-St complex was examined in a py(20 vol%)-organic solvent (80) mixture; E value: py-benzene (Bz) 0.342, py-chlorobenzene (CB) 0.399, py-DCB 0.431, and py-nitrobenzene (NB) 0.476. The polymerization rate decreased with an increase in the solvent polarity, while the reduced viscosity of PPO was independent of the solvent polarity in the E range 0.342—0.476.

Then, the catalytic actions in a water (10 vol%)-DMSO (90) mixture (E 0.486) and in a MeOH (10 vol%)-DCB (90) mixture (E 0.441) were examined (Table 3). The polymerization rates of XOH in an MeOH-DCB mixture were higher than that in a water-DMSO mixture. Moreover, the catalytic actions in an MeOH (10 vol%)-DMSO (90) mixture (E 0.484) and in an MeOH (10 vol%)-Bz (90) mixture (E 0.371) were evaluated by using the L5.1VP8.7Q complex. The polymerization rates were as follows: In MeOH-Bz>MeOH-DCB>water-DMSO>MeOH-DMSO. The order of these rates was according to the order of solvent polarities, except for the water-DMSO mixture. It was proven by Tsuchida et al. that the rate-determining step for the oxidative polymerization of XOH using the VP-Q polymer complex was the reoxidation step in a polar solvent and was the electron-transfer step in a nonpolar solvent. Also, the total polymerization rate was fast in a nonpolar solvent.[4] However, the rate using the L5.1VP8.7Q complex in a polar water-DMSO mixture was higher than that in a less polar MeOH-DMSO mixture. The cmc of L5.1VP8.2Q complex in 3—10 vol% water in DMSO was found but that in an MeOH-DMSO mixture was not. Therefore, the higher rate in the water-DMSO mixture was presumably due to the concentration of XOH to the reversed-micelles. In these solvents the polymerization rate using the L5.1VP8.7Q, L0.8VP3.2Q1.6MA or L-VP-Q-St complex was faster than that using the 34VP51Q or pyridine complex because of the large aggregation.

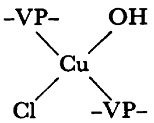
Effect of Pyridine. The oxidative polymerization of XOH was considerably affected by adding pyridine.[4] The catalytic actions in MeOH-DCB-py solutions are shown in Table 4. Although the E values of these solutions are nearly equal to 0.44 (0.441—0.449), the polymerization rate and the reduced viscosity of PPO

Table 5. Polymerizations of XOH by Cu(I) Complexes in MeOH-DCB-py Mixture

Ligand	Solvent vol%			Polymerization Rate $\mathrm{mm^3\,min^{-1}}$	Polymerization Time h	PPO Yield wt%	PPO Reduced viscosity $(\eta_{sp}C^{-1})$	DQ Yield wt%
	(MeOH-DCB-py)							
L5.1VP8.7Q	20	70	10	70	2	75	0.74	4
L5.1VP8.7Q	50	40	10	80	2	72	0.51	7
L5.1VP8.7Q	80	10	10	76	2	68	0.38	8
34VP51Q	20	70	10	120	1	73	0.69	4
34VP51Q	50	40	10	99	1	61	0.48	7
34VP51Q	80	10	10	66	2	47	0.20	9
None	20	70	10	255	0.7	77	0.57	4
None	50	40	10	160	1	60	0.49	7
None	20	60	20	70	3	63	0.55	4
None	20	50	30	10	10	82	0.69	5
	(MeOH-CB-py)							
L5.1VP8.7Q	20	70	10	146	1.3	77	0.75	3
None	20	70	10	430	0.5	79	0.62	4
	(MeOH-Bz-py)							
L5.1VP8.7Q	20	70	10	205	1	78	0.79	3
None	20	70	10	520	0.3	79	0.66	3

XOH: 0.2 mol dm^{-3}; CuCl: 5X10^{-3} mol dm^{-3}; [VP unit]/[Cu]=2. Volume: 40 cm^3; Temp: 30 °C; Oxidation: under oxygen atmosphere.

using the L5.1VP8.7Q complex increased at 3 vol% of the pyridine content. A similar result was also obtained upon using the L-VP-St complex. On the other hand, the catalytic actions without the telomer-type surfactants were, on the whole, less. Catalysts for the oxidative polymerization of XOH are known to possess the following structures:[4,12]



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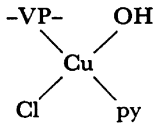

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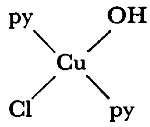

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Presumably, the **2** that formed upon adding pyridine (3 vol%) was easier to use for forming complexes with XOH than **1** with a rigid structure; also, oxygen was more easy of access to the resulting **2**-XOH complex because of less steric hindrance.[12] Consequently, the addition of pyridine would accelerate the polymerization rate. However, in a large excess of the pyridine content (80 vol%) the polymerization rate using the L5.1VP8.7Q complex was slow and the reduced viscosity of PPO was low. By a further addition of pyridine, the structure of **2** could be converted to the inactive structure VP-CuCl(py)$_2$ etc. Similarly, the polymerization rate became slow when the VP-unit ratio in the L0.8VP3.2Q1.6MA to the copper was increased, i.e., 31.9 mm^3 min^{-1} at ratio 5, 4.6 mm^3 min^{-1} at ratio 7, and 1.8 mm^3 min^{-1} at ratio 10. On the other hand, the rate without the L5.1VP8.7Q in the 3 vol% of pyridine content was very slow and the rate in the 80 vol% of pyridine content was fast but the reduced viscosity was very low. The structures would be CuCl(OH)py and **3** or CuCl(py)$_3$.

Polymerization under Oxygen Atmospere. The polymerization of XOH was examined by using a Cu(I) complex under an oxygen atmosphere instead of the Cu(II) complex under aerobic conditions (Table 5). The polymerization rates using the 34VP51Q polymer and the pyridine monomer complexes were very fast in comparison with that using the L5.1VP8.7Q telomer complexes. Their catalytic actions in MeOH-DCB-py solutions became more active at a lower MeOH content and the order of the catalytic actions was in MeOH-Bz-py>MeOH-CB-py>MeOH-DCB-py. The polymerization-rate ratio (using L5.1VP8.7Q to the rate using the pyridine complex in the MeOH-DCB-py (10 vol%) mixture) was larger than the ratio in the MeOH-CB-py or the ratio in the MeOH-Bz-py mixture. The Cu(I) complex of a telomer-type surfactant would aggregate or form reversed-micelles in these solutions. The approach of oxygen to the surfactant complex would be more difficult than the pyridine complex because of a steric hindrance, even if the oxygen pressure increased. Then, the rate-determining step in a polar solvent was the reoxidation step and that in a nonpolar solvent was the electron-transfer step.[4] Therefore, the dependence of the polymerization rate on the catalyst in the more polar solvent (MeOH-DCB-py) would be larger than that in the more nonpolar solvent (MeOH-Bz-py). Nevertheless, the reduced viscosity of PPO using the L5.1VP8.7Q complex was the highest in the MeOH-DCB-py mixture. Furthermore, the increase of pyridine made the polymerization rate slow, but made the reduced viscosity high. The structure of the complex would become **3**. Naturally, the polymerization rate

Table 6. Effects of Hexadecyltrimethylammonium Bromide

Ligand	HTAB	Polymerization rate	PPO Yield	PPO Reduced viscosity	DQ Yield
	mol dm^{-3}	mm^3 min^{-1}	wt%	($\eta_{sp}C^{-1}$)	wt%
L5.1VP8.7Q	0	70	75	0.74	4
L5.1VP8.7Q	0.025	26	76	0.86	5
34VP51Q	0	120	73	0.69	4
34VP51Q	0.025	28	69	0.85	3
None	0	255	77	0.57	4
None	0.025	32	78	0.67	4

XOH: 0.2 mol dm^{-3}; CuCl: 5×10^{-3} mol dm^{-3}; [VP unit]/[Cu]=2. HTAB: hexadecyltrimethylammonium bromide; Solvent: 40 cm^3 of MeOH(20 vol%)-DCB(70)-py(10) mixture; E: 0.451; Temp: 30 °C; Oxidation: under oxygen atmosphere.

increased under an oxygen atmosphere, and the rate when using the telomer-type surfactant was relatively disadvantageous in comparison with the rate when using pyridine. However, the characters of the telomer-type surfactants for the polymerization of XOH were substantially similar to that under aerobic conditions.

Then, the effects of hexadecyltrimethylammonium bromide (HTAB) on the oxidation polymerization of XOH were examined (Table 6). By the addition of HTAB, the reduced viscosity of PPO became high. However, the yields of PPO and DQ were nearly constant, and all the polymerization rates became slow (about 30 mm^3 min^{-1} while the reaction time became long). These results suggested that the HTAB interfered with the formation of catalyst-XOH complex because the HTAB attracted the XOH anions, and that the HTAB kept the growing PPO highly dispersed.

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